



**PERFORMANCE EVALUATION OF CHEMICALLY MODIFIED SAWDUST
AS LIGNOCELLULOSIC ADSORBENT FOR AQUEOUS ETHANOL
PURIFICATION**

By

OLADELE, OLANIKE FEYISAYO

B. Tech. (Chemical Engineering)

Ladoke Akintola University of Technology,

Ogbomoso, Oyo state.

**BEING A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE AWARD OF DEGREE IN M.Sc.**

IN CHEMICAL ENGINEERING

FACULTY OF TECHNOLOGY AND ENGINEERING,

OBAFEMI AWOLOWO UNIVERSITY

ILE-IFE, OSUN STATE

2016



CERTIFICATION

We certify that this project was carried out by Olanike Feyisayo OLADELE (TP13/14/H/1623) of the Department of Chemical Engineering in partial fulfillment of the requirements for the award of M.Sc. Degree in Chemical Engineering of the Obafemi Awolowo University, Ile- Ife.

.....

Dr. E. A. Taiwo

(Supervisor)

.....

Date

.....

Dr. O. A. Sanda

(Co- supervisor)

.....

Date

.....

Dr. E. F. Aransiola

(Chief Examiner)

.....

Date



OBAFEMI AWOLOWO UNIVERSITY, ILE - IFE, NIGERIA

HEZEKIEL OLUWASANMI LIBRARY

POSTGRADUATE THESIS

AUTHORIZATION TO COPY

AUTHOR: OLADELE OLANIKE FEYISAYO

TITLE: PERFORMANCE EVALUATION OF CHEMICALLY MODIFIED
SAWDUST AS LIGNOCELLULOSIC ADSORBENT FOR AQUEOUS
ETHANOL PURIFICATION

DEGREE: M. Sc (CHEMICAL ENGINEERING)

YEAR: 2016

I, OLADELE Olanike hereby authorize the Hezekiel Oluwasanmi Library to copy my thesis,
in parts or whole, in response to request from individual researchers and organizations for the
purpose of private study or research.

Signature: _____

Date: _____



DEDICATION

This research work is dedicated to the Lord of lords and King of kings who made it possible for me to undergo this programme. Also to baby Oladele Samson who came to the world in the course of this work. Glory be to God



ACKNOWLEDGEMENT

I give praise and adoration to the Lord Almighty for his great love and mercy towards my life. He was the source of strength and hope for me all through the period of this study. I acknowledge the supervision and guidance of my supervisors, Dr. E.A. Taiwo and Dr. O. Sanda respectively, whose encouragement and insightful contributions led to the success of this work. May the Lord take you to the peak of your career in life.

I appreciate my parents, Chief and Mrs J.O. Adetunji who initiated the idea of this study and gave me their maximum support in the course of the work. I also express deep appreciation towards my darling husband, Rev. Solomon Oladele for his moral, spiritual and financial support which greatly contributed to my success.

I will like to say a big thanks to my daddy and mummy in the Lord, the Lord Bishop of Osun North East Diocese, The Rt. Rev'd Dr. H.B. Olumakaiye and Dr. Mrs. M.F. Olumakaiye for encouragement and financial support they rendered towards the accomplishment of this programme. May God continue to increase and bless them.

I express my sincere appreciation to the Head of Department of Chemical Engineering, Dr. (Mrs.) E.F. Aransiola and every member of Staff of the department, most especially Prof. A.N. Anozie, Prof. S.K. Layokun, Prof. J.A. Sonibare, Dr. O.J. Odejebi, Mr. A. Bamimore, Mr. F.O. Adedokun, Mr. O.F. Ola, Mrs. Olayemi and others. I am most grateful to Prof. Ibitayo for his financial contribution to my work.

