REMOVAL OF HYDROGEN SULFIDE FROM BIOGAS USING CeO_2/NaOH/PSAC: SYNTHESIS AND PERFORMANCE FROM LABORATORY SCALE TO SCALE UP PROCESS DESIGN

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by

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LIST OF ABBREVIATIONS

AC	Activated carbon
ACF	Activated carbon fibre
BET	Brunauer-Emmett-Teller
BOD	Biochemical oxygen demand
CER	Certified emission reduction
CDM	Clean development mechanism
CNT	Carbon Nanotube
COD	Chemical oxygen demand
CPO	Crude palm oil
DBT	Dibenzothiophene
DTG	Derivative Thermogravimetric Analysis
FFB	Fresh fruit bunch
FTIR	Fourier Transformed Infrared Spectroscopy
IP	Isotherm parameter
IWI	Incipient wetness impregnation
MDEA	Methyl–diethyl–amine
MTC	Mass transfer coefficient
PEMFC	proton exchange membrane fuel cell
POME	Palm oil mill effluent
ppm	Part per million
PSAC	Palm shell activated carbon
SCR	Selective catalytic reduction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

TGA	Thermogravimetric Analysis
TNB	Tenaga National Berhad
UDS1	Upwind differencing scheme 1
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy

LIST OF SYMBOLS

A	Pre–exponential factor
a_F	Freundlich isotherm constant
A_T	Temkin isotherm constant
a_{RP}	Redlich–Peterson isotherm constant
β_a	Kinetic coefficient of external mass transfer
b_F	Freundlich isotherm constant
b_{RP}	Redlich–Peterson isotherm constant
b_T	Temkin isotherm constant
C_e	Equilibrium H_2S concentration
c_o	Inlet H_2S concentration
c	Outlet H_2S concentration
D_p	Effective particle diameter
ΔG	Gibbs free energy
ΔH	Enthalpy change
ΔS	Entropy change
ε	Polanyi potential
ε_i	Interparticle voidage
E	Mean free energy of sorption
E_a	Activation energy
F	Total gas flow rate
G'	Mass flux
K_a	BDST rate constant
k_{BA}	Bohart–Adams rate constant
k_{DR}	Dubinin–Radushkevich isotherm constant

k_{Th}	Thomas rate constant
k_{YN}	Yoon–Nelson rate constant
k_1	Pseudo–first order rate constant
k_2	Pseudo–second order rate constant
K_L	Langmuir isotherm constant
K_{RP}	Redlich–Peterson isotherm constant
M	Amount of sorbent
M_w	Molecular weight of H_2S
n	Number of experimental data
q_b	Breakthrough sorption capacity
Q_{DR}	Maximum sorption capacity
q_{BA}	Bohart–Adams sorption capacity
Q_e	Equilibrium sorption capacity
Q_m	Langmuir monolayer sorption capacity
Q_t	Sorption capacity at time t
q_{Th}	Thomas sorption capacity
q_w	Wolborska sorption capacity
R^2	Correlation coefficient
Re	Reynolds number
r_p	Particle radius
SS_{res}	Residual sum of squares
SS_{tot}	Total sum of squares
σ	Standard deviation
τ	Time when $c/c_0 = 0.5$
t_b	Breakthrough time

μ	Viscosity of fluid
v	Linear velocity
V_m	Molar volume
Ψ	Shape factor
w	Weight of the sorbent
x_i	Experimental data
$\hat{x}_i$	Calculated data
$\bar{x}_i$	Mean of experimental data
Z	Bed height
erf(t)	Error function of t

PENYINGKIRAN HIDROGEN SULFIDA DARI BIOGAS MENGGUNAKAN CeO_2/NaOH/PSAC: PENGHASILAN DAN PRESTASI DARI SKALA MAKMAL KE REKA BENTUK PROSES SKALA NAIK

