

**CALCIUM CHLORIDE SUPPORTED ON PURIFIED SPENT BLEACHING
EARTH AS POTENTIAL ADSORPTIVE MATERIAL FOR AIR
DEHUMIDIFICATION APPLICATION**

By

Mathaga Kihara John (B.Ed.Science)

**A Thesis Submitted in Partial Fulfillment for the Requirement for the Award of the
Master of Science Degree of the School of Pure and Applied Science of Kenyatta
University**

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DECLARATION

I, Mathaga Kihara John hereby declare that this thesis is my own original work and it has not been submitted for an award of degree or any other award in any institution

Signature.....Date.....

We approve that the work reported in this thesis was carried out by the candidate under our supervision

Professor Gerald K. Muthakia

Signature.....Date.....

Kimathi University College of Technology

Professor Thomas F.N. Thoruwa

Signed.....Date.....

Department of Energy Engineering
Kenyatta University

DEDICATION

I dedicate this study to Kihara's family and in particular to my mother Wambui and
Cyrus

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

A	Adsorbed Species
α	Alpha
q	Amount Adsorbed
x _m	Amount of Adsorbates Equivalent to Complete Monolayer Coverage
Z	Atomic Number
Φ_b	Bulky Density
M_b	Bulky Mass of the Particles that Constitute the Adsorbent in Kg
Δ	Change
C _{onc}	Concentration
⁰ C	Degree Celsius
eV	Electron Volts
Q _e	Equilibrium Adsorption Capacity (g/g)
C _e	Equilibrium Concentration of the Adsorbates
θ	Fraction of the Adsorbent Surface Sites
n	Freundlich Constant Related to the Intensity of the Adsorption
K _f	Freundlich Constant Relative to the Affinity for the Adsorbates
F	Function
γ	Gama
kJ	Kilojoules
kV	Kilovolts
kW	Kilowatts
K _L	Langmuir Constant Related to the Affinity of the Adsorbent
Q _{max}	Langmuir Monolayer Capacity of the Adsorbent
M_p	Mass of the Particles that Constitute the Adsorbent in Kg
μm	Micro Meter
M	Molarity
mol	Mole
nm	Nanometre
ρ	Para
Φ_p	Particle Density
ppm	Parts per Million
%	Percentage
P	Pressure
R ²	Regression Analysis
Φ	Relative Humidity
P/P ⁰	Relative Vapor Pressure (RH)
T	Temperature
R	The Universal Gas Constant
P ⁰	Vapour Pressure Above a Layer of Adsorbates
V _{mon}	Volume Corresponding to Monolayer Coverage
V _m	Volume in Cubic Metres
λ	Wavelength
wt.	Weight

ABBREVIATIONS AND ACRONYMS

AOCS	American Oil Chemical Society
AV	Acid Value
BE	Bleaching Earth
BET	Brunauer, Emmett, Teller
db	Dry Bulb
df	Fractal Dimension
DI	Deionized Water
g/cc	Grams per Centimeter Cubic
HCs	Hydrocarbons
Hex	Hexane
IUPAC	International Union of Pure and Applied Chemistry
Log	Logarithm
MCM	Mobil Composite Material
ml/g	Milliliter per Gram
OM	Organic Matter
PAH	Polynuclear Aromatic Hydrocarbons
PH	Potential Hydrogen
PV	Peroxide Value
RH	Relative Humidity
RPM	Rate per Minute
PSBE	Purified Spent Bleaching Earth
SBE	Spent Bleaching Earth
STDEV	Standard Deviation
STP	Standard Temperature and Pressure
SV	Saponification Value
VBE	Virgin Bleaching Earth
wt	Weight
XRF	X-Ray Fluorescence
XRFA	X-Ray Fluorescence Analysis

ABSTRACT

The cosmic limitation of high humid environment in tropic regions spurs a lot of interest to the development of low cost desiccants. Calcium chloride has been indicated as the oldest adsorbent desiccant among chemicals and gas dehydration industries. However, calcium chloride dissolution behaviour makes it difficult to be utilized well as desiccant. The first attempt to suppress deliquescence behavior for dehumidification purpose was in 1976 where silt loam was used as the host material. Further work has been presented to achieve the same goal using pure clay. The pollution effect of the spent bleaching earth (SBE) necessitated an investigation to determine whether SBE could be used to eradicate the deliquescence behaviour of calcium chloride. The spent bleaching earth was purified to remove the entrained hydrocarbons through three steps; solvent extraction using hexane, oxidation of the hexane residues using 30% hydrogen peroxide and thermal oxidation. The ratio of 1 gram spent bleaching earth to 5 ml hexane and reactivation temperature of 550 °C in thermal oxidation were established as the optimal conditions for reactivation of spent bleaching earth. Hexane was found to remove about 25% of the entrained hydrocarbons mainly oil which was characterized. The results for the characterization indicated that the oil recovered could be utilized in non-food applications such as bio-lubricant, detergents, soap and other oleochemicals. Hydrogen peroxide removed about 10% of the remaining hydrocarbons after hexane extraction and thermal treatment about 5% after the two preceding steps. Laboratory studies were conducted to assess the mixing ratio of the inorganic salt, auxiliary binder and purified spent bleaching earth in the development of the composite adsorbent. Samples with different ratios were subjected to a humid environment of 88% relative humidity, by preparing a saturated solution of potassium chromate in a sealed beaker. The samples which recorded minimum surface wetting, spalling and cracking as well as high water uptake were further subjected to multiple sorption cycle tests. For all the tests performed, sample ratio of 3 :1 :0.25 of PSBE :CaCl₂ :starch recorded the best results and was further tested for its sorption properties at different relative humidity's. Sorption properties were carried out in a humidity chamber at 11.3, 32.78, 43.16, 52.89, 75.5 and 93.58% relative humidity where the sorption capacity recorded 14.88, 17.60, 20.95, 24.40, 33.40 and 45.55% water uptake respectively. The desiccant developed was found to be effective in high moisture content and thus viable in tropic regions where such environs are common. The sorption data obtained were subjected to the Langmuir, Freundlich and Brunauer-Emmett-Teller (BET) adsorption models in order to determine the type of adsorption isotherm that best interpreted water sorption by the material. Results indicated that, water adsorption onto adsorbent developed followed BET and Langmuir type III isotherm which indicated the formation of multilayer. The sorption capacity of the adsorbent matrix developed recorded 40 to 45% water uptake which cohered with commercially available desiccant such as silica gel. Since the spent bleaching earth is normally disposed on potential land and limitations for this method of disposal is enormous, it is recommended that, oil manufacturing industries should emphasis on regenerating and re-using this waste in making products such as desiccants instead of disposing it in potential land, which they can use to preserve their products as well as sell to other consumers.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Problem

