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 **Date**

(Supervisor)

…………………………. …………………………

Dr. O. A. Sanda **Date**

(Co- supervisor)

…………………………… ………………………..

Dr. E. F. Aransiola **Date**

(Chief Examiner)

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 Oanike 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

ACKNOWLEGEMNT

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. Odejobi, 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.

TABLE OF CONTENTS

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSION

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

Figure Title

page

LIST OF PLATES

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 H_2O/weight of adsorbent) H_2SO_4 and 15% (weight of H_2O/weight of adsorbent) $CaCl_2$ at temperature range of 30 – 90 ^{0}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) $CaCl_2$ (MC90) and 25% (w/w) H_2SO_4 (MH90) had the highest adsorption capacities of 0.774 and 0.731(g H_2O 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 (CH_3CH_2OH) 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