I appreciate my course mates, Miss Tosin Akinrinade, Mr. Yinka Olabiyi, Ope Sole Olaoye, Tope Bello, Omolola Odesola and others. I also thank Mr and Mrs Faith Adeosun for accommodating me throughout the duration of this programme, Mrs Janet Osin for her kind gesture towards my baby. May God reward them abundantly. I am grateful to Mr. R.B. Ajala,



Mr. F.I. Alo and Mr. O. Omolayo in Material science and Engineering department for the assistance rendered over my project work.

OBAFEMI AWOLOWO UNIVERSITY



TABLE OF CONTENTS

Title	
Page	
Certification	i
Authorization to Copy	ii
Dedication	iii
Acknowledgement	v
Table of Contents	vii
List of Tables	xiii
List of Figure	xiv
List of Plates	xvii
Abstract	
xviii	

CHAPTER ONE: INTRODUCTION

1.1	Background of the Study	1
1.2	Research Objectives	4
1.3	Scope of the Study	5
1.4	Significance of the study	5

1.5	Justification of the Study	6
-----	----------------------------	---

CHAPTER TWO: LITERATURE REVIEW

2.1	Ethanol Production	7
2.2	Ethanol Purification	10
2.2.1	Distillation process	12
2.2.2	Ozonation process	14
2.2.3	Adsorption process	15
2.3	Adsorption Process and Phases	16
2.4	Application of Adsorption	17
2.5	Types of Adsorbents	18
2.5.1	Activated carbon	19
2.5.2	Activated alumina	22
2.5.3	Silica gel	22
2.5.4	Molecular sieves	25
2.5.5	Biomass adsorbent	25
2.6	Choice of Suitable Adsorbent	25
2.6.1	Physical property of adsorbent	26
2.6.2	Chemical selectivity of adsorbent	30

2.6.3	Adsorption capacity	31
2.6.4	Removal efficiency	32
2.6.5	Design of adsorption column	33
2.6.6	Regeneration capacity	34
2.7	Starch Adsorbent	35
2.8	Lignocelluloses Adsorbent	40
2.8.1	Composition of wood	42
2.8.2	Types of wood	43
2.8.3	Pretreatment of lignocellulosics	45
2.9	Adsorption Model	50
2.9.1	Adsorption kinetic model	50
2.9.1.1	Pseudo first order model	51
2.9.1.2	Pseudo second order model	51
2.9.1.3	Intraparticle diffusion model	52
2.9.2	Adsorption equilibrium model	53
2.9.2.1	Langmuir isotherm	53
2.9.2.2	Freundlich isotherm	55
2.9.2.3.	Sips isotherm	56
2.9.2.4	Brunauer-Emmett-Teller (BET) theory	56

2.9.3	Mass transfer mechanism	58
-------	-------------------------	----

CHAPTER THREE: METHODOLOGY

3.1	Preparation of Reagents	60
3.2	Preparation of Sawdust Adsorbents	60
3.2.1	Collection of sawdust adsorbent	61
3.2.2	Screening of sawdust adsorbent	61
3.2.3	Washing of sawdust adsorbent	61
3.2.4	Chemical pretreatment of sawdust as adsorbent	62
3.2.5	Surface structure of sawdust samples	62
3.3	Standard Adsorbent	64
3.4	Physical Characterization of Sawdust Adsorbent	64
3.4.1	Bulk density determination	64
3.4.2	Moisture content determination	65
3.4.3	Pore volume and porosity determination	65
3.5	Experimental Procedure for Liquid-phase Adsorption	66
3.6	Analysis of Samples	68
3.6.1	Refractometry determination	68

3.6.2	Density determination	69
3.7.	Statistical Evaluation of the Methods	69

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	Sawdust Samples Characterization	72
4.1.1	Bulk density of sawdust samples	72
4.1.2	Moisture content of sawdust samples	72
4.1.3	Pore volume and porosity of sawdust samples	74
4.2	Optimum Operating Conditions for Adsorption	74
4.2.1	Liquid phase batch kinetic studies	74
4.2.2	Liquid phase batch equilibrium studies	90
4.3	Evaluation of the Performance of the Sawdust Adsorbents	91
4.3.1	Parameters and statistical evaluation of kinetic models	91
4.3.2	Evaluation of adsorption isotherm parameters.	101
4.4	Microscope Structure of Sawdust Adsorbent	112