Dehumidification is a process of water removal from the atmosphere which involves absorption by liquid desiccants and /or adsorption by solid desiccants which maintains the relative humidity to the desired level. Desiccants are frequently used to protect moisture-sensitive products from water initially present during manufacturing and packaging operations as well as moisture permeating into the package over time (Kontny and Mulski, 1992; Kenneth *et al.*, 1992). Processing industries such as pharmaceutical, agricultural, food, textile, and computer chip among others uses desiccants at varying extents (Watts *et al.*, 1986). In the past forty years, the use of desiccant for dehumidification applications has expanded to new venues including hospitals, hotels, and supermarkets for building comfort as described by Ahmed (2005). The wide acceptance of desiccant technology, coupled with expanding markets for these materials has created a competitive production environment. This in turn has necessitated the air conditioning industry to continually look for improved dehumidification devices (Wang and Claridge, 2007; Florides *et al.*, 2003), by developing composite adsorbents such as calcium chloride impregnated in Silica-gel (Zhang *et al.*, 2005) and clay (Thoruwa *et al.*, 2000). These adsorbents record improved sorption properties of the host material.

Traditionally, ceramic materials dominated the desiccant market due to their availability, low cost as well as their ability to take on water, as a result of their porous construction as reported by Mooney *et al.* (1952). However, they do lack certain desirable characteristics in desiccant applications due to their low hygroscopic capacity (Likos and Lu, 2002).

Their ability to adsorb water can be enhanced by impregnating them with hygroscopic inorganic salts such as anhydrous CaCl_2 as reported by Thoruwa *et al.* (2000).

Appreciable world revenue in research is spent on moisture adsorption studies based on low cost and waste adsorbents (Likos and Lu, 2002). In the present work, studies on re-use of spent bleaching earth (clay mineral), an industrial waste from vegetable oil refineries, in the dehumidification process is investigated when impregnated with CaCl_2 to develop a composite adsorbent as well as characterization of the residual oil recovered.

1.2 Problem Statement

Dehumidification is recognized as an essential component in several industrial and agricultural operations for moisture removal, and thus considered a key factor in assuring energy efficiency and productivity. The high humidity in tropical regions, which is often over 80% and average temperature of 27 °C slows effective drying of harvested crops and makes packaging extremely difficult hence resulting to huge losses in many industries and agricultural firms. Sharp diurnal temperature changes results in condensation and resultant wetting of the grains in aerated storage and drying system, which nullifies any grain made in previous drying operations. High Relative Humidity (RH) leads to poor performance and increased respiratory diseases, hence low animal products, while in greenhouses, during winter periods, it causes decrease in plant transpiration rates and nutrient uptakes hence low productivity.

On the other hand, spent bleaching earth disposal protocol is a problem to our environment. The dissolution phenomena of calcium chloride also limit its application as desiccant material. The cosmic limitations of the high relative humidity, dissolution of

calcium chloride coupled with the spent bleaching earth disposal pollution prone method have prompted scientists to relentlessly devise dehumidifiers based on low-cost available materials.

1.3 Justification

Most parts of the tropics are characterized by high humidity, often over 80% which has vast effects on packaging of industrial products and drying of harvested crops. This has impelled the need to devise adsorbent materials that can reduce the undesired relative humidity in these regions. The inadequate electric power supply in most parts of the tropics and the high cost of fossil fuels favors the use of desiccant for dehumidification over refrigeration (Hamed, 2002).

Composite adsorbent consists of a porous host matrix with open pores and a hygroscopic substance (commonly an inorganic salt) impregnated into its pores as reviewed by Zhang *et al.*, (2005). The composite adsorbent is characterized by high hygroscopic capacity and saturated adsorption rate as compared to plain host matrix, thus recording high water uptake. Studies in the past have focused primarily on the CaCl_2 composite adsorbent based on relatively pure clay minerals (Thoruwa *et al.*, 2000; Kontny *et al.*, 1992) and silica-gel (Zhang *et al.*, 2005), in order to eradicate the dissolution phenomena of CaCl_2 . The present work investigates sorption properties of a composite adsorbent of CaCl_2 impregnated on purified spent bleaching earth (PSBE) as a remedy to the dissolution of CaCl_2 as an adsorbent as well as devise an alternative environmentally acceptable disposal protocol for spent bleaching earth (SBE).

