STUDIES OF AMINE FUNCTIONALIZED BIOCHAR BASED DESICCATED COCONUT WASTE FOR CARBON DIOXIDE ADSORPTION

by

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LIST OF ABBREVIATIONS

APTES	3-aminopropyl (triethoxysilane)
APTES-Co	3-aminopropyl(triethoxysilane) and cobalt particle
ATMP	Methylenephosphonic acid
BDC	1, 4-benzenedicarboxylic acid
BET	Brunauer-Emmett-Teller
B3LYP	Becke, 3-parameter, Lee-Yang-Parr
CB	Carbon black
CH_4	Methane
CN	Modified urea
CO (NO_3) $2.6H_2O$	Cobalt nitrate hexahydrate
CO_2	Carbon dioxide
CS	Corn stalk
DCW	Desiccated coconut waste
DEA	Diethanolamine
DETA	Diethylenetriamine
DFT	Density Functional Theory
DT	Diethylenetriamine-trimethoxysilane
EDA	Ethylenediamine
EDX	Energy dispersive X-Ray spectroscopy
FM	Magnetite fine particles
FMO	Frontier molecular potential
FTIR	Fourier Transform Infrared Spectroscopy
GHG	Global greenhouse gas
HC	Hydroochar
HC-APTES	Hydrochar-(3-aminopropyl(triethoxysilane)
HMMP-1	High-valence metal-induced microporous polymer filler nanoparticle
HNO_3	Nitric acid
HOMO	Highest occupied molecular orbital
HPC	High performance computing
HW	Hickory wood

H_2O_2	Hydrogen peroxide
KOH	Phosphoric acid
K_2CO_3	Potassium carbonate
LUMO	Lowest unoccupied molecular orbital
MCM-41	Mobil Composition of Matter-41
MCO	Movement control order
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MEP	Molecular electrostatic potential
MgO	Magnesium oxide
MIM	2-methylimidazolate
MMM	Mixed matrix membranes
MNPs	Metal nanoparticles
MOF	Metal-organic frameworks
Mt	Million tonnes
N	Nitrogen
NaOH	Sodium hydroxide
NH_3	Ammonia
NS	Walnut shell
N_2	Nitrogen gas
N_2O	Nitrous oxide
OH	Hydroxyl
PEHA	Polyethylenehexamine
PEI	Polyethyleneimine
PFO	Pseudo-first order
ppmv	parts per million volumes
PSO	Pseudo-second order
PW	Pine wood
RS	Rape straw
SBA-16	Santa Barbara Amorphous-16
SEM	Scanning electron microscope
SFGs	Surface functional groups
SS	Soybean straw
TEPA	Tetraethylenepentamine

TETA	Triethylenetetramine
TGA	Thermogravimetric analysis
TOAB	Tetraoctylammonium bromide
WS	Wheat straw
ZIF	Zeolitic imidazolate framework
Zr	Zirconium

LIST OF SYMBOLS

a.u	Atomic unit
d.p	Number of the PLS or PCA component
E	Energy
E_{HOMO}	Energy values of highest occupied molecular orbital (HOMO)
E_{LUMO}	Energy values of lowest unoccupied molecular orbital (LUMO)
eV	Electron volte
Beg	Gram
k_1	Rate constant of pseudo-first-order, 1/minf
k_2	Rate constant of pseudo-second-order, mg(g/min)
mg	Miligram
mmol	Millimole
q_e	Adsorption capacity at equilibrium, mg/g
q_t	Adsorption capacity at any time, mg/g
t	Time, min
T	Temperature,K
wt%	Weight percent
°C	Degree Celcius
ΔE_{ads}	Adsorption energy
ΔE_{gap}	Energy gap

Kajian Amina Berfungsikan Bioarang Berasaskan Hampas Kelapa untuk Penjerapan Karbon Dioksida

ABSTRAK

Masalah alam sekitar seperti perubahan iklim dan pemanasan global yang disebabkan gas rumah hijau terutamanya gas karbon dioksida (CO_2) telah menjadi topik yang membimbangkan seluruh dunia. Penjerapan merupakan kaedah yang efisien untuk penangkapan CO_2. Dalam penyelidikan ini, satu siri rantaian amina berfungsikan bioarang berasaskan hampas kelapa (amina-bioarang@DCW) iaitu penjerap ethylenediamine (EDA-bioarang@DCW) diethylenetriamine berfungsikan bioarang@DCW (DETA-bioarang@DCW), triethylenetetramine berfungsikan bioarang@DCW (TETA-bioarang@DCW), tetraethylenepentamine berfungsikan bioarang@DCW (TEPA-bioarang@DCW), and pentaethylenehexamine berfungsikan bioarang@DCW (PEHA-bioarang@DCW) telah disintesis dan dicirikan. Siri penjerap amina-bioarang@DCW mempunyai struktur liang yang lebih baik dan luas permukaan spesifik yang lebih besar daripada hampas kelapa yang asli (DCW) apabila dianalisa mengunakan pengimbasan mikroskop elektron (SEM) dan Brunauer-Emmett-Teller (BET). Di samping itu, analisis Sinar-X Penyebaran Tenaga (EDX) dan Spektroskopi Inframerah Transformasi Fourier (FTIR), masing-masing mengesahkan kejayaan menfungsikan siri amina terhadap biochar berasaskan hampas kelapa (biochar@DCW). Daripada analisa prestasi penjerapan CO_2, TETA-bioarang@DCW mempunyai kapasiti penjerapan CO_2 yang lebih tinggi (61.78 mg/g) daripada penjerap lain yang telah disintesis kerana luas permukaan spesifiknya yang lebih besar dan isipadu liang yang lebih besar iaitu 31.7 m^2/g dan 0.0029 cm^3/g, masing-masing. Nisbah bioarang@DCW:amina yang terbaik untuk penjerapan CO_2 adalah 1:2. Kinetik penjerapan pada TETA-biochar@DCW berpadanan baik dengan model pseudo-kedua, mencadangkan proses penjerapan berlaku melalui penjerapan kimia. Tambahan pula, TETA-biochar@DCW menunjukkan selektiviti yang tinggi terhadap gas CO_2 dan kebolehgunaan semula yang baik selepas lima kitaran penjerapan-penyahjerapan CO_2. Kajian teori daripada Teori Fungsi Ketumpatan (DFT) mendedahkan bahawa TETA-biochar@DCW adalah penjerap yang reaktif dan stabil untuk penjerapan CO_2. Analisis daripada pengoptimuman geometri dan orbital molekul sempadan (FMO) membuktikan TETA-bioarang@DCW adalah penjerap yang stabil kerana memiliki nilai jumlah tenaga dan momen dipol yang paling rendah dan jurang tenaga yang lebih besar setelah penjerapan CO_2 berlaku. Manakala, kajian daripada keupayaan elektrostatik molekul (MEP) melaporkan TETA-biochar@DCW adalah penjerapan yang reaktif setelah penyerapan proses berlaku dengan memiliki nilai potensi elektrostatik tertinggi ($7.146e^{-2}$ eV) berbanding penjerap amina-bioarang@DCW yang lain, menunjukkan TETA-bioarang@DCW mempunyai interaksi yang kuat terhadap gas CO_2. Dapatan daripada kajian ini sekaligus menyokong baik dapatan daripada eksperimen yang menunjukkan TETA-biochar@DCW adalah penjerap yang paling optimum terhadap CO_2 rentetan sifat fizikokimianya yang hebat dan ciri molekulnya yang reaktif dan stabil. Secara konklusinya, TETA-bioarang@DCW boleh digunakan sebagai penjerap alternatif untuk penjerapan CO_2.

Studies of Amine Functionalized Biochar based Desiccated Coconut Waste for Carbon Dioxide Adsorption

ABSTRACT

Environmental problems such as climate change and global warming caused by greenhouse gases, mainly CO_2, have become a worldwide topic of concern. Adsorption is a promising method for CO_2 capture. In this research, a series of amine functionalized on biochar based desiccated coconut waste (amine-biochar@DCW) namely ethylenediamine functionalized biochar@DCW (EDA-biochar@DCW), diethylenetriamine functionalized biochar@DCW (DETA-biochar@DCW), triethylenetetramine functionalized biochar@DCW (TETA-biochar@DCW), tetraethylenepentamine functionalized biochar@DCW (TEPA-biochar@DCW), and pentaethylenehexamine functionalized biochar@DCW (PEHA-biochar@DCW) adsorbents were synthesized and characterized. From the Scanning Electron Microscopy (SEM) dan Braeuer-Emmett-Teller (BET) analysis, series of amine-biochar@DCW adsorbents had better developed pore structure and larger specific surface area than that of pristine desiccated coconut waste (DCW). Besides, Energy Dispersive X-ray (EDX) dan Fourier Transform Infrared Spectroscopy (FTIR), confirmed the successful functionalization of series of amine towards biochar based desiccated coconut waste (biochar@DCW). From the CO_2 adsorption experiment, TETA-biochar@DCW had higher CO_2 adsorption capacity (61.78 mg/g) as it has the largest specific surface area and highest total pore volume with 31.7 m^2/g dan 0.0029 cm^3/g, respectively. The best ratio of biochar@DCW:amine for the CO_2 adsorption is 1:2. The adsorption kinetics on the TETA-biochar@DCW was best fitted by the pseudo-second model, suggesting the adsorption process occurs through chemisorption. Furthermore, TETA-biochar@DCW depicts high selectivity towards CO_2 gas and good reusability after five CO_2 adsorption–desorption cycles. From theoretical study using Density Functional Theory (DFT) approach reveals that TETA-biochar@DCW as the reactive and stable adsorbent for CO_2 adsorption. Analysis from the geometry optimization and frontier molecular orbital (FMO) proved that TETA-biochar@DCW as stable adsorbent because it has the lowest total energy and dipole moment and has large energy gap after the CO_2 adsorption occurs. While, the study of molecular electrostatic potential (MEP) shows that TETA-biochar@DCW is a reactive CO_2 adsorbent with the the highest electrostatic potential value (7.146 e^{-2} eV) compared with other amine-biochar@DCW adsorbents, suggesting the strong adsorption of TETA-biochar@DCW towards CO_2 gases. Outcomes from theoretical study well support the findings from experimental which showed TETA-biochar@DCW as optimum adsorbent for CO_2 due to its great physicochemical properties and its reactive molecular characteristics. As conclusion, TETA-biochar@DCW can be used as an alternative adsorbent for CO_2 adsorption.

CHAPTER 1 : INTRODUCTION

1.1 Background of Study

The temperature of the earth gradually increased, beginning with the Industrial Revolution in the early 20th century. Recent weather conditions have intensified the debate about rising global temperatures. Temperatures are explained by high manufacturing and economic activity levels including major emissions (Mikhaylov et al., 2020). The main source of greenhouse gas emissions is from human activities, for instance, the combustion of fossil fuels for electricity, food, and transport. If uncontrolled emissions are not reduced, the current CO_2 level of 394.5 parts per million volume (ppmv) is predicted to increase to 500 ppmv by 2050 (Thakur et al., 2022).

Several techniques have been introduced to minimize the concentration of CO_2 in the environment, such as absorption, membrane separation, and cryogenic separation. However, all these methods are costly and not environmentally friendly (Zubbri et al., 2020). The solid adsorption method is widely used for its advantages of low cost, simple operation, high stability, low renewable energy consumption, and low equipment corrosion (Chen et al., 2021; Nie et al., 2018). Common adsorbents have been synthesized for CO_2 adsorption, including porous polymer materials, metal-organic framework, porous metal oxide, and mesoporous silica. However, these adsorbents have several drawbacks such as low CO_2 uptake, expensive and poor recyclability performance (Shafawi et al., 2021)

Recently, more attention has been focused on utilizing emerging carbonaceous adsorbent, biochar as CO_2 adsorbents. For biochar, various biomass wastes can be used as feedstock, such as agricultural waste. Desiccated coconut waste (DCW) is one of the promising raw materials for biochar production as it has higher cellulose, hemicellulose, and lignin contents. DCW is an attractive choice because of its high availability, cheap and easily regenerable, and the fact that DCW requires minor preparation before it is utilized (Rahim et al., 2020). In addition, using DCW promotes the management of biomass wastes for biochar production. As the utilization of DCW based biochar has been rarely reported for CO_2 adsorption application, it is a good idea to explore biomass from DCW as raw materials to develop biochar as an adsorbent for CO_2 capture.

In addition, properties of biochar such as surface area, porosity and surface functional groups need to be further improved to enhance CO_2 capture. Thereby, surface modification and grafting of functional groups onto the surface of the material may be an effective approach to improve the adsorption performance of biochar toward CO_2 adsorption. In the present study, amine functionalization on the surface of biochar was used to modify the surface of biochar. A series of amines, namely ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA) were chosen to functionalize the surface of biochar. These amine series were selected based on the alkyl chain with different numbers of nitrogen (N) elements because Liu et al. (2015) reported that the nitrogen site of amine provided active sites for the adsorption of CO_2. The synthesized adsorbents were further characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Energy dispersive X-Ray (EDX) spectroscopy, Brunauer-Emmett-Teller (BET) and Thermogravimetric Analysis

(TGA). The CO_2 adsorption capacity of the series amine-biochar@DCW adsorbents was screened using thermogravimetric analysis (TGA).

The optimum adsorbent with the highest CO_2 adsorption capacity has been further used to evaluate kinetic, selectivity, and regeneration studies. Additionally, the investigation on the adsorption mechanisms of series amine-biochar@DCW with CO_2 molecules was detesrmined thoroughly using theoretical Gaussian 09 software employing Density Functional Theory (DFT) approach. The detail fundamental level of the adsorption energy and interacting site of adsorbents with CO_2 were examined from computational calculation via geometry optimization, molecular electrostatic potential (MEP), frontier molecular orbitals (FMO), and their adsorption energy.

1.2 Problem Statement

CO_2 is one of the greenhouse gases (GHGs) that has contributed to extreme climate change, such as global warming. Climate change has the potential to lead to catastrophic flooding, landslides brought on by rain, and excessive precipitation, all of which can harm both private property and public infrastructure. Climate change also endangers the health of the earth, the human race, and the global economy. Finding an alternative means of capturing CO_2 is imperative for the sustainability of the environment.

Several CO_2 capture techniques have been studied to reduce the CO_2 emission in the atmosphere including absorption, membrane separation, and cryogenic separation. Although these implemented techniques effectively capture carbon dioxide, they have

several drawbacks, such as high cost, poor thermally stable and recyclability (Kamran & Park, 2021).

Adsorption has become a promising technique owing to its simplicity and low-cost operation. Various adsorbents were synthesized for the adsorption of CO_2 including metal-organic frameworks (MOF) and mesoporous silica. Nevertheless, these adsorbents faced some limitations in being effective CO_2 adsorbents due to low CO_2/N_2 selectivity, low CO_2 uptake and require high cost for synthesis.

Biochar, the immediate carbon-based solid adsorbents obtained through biomass thermochemical conversions, is one of the potential and cheap CO_2 adsorbents. Agricultural waste is a suitable precursor for the production of biochar. In this research, desiccated coconut waste (DCW) is chosen as raw material for the preparation of biochar as it has high content of cellulose, lignin, and hemicellulose, quick sorption kinetics, easily regenerable, and low-cost material (Rahim et al., 2020). However, the original biochar generally has a low saturation adsorption capacity (Wang et al., 2022). Many researchers have attempted to modify the biochar surface to solve this problem.

One of the techniques is the surface chemical modification, which makes biochar have more active sites with specific adsorption functions by improving the functional groups and the surface of biochar. Dozens of researchers have paid attention to the modification of biochar to increase the amount of surface functional groups, and amine groups have been proven to have an excellent effect on improving the adsorption capacity of biochar. A series of amines with different chain lengths, including EDA, DETA, TETA, TEPA, and PEHA, were selected to functionalize biochar as amine provides

active sites for selective CO_2 gases. Characterizing the modified biochar in terms of the functional group, surface morphology, elemental, thermal stability, and pore size analysis is important because the amine functionalization towards biochar surface can be confirmed from these results.

The essential characteristic of synthesized modified biochar is its adsorption capacity, which the amine modifying agents greatly influence on biochar. The reason for the varying results in this study is due to the use of different-length amine chains as modifying agents. The uptake capacity of the synthesized adsorbents mainly depends on the elemental N of the amine, as it provides active sites for the adsorption of CO_2. Thus, screening the performance of the synthesized adsorbents functionalized with a series amine modifying agent is necessary to observe their behaviour in terms of CO_2 adsorption capacity.

Since only a few studies support their experimental data with a theoretical approach, this research takes a step toward validating experimental outcomes at the molecular level using computational study. Density Functional Theory (DFT) investigated the interaction site and binding energy between a series of amine-biochar@DCW and CO_2. DFT approaches can provide insight into the reaction mechanisms of adsorption processes and accurately predict the adsorption energy and geometry of molecules on surfaces. Therefore, this outcome contributes insight into fundamental understanding for further advancement in adsorbent material for environmental remediation, mainly CO_2.

1.3 Research Questions

i) What are the characteristics of the adsorbents developed in this study?

ii) How does the performance of synthesized adsorbents towards CO_2 adsorption in kinetic, regeneration and selectivity studies?

iii) What is the correlation between the experimental and theoretical analysis of synthesized adsorbents with CO_2 in terms of adsorption energy using the Density Functional Theory (DFT) approach?

1.4 Objectives Study

i) To synthesis and characterize a series of amine-functionalized biochar based desiccated coconut waste (amine-biochar@DCW) adsorbents for CO_2 adsorption.

ii) To evaluate the performance of synthesized amine-biochar@DCW adsorbent towards CO_2 adsorption in terms of kinetic, regeneration and selectivity studies.

iii) To assess the adsorption study of series amine-biochar@DCW adsorbents with CO_2 using Density Functional Theory (DFT) approach.

1.5 Research Scope

The present work highlights the use of DCW as raw material to develop biochar for CO_2 adsorption. A series of amines with different amine chain lengths including ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA),

tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA) were introduced on the surface of the synthesized biochar@DCW to produce series amine-biochar@DCW adsorbents including EDA-biochar@DCW, DETA-biochar@DCW, TETA-biochar@DCW, TEPA-biochar@DCW and PEHA-biochar@DCW to enhance the performance of the biochar based DCW (biochar@DCW) towards CO_2 adsorption. The structure of the series of amine-biochar@DCW was characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray (EDX) spectroscopy, Braeuer-Emmett-Teller (BET) and Thermogravimetric Analysis (TGA) analyses.

As characterization studies confirmed the physicochemical properties of fabricated series amine-biochar@DCW adsorbents, the performance of these adsorbents was screened towards CO_2 adsorption. The adsorbent with high adsorption CO_2 capacity was selected for further kinetic, selectivity, and regeneration evaluation. The kinetic study examined the adsorption mechanism of amine-biochar@DCW adsorbent towards CO_2 using pseudo first order and pseudo second order models. In addition, a selectivity study was assessed in this research to investigate the selectivity performance of amine-biochar@DCW adsorbent towards CO_2 gases over other gases such as N_2, CH_4, and air. The stability of amine-biochar@DCW adsorbent after five cycles of CO_2 adsorption-desorption was evaluated using a regeneration study.

The interaction between the functionalized series of amine-biochar@DCW (EDA-biochar@DCW, DETA-biochar@DCW, TETA-biochar@DCW, TEPA-biochar@DCW and PEHA-biochar@DCW) adsorbent with CO_2 were assessed using density functional theory (DFT) by employing Becke, 3-parameter, Lee-Yang-Parr