ABSTRAK

Dalam penyelidikan ini, bahan serap CeO_2/NaOH/PSAC telah berjaya dihasilkan dan digunakan dalam penyingkiran hidrogen sulfida dari biogas. Penyelidikan awal menunjukkan laluan penghasilan terbaik adalah menggunakan kaedah rendaman untuk impregnasikan serium oksida dan natrium hidroksida ke karbon teraktif tempurung kelapa sawit (PSAC). Di samping itu, proses pengkalsinan mesti dilakukan sebagai langkah penyediaan terakhir kerana proses ini meningkatkan kapasiti serapan. Parameter penyediaan yang dikaji ialah masa impregnasi (0 – 180 minit), jumlah serium (1 – 10% wt serium), kepekatan natrium hidroksida (0.2 – 1.0M NaOH), suhu (250 – 500^{o}C) dan tempoh pengkalsinan(1 – 4 jam). Pengoptimuman parameter penyediaan bahan serap telah dilakukan dengan nilai optimum ialah 1.5 jam masa impregnasi, 5 wt% serium, 1.0 M NaOH, 400^{o}C suhu pengkalsinan dan 3 jam masa pengkalsinan. Parameter operasi yang mempengaruhi kapasiti serapan ialah suhu serapan, kepekatan H_2S, jumlah bahan serap dan kadar aliran. Nilai maksimum kapasiti serapan boleh dikenalpasti untuk setiap parameter operasi. Selain itu, komponen gas lain seperti air, karbon dioksida dan metana juga boleh mempengaruhi kapasiti serapan dengan berbeza. Analisa data menunjukkan isoterma serapan Freundlich paling sesuai untuk menggambarkan tingkah laku serapan. Penyelidikan termodinamik menunjukkan perubahan entalpi (ΔH) dan perubahan entropi (ΔS) dikirakan sebagai –6.0 kJ/mol dan 25.7 J/mol.K. Serapan adalah pseudo peringkat kedua dengan tenaga pengaktifan 11.7 kJ/mold dan kadar tetap adalah antara 2.387–4.066 X 10^{-6} g/mg.min untuk suhu 30–70^{o}C. Lengkung bulus disesuaikan dengan bagus dengan menggunakan model lengkung bulus yang dibangunkan oleh Chu (2004). Sehingga 78% kapasiti serapan asal dapat dicapai dalam penyelidikan penjanaan semula dengan mengunakan rawatan haba di bawah atmosphere lengai. Suhu dan masa penjanaan semula adalah 500^{o}C dan 4 jam masing masing. Skala naik proses serapan dengan bahan serapan CeO$_2$/NaOH/PSAC telah berjaya direkabentuk dengan kadar pulangan (ROR) selama dua tahun. Penyelidikan simulasi juga dijalankan dan didapati kenaikan kecekapan berlaku pada kadar aliran yang lebih tinggi dan kolom serapan yang lebih kecil.

REMOVAL OF HYDROGEN SULFIDE FROM BIOGAS USING CeO_2/NaOH/PSAC: SYNTHESIS AND PERFORMANCE FROM LABORATORY SCALE TO SCALE UP PROCESS DESIGN

ABSTRACT

In this study, CeO_2/NaOH/PSAC sorbent was successfully synthesized and applied in hydrogen sulfide removal from biogas. Preliminary study showed that the best synthesis route was using soaking method to impregnate cerium oxide and sodium hydroxide onto palm shell activated carbon (PSAC). In addition, calcination must be applied as final step of the preparation because it increased the sorption capacity. Preparation parameters studied were impregnation time (0 – 180 min), cerium amount (1 – 10% wt Ce), sodium hydroxide concentration (0.2 – 1.0M NaOH), calcination temperature (250 – 500°C) and duration (1 – 4 hours). Optimization of sorbent preparation parameters was successful and the optimum values were 1.5 hours impregnation time, 5 wt% cerium, 1.0 M NaOH, 400°C calcination temperature and 3 hours of calcination time. Operating parameters that were found to affect the sorption capacity were sorption temperature, H_2S concentration, sorbent amount, and flow rate. Maximum value of sorption capacity can be identified for each of these operating parameters. Moreover, other gas components such as water, carbon dioxide and methane can also affect the sorption capacity differently. Data analysis showed that Freundlich sorption isotherm can best described the sorption behavior. Thermodynamic study showed that enthalpy change (ΔH) and entropy change (ΔS) were calculated to be –6.0 kJ/mol and 25.7 J/mol.K. The sorption was pseudo–second order with activation energy 11.7 kJ/mol and rate constant was between 2.387–4.066 X 10^{-6} g/mg.min for temperature 30–70°C. Breakthrough curve was fitted well by using breakthrough model developed by Chu (2004). Up to 78% of original sorption capacity was achieved in the regeneration study using heat treatment under inert atmosphere. The regeneration temperature and time were 500°C and 4 hours, respectively. Scale up sorption process using the developed CeO_2/NaOH/PSAC sorbent was successfully designed with a rate of return (ROR) of two years. Simulation study was also performed and increased efficiency at higher flow rate and smaller sorption column was discovered.