The new adsorbent was anticipated to be of low initial cost since SBE was available waste material from oil processing industries. The use of regenerated spent bleaching earth was projected to facilitate the design of waste containment system for 600,000 plus tones of spent bleaching earth (SBE) (Mana *et al.*, 2008; Ng *et al.*, 1997) in order to circumvent the current pollution-prone disposal methods. The new adsorbent material was anticipated to be solar regenerated thus reducing dependency on electrical energy.

1.4 Objectives

1.4.1 General Objective

The general objective of this study was to investigate the water sorption properties of calcium chloride supported on purified spent bleaching earth and the feasibility of re-use of spent bleaching earth in the development of low cost adsorptive material for air dehumidification.

1.4.2 Specific Objectives

The specific objectives of this study are to;

1. Investigate properties of spent bleaching earth and by products by;
 - i. Determining; the surface composition, the ash content, the moisture content, organic matter content and the pH value of the spent bleaching earth.
 - ii. Determining; the peroxide value, acid value, saponification value, unsaponifiable matter and purity of the entrained oil.
2. Investigate the potential of purified spent bleaching earth (PSBE) in the development of solid desiccant by determining the mixing ratio of PSBE, calcium chloride and auxiliary binder that give the best adsorbent.

3. Determine the effect of the acid activation on the sorption characteristic of the adsorbent
4. Investigate the potential of the PSBE-CaCl₂ desiccant on air dehumidification by;
 - i. Determining the moisture sorption equilibrium capacity of the CaCl₂-PSBE desiccant.
 - ii. Applying Langmuir, Freundlich and BET isotherms to the adsorbent sorption data obtained to elucidate the adsorption mechanism involved.
 - iii. Comparing the sorption capacity of the CaCl₂-PSBE desiccant with silica gel
5. Determine the thermo-physical properties of the solid adsorbent.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dehumidification

Dehumidification is a process in which the moisture or water vapour or the humidity is removed from the air thus keeping its dry bulb (db) temperature constant. Like the pure humidification process, in actual practice the pure dehumidification process is not possible, since the latter is always accompanied by cooling or heating of the air. Dehumidification process along with cooling or heating is used in a number of air conditioning applications as discussed later in this section. Essentially, there are two ways in which air dehumidification may be accomplished: cooling and dehumidification process as in the case of refrigerant and heating and dehumidification process as presented by hygroscopic substances (Khemani, 2009; Sumathy *et al.*, 2003).

2.1.1 Cooling and Dehumidification Process

Using refrigeration to remove moisture from the atmosphere is the most common method for dehumidifying air that works by drawing moist air over a refrigerated coil with a small fan. Since the saturation vapour pressure of water decreases with decreasing temperature, the water in the air condenses and drips into a collecting bucket. The air is then reheated by the warmer side of the refrigeration coil (ASHRAE, 1983). This method is effective in dehumidifying comparatively warm air with high humidity ratio to produce air with a dew point above 5 °C. The major disadvantage of dehumidification by refrigeration is high energy requirements and ice building up on the coils at temperatures below 0 °C (Sumathy *et al.*, 2003). However, combination of sorption dehumidification

and refrigeration unit produces the desired air humidity and dew points at relatively low cost (Sumathy *et al.*, 2003; Srihirin *et al.*, 2001; Ashrae, 1983).

2.1.2 Heating and Dehumidification Process

Desiccants are materials with high affinity for water and hence scavenge moisture from the atmosphere (Zhang *et al.*, 2003; Dai *et al.*, 2001). Dehumidification using desiccants on the other hand is a process by which liquid or solid sorbent materials extract moisture from the surrounding air. Typically, the sorbent moisture content is a function of the relative humidity (RH) of the surrounding air as presented by Ahmed (2005). The driving force for moisture absorption is the vapour pressure differential attributed to lower vapour pressure on the sorbents compared to the surrounding air. When exposed to low moisture content, low vapour pressure builds which results in attainment of equilibrium upon exposure to high RH environment. Virtually, all hygroscopic materials exhibit desiccant behavior but the term desiccant is reserved for materials whose behavior can be exploited to produce some practical and useful result (Zhang *et al.*, 2003; Kontny *et al.*, 1992).

Two major categories of desiccant exist namely, adsorbent and absorbent. Absorbent are liquid sorbents such as lithium chloride glycol solution, lithium bromide, concentrated sulphuric acid and calcium chloride solution among others. Absorbents undergo a chemical change as they attract and retain water vapour due to the formation of the hydrogen bonds (Factor and Grossman, 1980). Adsorbent materials on the other hand hold water molecules in pores at their surface and no chemical change results (Mei *et al.*,

1979). Silica-gel, molecular sieves, activated alumina, zeolites, activated charcoal and composite adsorbents are good examples of adsorbent materials.

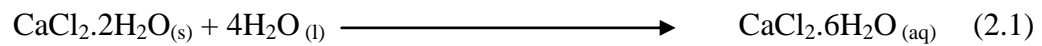
2.1.3 Merits and Demerits on use of Adsorbents over Absorbents

Removal of moisture from air at atmospheric pressure using both solid and liquid desiccants constitutes sizeable market in chemical, equipment manufacturing and processing industries. However, solid desiccants are more preferred over liquid due to the following properties; high drying potential, high energy storage, high capability in regeneration and continual use over a longer lifespan, high dissipation of hydration heat, exhibition of lower pressure drop on passing of air through a desiccant bed, ease in handling due to their solidity nature and relatively low dehumidification costs when regenerated with solar energy (Zhang *et al.*, 2005; Thoruwa *et al.*, 2000). In spite of the above advantages, solid desiccants have their own short comings which include; bulkiness, high cost of production or fabrication and relatively high regeneration energy requirements. The following study addresses the above shortcomings of solid desiccants in that, the material used is a waste material which reduces the cost of production and on regeneration, the adsorbents could be solar restored.

2.2 Calcium Chloride Composite adsorbents

Composite adsorbents are materials made up of a porous host matrix and hygroscopic salts such as CaCl_2 impregnated in their pores (Aristov *et al.*, 1996a, b). The composite adsorbents have high hygroscopic capacity since their physical structure takes an immediate position between solid adsorbent and pure hygroscopic salt as observed by Zhang *et al.* (2005) and Jia *et al.* (2007). The adsorbent sorption is characterized by three sorption properties; solid adsorption by the host matrix and solid anhydrous salt, liquid

absorption by the aqueous solution formed when salt dissolves in the absorbed moisture and finally chemical reaction. Industrial calcium chloride is essentially dehydrating ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). Armstrong and Bruswitz (1984) indicate that CaCl_2 is one of the oldest absorbent desiccants among chemicals and gas dehydration industries. It exhibits deliquescent behavior on exposure to water vapor to form a supersaturated solution as represented in equation 2.1 (Armstrong and Bruswitz 1984).



Sorbents mixture of silt loam with CaCl_2 proves essential in producing dehumidified air for aeration of grains under the humid tropics conditions (Odigboh, 1976). The sorbent placed in a packed bed indicated the capability of reducing RH from 85 to 32% and regeneration at temperatures as low as 27 °C. CaCl_2 -Clay composite have also been tested and proved to have an enhanced performance (Thoruwa *et al.*, 2000). Physicochemical properties based on classical kinetics and adsorption theories such as Polanyi-dubinin for the desiccant materials are also in literature (Liu and Wang, 2003; Aristov *et al.*, 2002). Composite adsorbents thus have spurred investigation on other micro porous materials due to their improved performance in comparison with micro porous non-impregnated adsorbents (Jia *et al.*, 2007; Zhang *et al.*, 2005).

Thoruwa *et al.* (2000) developed a clay- CaCl_2 adsorbent material with a mixture ratio of 1:3:0.44 of calcium chloride, Kaolinite and Vermiculite, respectively. The desiccant developed was found to exhibit a maximum moisture sorption of 45% under an 81% RH static environment and a moisture sorption of 8 to 11% dry bulb (db) under dynamic conditions with air entering at 30 °C and 85% RH over a period of 12 hrs. The desiccant

was found to be regenerated in 4 to 6 hrs at 50 °C. Three clay calcium chloride desiccants were developed and tested for moisture sorption and regeneration characteristics at 25 °C / 85% RH and 50 °C / 20% RH respectively. This study showed that the sorbent had maximum moisture sorption ranging from 30 to 40% (db) which were comparable to commercially available desiccants at an estimated production cost of 1/9th that of silica gel desiccant. Over one year of continuous testing, Kaolinite based composite adsorbent did not have substantial decrease in performance or structural integrity and hence the author settled on this particular material.

Aristov *et al.* (2000) and Tokarev *et al.* (2002) studied composite desiccant based on calcium chloride. Aristov *et al.* (2000) impregnated a sample of expanded vermiculite with 40% (wt) solution of CaCl₂. This sample was found to contain 57.3% calcium chloride content when dried. Its sorption isobars, isostere, and isotherms at varying temperatures and vapour pressures were determined. It was shown from this study that crystalline hydrates were formed in the pores of the vermiculite.

Tokarev *et al.* (2000) developed a desiccant consisting of calcium chloride in a matrix of Mobil Composite Material (MCM). The dry MCM was impregnated with saturated solution of calcium chloride until the pores were filled. The material contained 37.7% (wt) content of calcium chloride when dried. This desiccant recorded a moisture sorption characteristic of 70 to 75 % (db) when exposed to 70% RH. The adsorbent could be regenerated at temperatures of 70 to 120 °C. Aristov *et al.* (2002) carried a separate study on different combination of silica gel and inorganic salts and performed experiments to determine the moisture sorption properties. The composite sorbent that performed well in

this study over the static testing condition constituted of silica gel with an average pore size of 7.5 nm and calcium chloride with a final salt content of 33.7% (db). The adsorbent was found to release almost all sorbed moisture at 110 °C and to perform well even at regeneration temperatures as low as 60 °C.

Zhang *et al.* (2005) has worked and reported on a composite desiccant material which consisted of silica gel and calcium chloride. The purpose of the composite material developed by Zhang *et al.* (2005) group was to alleviate the dissolution phenomena of the calcium chloride in the absorbed water, which occurs after the formation of solid crystalline hydrate $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The author applied silica gel to corrugated paper which was then immersed in a 10% by weight calcium chloride solution for 2 hrs and then dried. Hygroscopic capacity of the composite material was monitored over time and a comparison made with other desiccant materials such as silica gel and calcium chloride. The material was also installed on a desiccant wheel containing silica gel. The new desiccant recorded an improvement of up to 50% as compared to silica gel alone at regeneration temperature of 60 to 120 °C and inlet conditions varying between 27.5 to 35 °C and 39.0 to 63.8% RH. The flow rates used for the experiments were 790 and 263 m^3/hr for the process and regeneration air, respectively.

Jia *et al.* (2007) measured and compared performances of two desiccants wheels. One of these desiccant wheels was coated with silica gel and the other with a composite desiccant material made with silica gel and lithium chloride. The author determined that the optimal regeneration temperature for the composite desiccant wheel was 20 °C lower (80 °C) than the wheel that used silica gel (100 °C).

Tretiak and Abdallah (2009) have determined the sorption and desorption properties of 3:0.44 mixture of commercial kaolin clay and vermiculite sorbent for use in a residential environment. Water was added to the mixture to form a paste which was moulded into spherical sorbents of approximately 16.5 mm and dried. After cooling, the clay spheres were submerged in a saturated solution of calcium chloride for one hour and dried. The final calcium chloride content of the desiccant was found to be 18.5% (db) effective.

Based on the above literature on composite desiccants, most of the studies report an improvement on the performance and structural integrity of calcium chloride impregnated on clay host matrix. Spent bleaching earth has been shown to regain the properties of the virgin bleaching earth once regenerated (Wachira *et al.*, 2005). The regenerated spent bleaching earth has been utilized in different sorption application as discussed later in 2.4.4 but none has been reported on the sorption of moisture by the material or desiccant development. The present work reports the sorption results of composite desiccant where PSBE was used as a host matrix for the CaCl_2 salt.

2.3 Dehumidification Applications

Dehumidification has a wide application ranging from preservation of stored material, industrial processes, condensation prevention and icing, humidity control in air-conditioned spaces such as offices and supermarkets. The presence of moisture in the manufacturing industries, storage areas such as; silos, warehouses and packaging areas of manufactured products leads to excessive losses due to corrosion damages and loss of products. Preservation of materials by dehumidification is effectively accomplished in these areas by the use of dehumidification systems by employing liquid and solid desiccants which extract the moisture and curb the corrosion processes. Other operations

relying on the similar systems for application include commercial storage operations such as beer making industry, meat storage, pharmaceutical packaging, penicillin processing as well as storage of; machine tools, candy, food products, furs, furniture, seeds, paper work stock, electronics and chemicals (Zhang *et al.*, 2003).

Many industrial processes require low humidity environment during processing which is usually accomplished by the use of desiccant dehumidifiers. Chemicals, pharmaceuticals, hygroscopic materials, dry food products such as milk, drink mixes, fertilizers, animal food, batteries, laminated glasses, hermetic compressors, electronic components, motors and transformers are among the products which are processed and produced in low humidity environments where dehumidification applications are practical and useful (Hamed, 2005).

The air conditions desired for human comfort range between 40 to 60% RH and 20 to 22 °C temperatures (Croome-Gale and Roberts, 1975), which are normally maintained through air-conditioning units by employing refrigeration systems as reported by Zhang *et al.* (2005) and Thoruwa *et al.* (2000). Space conditioning in high occupancy areas such as supermarkets, offices and other places of assembly is paramount since the latent heat load is much larger than the cooling load. In these areas, humidity control is effectively achieved at minimum cost by using desiccant dehumidifiers coupled to refrigeration system (Zhang *et al.*, 2003).

Liquid desiccants operated systems employing adsorbents such as lithium chloride impregnated on a disc or drum or wheel render their application mostly in air dehumidification and space-conditioning in commercial and residential applications

(Matsuki and Saito, 1988). Liquid desiccants operated dehumidifiers have in particular been successful in space conditioning, especially in hospitals, nursing homes and animal laboratories, providing not only improved humidity control, but also bacteria control (Wilkinson *et al.*, 1988). Similarly, solid desiccants such as silica gel or activated alumina placed on a rotary wheel or in a packed bed render their application useful mostly in air dehumidification and space-conditioning. Solid desiccants have been proven suitable for cooling of cold storage display in supermarkets as reported by Ahmed (2005). The process is enhanced through shifting of the cooling load to the ambient air while at the same time extracting moisture from the air around the display storage.

Desiccant technology applications in agricultural and food industry are a recent venture which has accelerated the need to explore more materials that can be exploited for this purpose. Odigboh (1976) devised dehumidifier material based on CaCl_2 -loam soil composite for dehumidified aeration of food grains under the humid tropical condition. Moreover, Fletcher (1980) placed CaCl_2 on a contactor wheel in order to produce dehumidified air for grain drying. Desiccants produce dehumidified air in the drying operations as well as creating drying potential through sensible heating and the two phenomena creates significant drying potential at reduced temperatures suitable for thermally sensitive biological products (Miller, 1985). When desiccants absorb water from the air, the process is usually exothermic hence some energy in form of heat is released which provides drying potential instead of drying using other heating mechanisms. All these applications of dehumidification process justifies the need to investigate more low cost adsorbent materials such as PSBE.

2.4 Clays

Clays to Geologists are weathered sedimentary rock particles with diameters 3.9 μm or less. They are so defined as disperse system of colloidal products of weathering in which the secondary mineral particles dimensions 2 μm and less predominate (Gastuche *et al.*, 1962; Grim, 1986). Clays have great variation in chemical composition and colour, but most are composed of silica, alumina and water (Van Thoor *et al.*, 1965). All clays have the following characteristics in general: When moist they are plastic; when dried at moderate/ ambient temperature, they become hard, rigid solid but regain their solubility when moistened; when dried at relatively high temp, they become mechanically strong and permanently non-plastic as reported by Van Der Marel and Beutelspacher (1979).

2.4.1 Clay Minerals

There are four commonly naturally occurring clay minerals namely Kaolinite, Montmollironite, Bentonites and ball clays. The kaolin consists of closed packed regular alteration of Si-O and Al-O sheets as represented by Figure 2.1 (Grim, 1986; Grimshaw, 1971; Gastuche *et al.*, 1962). Montmorillonite are alumino-silicate mineral in the group of Smectite, which are characterized by an expanding lattice except vermiculite. Their lattice consists of Al-O sheets sandwiched between Si-O sheets with inter-lamellar spaces punctuating each set of the sheets as observed in Figure 2.2 (van der Marel and Beutelspacher, 1979; Grimshaw 1971). The space allows water molecules into the structure causing the characteristic swelling on exposure to moisture as reported by Van Thoor *et al.*, (1965). Naturally they contain trace impurities of calcite, feldspar, zinc blends, apatite, sphenes and lemons with variable amounts of Mg and Fe replacing part of Al in the silicate structure giving the formulae; $(\text{Al, Mg, Fe})_4\text{Si}_8\text{O}_{20}(\text{OH})_4$ and

resulting in a net charge on the material. This charge is neutralized by association with exchangeable cations; Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and H^+ (van der Marel and Beutelspacher, 1979).

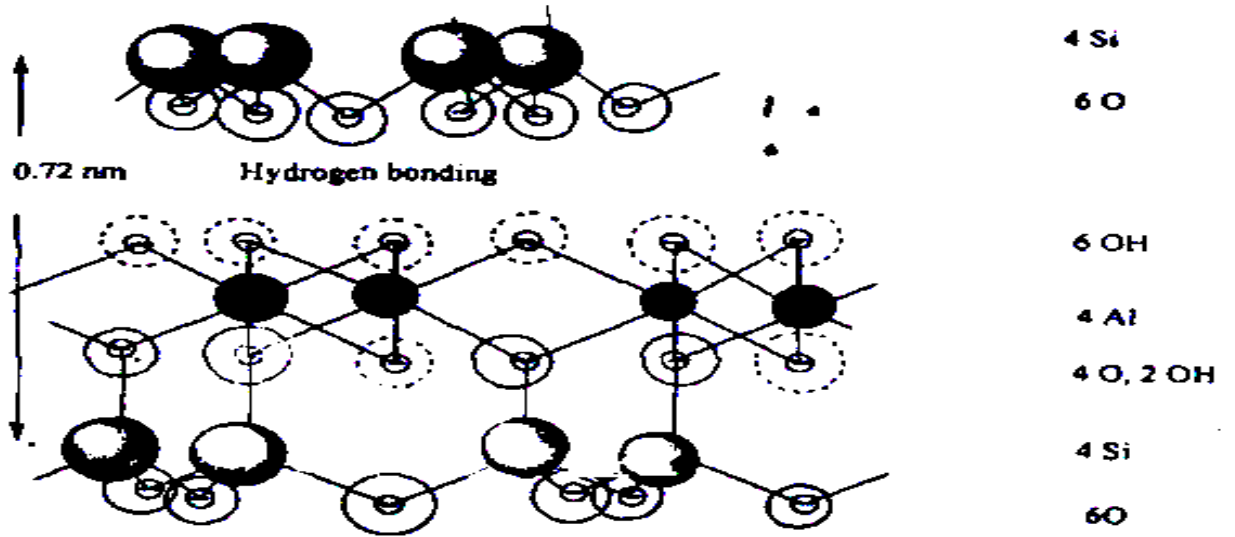


Figure 2.1: Kaolinite Structure

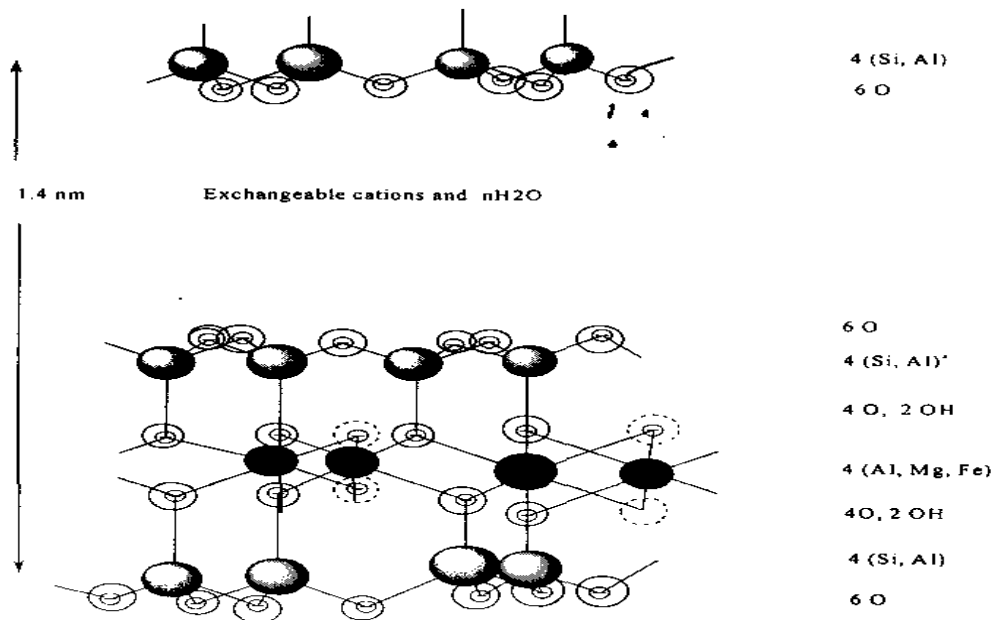


Figure 2.2: Montmorillonite Structure

Bentonites on the other hand are impure montmorillonite which are highly colloidal, plastic and possess unique characteristic of swelling several times over their origin volume when mixed with water (Watts *et al.*, 1986; Van Der Marel and Beutelspacher, 1979). Two types of bentonites do exist, Wyoming which carry Na^+ as the principal exchangeable cation and those that carry Mg^{++} as exchangeable cation and possess oil decolourization potential (Low *et al.*, 2003; Folleto *et al.*, 2002). Fullers earth are type of montmorillonite that have capacity to sorb colour, metal ions and other impurities from oil (Mana *et al.*, 2007; Low *et al.*, 2003; Ng *et al.*, 1997), they are generally used as universal oil bleaches. Their chemical and physical properties are presented in Table 2.1.

Table 2.1: Properties of Fullers Earth (Al-zahrani *et al.*, 2000)

Properties of Fullers Earth (Bleaching Earth)			
Physical Properties		Chemical Analysis	% w/w
Apparent Bulk Density [g/cc]	0.99	Silicon Oxide	64
Free Moisture (2hr, 110 °C) [%]	10 to 12	Aluminium Oxide	16
Loss on Ignition (Pre dried, 2hr, 1.0 °C) [%]	6 to 8	Iron (III) Oxide	1.20
pH (10% Suspension, Filtered)	5 to 5.3	Magnesium Oxide	2.10
Acidity [Mg KOH/g]	< 1	Calcium Oxide	1.20
Surface Area (B.E.T.) [m ² /g]	210	Sodium Oxide	0.00
Micro Pore Volume 0-80 nm [ml/g]	0.46		

2.4.2 Bleaching Earth

Bleaching earth refers to acid-activated bentonites, montmorillonite, or smectite clays in form of finely divided ground powders which is commonly used to sorb coloured pigments, such as carotenoids and chlorophyll as well as colourless contaminants such as phospholipids and hydro peroxides from edible and inedible oils (Al-Zahrani *et al.*, 2000, Ng *et al.*, 1997). They are essentially montmorillonite and to a lesser extent attapulgites.

The latter are similar to montmorillonite consisting inter-lamellar spaces in their structure as shown in Figure 2.3.

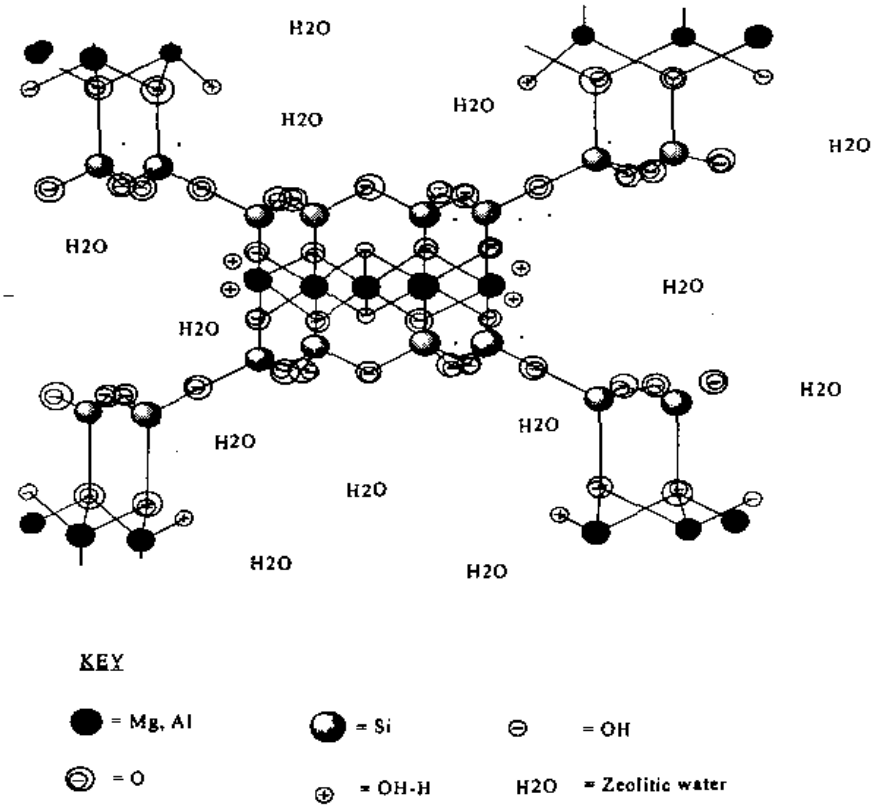
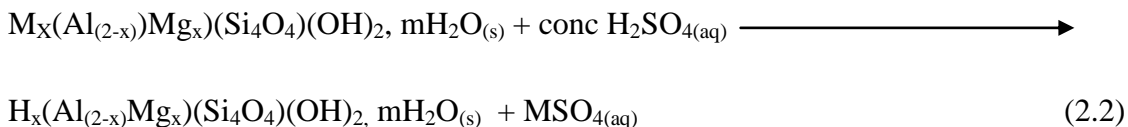


Figure 2.3: The Structure of the Attapulgites

The clays are usually reactivated at 200-300 °C and ground to various sizes for bleaching applications. The activity of the montmorillonite is enhanced by acid activation (Al-Zahrani *et al.*, 2000). Similarly, natural bentonites have limited sorbing capacity and hence are acid-activated by treating them with hot mineral acid solution such as H₂SO₄ or HCl where the hydrogen ions attack the alumino silicate layers via the interlayer region as presented by equation 2.2 (Tylor and Jonkins, 1987). This attack alters the structure, chemical composition and physical properties of the clay by exchanging Ca⁺⁺ and Mg⁺⁺

with H^+ which are good leaving group thus increasing the adsorption capacity (Wang and Lin, 2000; Mokaya *et al.*, 1993).



2.4.3 Bleaching of Edible Oils

Industrial manufacture of edible oil undergoes through four major processes namely: extraction, deodorization, bleaching, and refining. The extraction processes is usually realized by the use of solvent extraction where hexane is generally employed. The deodorization process involves the removal of the bad odour from the extracted oil. Bleaching process which is the third process refers to the adsorptive cleansing of edible oils; simply, it is the purification stage as reviewed by Patterson (1992). Many methods exist in oil bleaching including; alkali treatment and oxidative bleaching, hydrogenation and heat treatment at 220 °C. However, on an industrial scale, acid activated calcium montmorillonite clay commonly referred to as bleaching earth (BE) is prioritized in removing a variety of undesirable impurities which would otherwise impart colour, odour and taste to the refined product (Pollard *et al.*, 1993). The impurities include chlorophyll, β -carotene (and their derivatives), residual soaps, fatty acids, phosphatides and trace metals as reported by Pollard *et al.* (1993). Activated carbon is also periodically used in the admixture with virgin bleaching earth for the removal of trace quantities of polynuclear aromatic hydrocarbons (PAH) from edible oils. These contaminants, some of which are suspected human carcinogens, are sufficient to be of concern to edible oil processors (Patterson, 1992).

Bleaching processes employs two techniques namely; the percolation method in which the oil is filtered through granular product of 250 to 200 μm (or 10 to 60 mesh) essentially at low temperatures whereby the coloring matter get adsorbed by the soil as the oil passes through. Contact processes in which the oil is put in contact with finely ground clay of about 74 μm (or less than 200 mesh) for predetermined period of time to equilibrate. Filter pressing operation then separates the oil at temperatures in the range of 150 to 300 $^{\circ}\text{C}$ as reviewed by Wambu *et al.*, (2009). Over 200,000 tonnes of the bleaching earth are utilized globally by oil manufacturing industries in this stage of processing annually (Low *et al.*, 1998).

2.4.4 Spent Bleaching Earth (SBE)

Spent bleaching earth (SBE) is the filter cake obtained from the bleaching process which contains impurities adsorbed from crude oil (Wachira *et al.*, 2005; Patterson, 1989) with considerable quantities of entrained oil that is quantified approximately to 30 to 40% as reported by Wachira *et al.* (2005). Its disposal protocol poses an acute problem of management and storage. The residual oil in these principal solid waste products can rapidly oxidize to the point of spontaneous ignition as a result of clay-catalyzed auto-oxidation reactions (Pollard *et al.*, 1993).

Direct landfills are the most common current mode of disposal particularly in Kenya as shown in figure 2.4, which results in severe pollution problems (Wambu *et al.*, 2009). With a growing concern for the safe disposal of catalysts (McDermott *et al.*, 1989), a re-evaluation of waste management options for this material is paramount, which promotes the urgency to innovate other adsorptive purposes in addition to the oil recovery for other practical purposes (Folletto *et al.*, 2002).



Figure 2.4: Disposal site for spent bleaching earth in Mlolongo (Kenya)

The re-use of SBE which is an example of waste management strategy and the concomitant recovery of residue oil has been a recurrent focus of research within the edible oil industry for nearly 60 years (Patterson, 1989). Spent bleaching earth regeneration has been attempted by solvent extraction (Cheah and lion, 2002), solvent extraction followed by thermal processing (Boukerroi and Ouali, 2000), preliminary acid impregnation followed by thermal processing (Mana *et al.*, 2006; Wang and Lin, 2000), and the product obtained reported to possess similar properties as virgin bleaching clays. The regenerated spent bleaching earth (PSBE) has then found numerous applications such as removal of basic dyes from aqueous solution (Mana *et al.*, 2007), biological treatment

and land farming, fuel supplements (Daido, 1987), metals and organic group adsorption (Wambu *et al.*, 2009; