# DEVELOPMENT OF WATER ADSORBENT FROM SPENT BLEACHING EARTH FOR DEHYDRATION OF AZEOTROPE ETHANOL-WATER MIXTURE

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Doctor of Philosophy

UNIVERSITI MALAYSIA PAHANG



## SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy in Chemical Engineering.

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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

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# LIST OF SYMBOLS

Ad%	Single metal ion adsorption percentage
Ad <sub>tot</sub> %	The total metal ion adsorption percentage
b	Sorption energy related to monolayer adsorption
В	Temkin constant
d <sub>p</sub>	Mean pore size diameter
c	Outlet adsorbate concentration
c <sub>e</sub>	Adsorbate concentration in equilibrium
c <sub>F</sub>	Inlet concentration to adsorbent bed
С	Concentration of water after adsorption process
C <sub>ads</sub>	Amount of solute adsorbed per mass of adsorbent
C <sub>b</sub>	Concentration of adsorbate at the outlet of the bed
Ce	Equilibrium concentration
Ci	Initial concentration or concentration of adsorbate into the bed
Co	Initial concentration
C <sub>f</sub>	Final concentration
$C_{Ca}(0)$	Calcium ion concentration before phase separation
$C_{Ca}(t)$	Calcium ion concentration after phase separation
$\Delta H_{ads}$	Heat of adsorption
ε <sub>b</sub>	Bed void fraction
3	DKR isotherm constant
k <sub>c</sub>	Correction factor for Yoon and Nelson model
K <sub>ad</sub>	DKR isotherm constant
Κ	Freundlich constant related to operating temperaturel
Κ	Adsorption equilibrium constant in Klinkenberg model
K <sub>F</sub>	Freundlich constant
K <sub>L</sub>	Langmuir constant
K <sub>T</sub>	Temkin constant
k	Overall mass transfer coefficient
k'	Rate constant for Yoon and Nelson model
$\Gamma_{Ca}$	Calcium exchange capacity
М	Molecular weight
M <sub>CaO</sub>	Molecular mass of calcium oxide
n	Freundlich constant
Ν	Constant for adsorption system for Freundlich model
Р	Pressure
Po	Initial pressure
Q	Langmuir constant
q <sub>e</sub>	adsorption capacity per mass of the adsorbent in equilibrium
$q_s$	theoretical isotherm saturation capacity
$S_{BET}$	Total surface area using BET method
t	Sampling time
τ	Dimensionless time in Klinkenberg model
τ	Dehydration time at 50% (i.e $C_b/2$ ) in Yoon and Nelson model
20	X-ray diffractogram angle
u	Superficial velocity
V	Sample volume
Va	Aqueous phase volume

V <sub>micro</sub>	Micropore volume
V <sub>tot</sub>	Total pore volume
W <sub>ads</sub>	Weight of adsorbent in the vial
W <sub>eth</sub>	Weight of ethanol injected into vial
ξ	Dimensionless bed lenght
Z	The bed height

# LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
BET	Brunauer-Emmet-Teller
BFA	Bagasse fly ash
BJH	Barret-Joyner-Halenda
CBC	Calcium Binding Capacity
CEC	Cation Exchange Capacity
DKR	Dubinin-Kaganer-Radushkevich
DOE	Design of Experiment
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray
EDXS	Energy Dispersive X-ray Spectroscopy
FAU	Faujasite
FESEM	Field Emission Scanning Electron Microscopy
FIST	Faculty of Industrial Science and Technology
FTIR	Fourier Transformed Infrared
HSFA	High Silicon Fly Ash
ICDD	International Committee of Diffraction Data
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Llasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
IR	Infrared
IZA	International Zeolite Association
JCPDS	Joint Committee on Powder Diffraction Standards
KOH	Kalium Hydroxide
LTA	Linde Type A
MFI	Zeolite ZSM-5
MPOB	Malaysia Palm Oil Board
MOR	Mordenite
OVAT	One-Variable-At-a Time
PAL	Palygorskite
PEG	Polyethylene Glycol
PSA	Pressure Swing Adsorption
PTFE	Polytetrafluoroethylene
RBD	Refined, Bleached and Deodorized
SBE	Spent Bleaching Earth
SEM	Scanning Electron Microscopy
SC	Scanning Calorimetry
TGA	Thermogravimetric Analysis
UMP	Universiti Malaysia Pahang
UV	Ultraviolet
XRD	X-ray Diffractromery
XRF	X-ray Fluororescence
ZSM-5	Zeolite-Socony-Mobile-5

#### DEVELOPMENT OF WATER ADSORBENT FROM SPENT BLEACHING EARTH FOR DEHYDRATION OF AZEOTROPE ETHANOL-WATER MIXTURE

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#### ABSTRAK

SBE adalah bahan buangan dari loji penapisan minyak sawit dan kebiasannya di buang ke tapak pelupusan sampah. Etanol adalah bahan api alternatif dan mesti kering sebelum boleh digunakan dalam enjin petrol. Dalam kajian ini, penjerap air untuk penulinan campuran azeotrop etanol-air dihasilkan dari SBE mengunakan kaedah pelakuran terubahsuai. Pencirian penjerap air yang terhasil dilakukan menggunakan teknik XRD, FESEM-EDX, ICP-MS dan penganalisa luas permukaan dan keporosan bahan. Enam pembolehubah atau faktor (i.e. penambahan alumina, masa penuaan, suhu penuaan, penambahan KOH, penambahan air dan suhu pelakuran) mempengaruhi penjerapan air dikaji menggunakan teknik OVAT dan teknik faktor penuh berbilang aras DOE yang lebih berstruktur. Akhirnya, kedua-dua penjerap air yang dihasilkan dari SBE dan komersial di gunakan untuk penulinan campuran azeotrop ethanol air menggunakan radas penjerapan skala meja. Analisa XRD menunjukkan penjerap air yang dihasilkan dari SBE bukan dari jenis zeolit A. Walaubagaimanapun imej SEM, menunjukkan bahawa penjerap air tersebut terdiri dari beberapa fasa seperti zeolit A, X, MFI dan fasa amorfos. Tiada hubungkait diperhatikan dari keputusan analisa luas permukaan dan keporosan terhadap penjerapan air bahan penjerap tersebut. Menggunakan teknik OVAT, di dapati bahawa penambahan alumina terbaik adalah pada 80 g/g bahan, masa penuaan 5 hari, suhu penuaan 80°C, penambahan KOH adalah 71% berat bahan, suhu pelakuran 550°C dan penambahan air pada 65% berat bahan terlakur. Analisa varian teknik DOE menunjukkan kesan utama penambahan alumina, penambahan air, suhu pelakuran dan masa penuaan adalah signifikan. Kesan dua hala suhu pelakuran-suhu penuaan dan suhu pelakuran-suhu penuaan juga di dapati signifikan. Kombinasi pembolehubah terbaik adalah pada suhu pelakuran 550°C, suhu penuaan 80°C, masa penuaan 3 hari, penambahan air 65% wt, penambahan KOH 56% berat bahan dan penambahan alumina 80 g/g bahan. Jangkaan air yang diserap adalah 0.0343 g air/g penjerap. Model Yoon dan Nelson di dapati sesuai digunakan untuk data eksperimen lengkung dehidrasi kedua-dua bahan penjerap, untuk penganggaran masa terobos. Dianggarkan bahan penjerap dari SBE mempunyai keupayaan lebih kurang 66% keupayaan penjerap komersil dari segi masa terobos. Kajian ini menunjukkan penjerap berkos murah boleh dihasilkan dari SBE menggunakan kaedah pelakuran terubah suai dan berupaya untuk mengeringkan campuran etanol-air dengan ketulinan lebih 99% berat ethanol untuk digunakan sebagai bahan api bio di dalam enjin petrol.

#### ABSTRACT

SBE is a waste from palm oil refinery it is normally dumped into landfill. Ethanol is an alternative fuel and it must be anhydrous to be used in petrol driven engine. In this study, water adsorbent to dehydrate the azeotrope mixture of ethanol-water was synthesised from SBE using modified fusion method. The synthesised water adsorbent was characterized using XRD, FESEM-EDX, ICP-MS and surface area and porosity analyser. Six variables or factors (i.e. added alumina, aging time, aging temperature, added KOH, added water and fusion temperature) affecting the water-uptake were studied using OVAT technique followed by structured full multilevel factorial DOE method. Lastly, the synthesised and commercial water adsorbent was used to dehydrate azeotrope mixture of ethanol-water in bench top adsorption apparatus to produce dehydrated ethanol. XRD analysis showed that the water adsorbent was not the type of zeolite A. However from SEM images, it was believed that the water adsorbent consist of several types of phases such as zeolite A, X, MFI plus amorphous phase. No relationship was found between results from surface area and porosity experiments to the water-uptake capacity of the water adsorbent. Using OVAT technique, the best added alumina was found to be 80 g/100 g material, aging time of 5 days, aging temperature of 80°C, added KOH of 71% of material mass, fusion temperature was 550°C and the best added water was 65% of the weight of ground fused material. Analysis of variant of the DOE technique showed that the main effects of added alumina, added water, fusion temperature and aging time were significant. There were two way interaction effects between fusion temperature and aging temperature, and between fusion temperature and aging time. The best variables combinations were at fusion temperature of 550°C, 80°C aging temperature, 3 days of aging time, added water 65% wt, added KOH 56% of material mass and added alumina 80 g alumina/g material, with the expected water-uptake of 0.0343 g H<sub>2</sub>O/g adsorbent. Yoon and Nelson model can be used to model the experimental dehydration curve for prediction of breakthrough time. The performance of synthesised water adsorbent was approximately 66% of the commercial water adsorbent in terms of breakthrough time. This study showed that low cost water adsorbent can be produced from spent bleaching earth using modified fusion method and was able to dehydrate ethanol-water mixture more than 99% weight ethanol to be used as bio-fuel in petrol driven engine.

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