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

5.1	Conclusions	122
-----	-------------	-----

5.2	Recommendations	123
REFERENCES		124
APPENDICES		140

OBAFEMI AWOLOWO UNIVERSITY

LIST OF TABLES

Table	Title	page
1.1	Annual Bio-ethanol Production by Top Ten Countries	3
2.1	Chemical Components of Hardwood and Softwood	48
4.1	Physical Characterization of the Sawdust Samples	73
4.2	Estimated Parameters and Evaluation of Kinetic models	93
4.3	Estimated Parameters and Evaluation of Adsorption Isotherm	100
A1	Refractive Index and Density Calibration Ethanol Standard Solution	140
A2	Codes and Names of Adsorbent Samples	141
A3	Performance of Unmodified and H ₂ SO ₄ modified Sawdust in Aqueous Ethanol	142
A4	Performance of CaCl ₂ modified Sawdust in Aqueous Ethanol	144
A5	Particle size 1 Removal Efficiency	146
A6	Adsorption Equilibrium Data	147

LIST OF FIGURES

Figure Title

page

2.1	Schematic of dry milling ethanol production process	9
2.2	Schematic of wet milling ethanol production process	11
2.3	Chemical structure of amylose and amylopectin	38
2.4	Chemical structure of cellulose, hemicelluloses and xylan	46
2.5	Chemical structure of lignin and tannin	47
4.1	Plots of adsorption capacity for unmodified sawdust (UM)	75
4.2	Plots of adsorption capacity for MH30	76
4.3	Plots of adsorption capacity for MH70	77
4.4	Plots of adsorption capacity for MH80	78
4.5	Plots of adsorption capacity for MH90	79
4.6	Plots of adsorption capacity for MH30	80
4.7	Plots of adsorption capacity for MC70	81
4.8	Plots of adsorption capacity for MC80	82
4.9	Plots of adsorption capacity for MC90	83

4.10	Plots of adsorption capacity for MHP ₁	86
4.11	Plots of adsorption capacity for MCP ₁	87
4.12	Equilibrium adsorption of water onto H ₂ SO ₄ modified adsorbents	88
4.13	Equilibrium adsorption of water onto CaCl ₂ modified adsorbents	89
4.14	Pseudo first order kinetic model for CaCl ₂ modified adsorbents	94
4.15	Pseudo first order kinetic model for H ₂ SO ₄ modified adsorbents	95
4.16	Pseudo second order kinetic model for H ₂ SO ₄ modified adsorbents	96
4.17	Pseudo second order kinetic model for CaCl ₂ modified adsorbents	97
4.18	Intraparticle diffusion plot of H ₂ SO ₄ modified adsorbents	98
4.19	Intraparticle diffusion plot of CaCl ₂ modified adsorbents	99
4.20	Langmuir isotherm plot of unmodified adsorbent	103
4.21	Langmuir isotherm plot of MH90 adsorbent	104
4.22	Langmuir isotherm plot of MC90 adsorbent	105
4.23	Freundlich isotherms plot of unmodified adsorbent	106
4.24	Freundlich isotherm plot of MH90 adsorbent	107
4.25	Freundlich isotherm plot of MC90 adsorbent	108
4.26	BET adsorbent isotherm for water unmodified adsorbent	109

4.27	BET adsorbent isotherm for water MH90 adsorbent	110
4.28	BET adsorbent isotherm for water MC90 adsorbent	111

OBAFEMI AWOLOWO UNIVERSITY

LIST OF PLATES

Plate	Title	
page		
3.1	Screened sawdust samples of different particle size	63
3.2	Liquid – phase adsorption experimental set-up	67
4.1	Micrograph of UMP ₁	113
4.2	Micrograph of UMP ₂	114
4.3	Micrograph of UMP ₃	115
4.4	Micrograph of MCP ₁	116
4.5	Micrograph of MCP ₂	117
4.6	Micrograph of MCP ₃	118
4.7	Micrograph of MHP ₁	119
4.8	Micrograph of MHP ₂	120
4.9	Micrograph of MHP ₃	121

ABSTRACT

This research investigated the applicability of a lignocellulosic adsorbent such as chemically modified sawdust for aqueous ethanol purification with a view to producing fuel-grade ethanol. It also determined the optimum condition for water adsorption and evaluated the performance of the modified sawdust samples as alternative to the costly commercial adsorbents.

The sawdust were modified using 25% (weight of H₂O/weight of adsorbent) H₂SO₄ and 15% (weight of H₂O/weight of adsorbent) CaCl₂ at temperature range of 30 – 90 °C. The physical characterization of the screened sawdust were determined and used to select the likely optimum particle size for the adsorption process. The samples were analyzed using refractive index and density methods. Liquid phase adsorption experiments were conducted at room temperature with initial concentration of 92.85% (w/w) aqueous ethanol. Adsorption isotherm parameters were determined from equilibrium experiments carried out using different adsorbent doses of range 0.5 - 2.0 g. The adsorption performance of the modified sawdust samples were determined from the kinetic models using pseudo-first order, pseudo-second order kinetics and intraparticle diffusion as the rate controlling mechanism. The evaluation of the performance of the modified sawdust samples for equilibrium isotherm was done using Langmuir, Freundlich and Brunauer-Emmett-Teller (BET) adsorption isotherm.

The results showed that adsorption capacities at equilibrium for the 0.425 mm particles modified in 15% (w/w) CaCl₂ (MC90) and 25% (w/w) H₂SO₄ (MH90) had the highest adsorption capacities of 0.774 and 0.731(g H₂O g⁻¹ adsorbent) respectively and percentage water removal of 88.81 and 83.50% respectively. The acid and salt modified sawdust samples attaining

equilibrium within 50 min. The calculated adsorption capacities for pseudo-first order model (0.1910 – 0.9036 ml/g) were closer to experimented data (0.3080 – 0.7530 ml/g) than those obtained from pseudo-second order model (0.6620 – 0.9880 ml/g). Statistical evaluation of kinetic models showed that total error (Err^2) and standard deviation (SSE) for pseudo-first order (0.0084 – 0.0298) and (0.1726 – 0.1170) respectively were smaller compare to that of pseudo-second order model of range (0.0072-0.1253) and (0.354 – 0.0847). The adsorption parameter for Langmuir isotherm ranges between 0.9220-0.9695 and Freundlich isotherm ranges between 0.568 and 0.9251. Since conditions of $(0 < R_L < 1)$ and $(0 < 1/N_f < 1)$ were met by the process, this implied that the adsorption system is favorable.

The study concluded that $CaCl_2$ modified sawdust has higher adsorption performance than H_2SO_4 modified sawdust. The smallest particle sizes of $CaCl_2$ (MC90) modified adsorbent gave the highest yield of 0.774 g/g adsorption capacity using 92.85% w/w initial ethanol concentration. Pseudo-first order model and Freundlich adsorption isotherm were the most appropriate models that described the adsorption process.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is a clear liquid also known as ethyl alcohol or grain alcohol, the same type of alcohol found in alcoholic beverages. It is used as a solvent, germicide, beverage, antifreeze, fuel, depressant and as chemical intermediate for other chemicals (Bakalinsky and Penner, 1993). It is most often used as a motor fuel, mainly as a bio-fuel additive for gasoline (RFA, 2012). It is commonly made from biomass such as corn or sugarcane. It has a higher octane number than gasoline providing premium blending properties. Low octane gasoline is blended with 10% ethanol to attain the standard 87octane requirement. Ethanol is the main component in high – level ethanol blends (AFDC, 2015).

Nowadays, cars that are able to run using 100 % ethanol have been introduced in Brazil (ABRACICLO, 2011). World ethanol production for transport fuel tripled between 2000 and 2007 from 17 billion to more than 52 billion liters. From 2007 to 2008, the share of ethanol in global gasoline type fuel use increased from 3.7% to 5.4% (UNEP, 2009). Ethanol fuel is widely used in Brazil and in the United States, and together both countries were responsible for 87.1% of the world's ethanol fuel production in 2011. Worldwide ethanol fuel production reached 84.6 billion litres, with the United States as the top producer with 52.6 billion liters, accounting for 62.2% of global production, followed by Brazil with 21.1 billion liters as shown in Table 1.1 (RFA, 2012). Ethanol fuel has a "gasoline gallon equivalency" (GGE) value of 5.7 liters, which means 5.7 liters of ethanol, produces the energy of about 3.8 liters of gasoline (GGE, 2011). Since 1976, the

Commented [O1]: Reference not listed

Commented [O2]: Reference not listed

Brazilian government has made it mandatory to blend ethanol with gasoline, and since 2007 the legal blend is around 25% ethanol and 75% gasoline (E25) (UNICA, 2010).

Table 1.1: Annual Bio-ethanol production by Top Ten Countries (billions U.S. gallons)

World rank	Country	2011	2010	2009	2008	2007
1	US	13,900.00	13,900.00	10,938.00	9000.00	6,485.00
2	Brazil	5,573.24	6,921.54	6,577.89	6,472.20	5,019.20
3	EU	1,199.31	1,176.88	1,039.52	733.60	570.30
4	China	554.76	541.55	541.55	501.90	486.00
5	Thailand			435.20	89.80	79.20
6	Canada	462.30	356.63	290.59	237.70	211.30
7	India			91.67	66.00	52.80
8	Colombia			83.21	79.30	74.90
9	Australia	87.20	66.04	56.80	26.40	26.40
10	Others			247.27		
	World Total	22,356.09	22,946.87	19,534.99	17,335.20	13,101.70

Source: (Licht, 2011)

Commented [O3]: This was listed as Licht (2010). Check and correct.

As at December 2011, Brazil had a fleet of 14.8 million flex-fuel automobiles and light trucks (ANFAVEA, 2012) and 1.5 million flex-fuel motorcycles that regularly use neat ethanol fuel known as E100 (ABRACICLO, 2010).

Bio-ethanol is usually obtained from the conversion of carbon-based feedstock. Agricultural feed stocks are considered renewable because they get energy from the sun using photosynthesis, provided that all minerals required for growth (such as nitrogen and phosphorus) are returned to the land. Ethanol can be produced from a variety of feed stocks such as sugarcane bagasse, miscanthus, sugar beet, sorghum, grain, switchgrass, barley, hemp, kenaf, potatoes, sweet potatoes, cassava, sunflower fruit, molasses, corn, stover, grain, wheatstraw, cotton, other biomass, as well as many types of cellulose waste and harvesting, whichever has the best well-to-wheel assessment (Martins, 2008).

Distillation process can only remove water from aqueous ethanol to a maximum ethanol concentration of 95%. The azeotropic distillation has been used to overcome this problem for large scale production of anhydrous ethanol (Treybal, 1981). However, the inherent draw back such as the addition of a third component (called an entrainer) to the mixture, large cost of entrainer recovery, the inevitable entrainer losses and choices of materials of construction make the production of anhydrous ethanol by azeotropic distillation on a small scale not feasible. On a small scale, anhydrous ethanol can be obtained by an adsorption operation (Cooney, 1980).

Adsorption process is a separation technique utilizing a large surface area of adsorbent. Compounds are simply adsorbed on the adsorbent depending on their physical and chemical properties. When purification of ethanol is considered, non-polar surface and wide ranging pore distribution are favorable since ethanol is polar compounds and various sizes of particles could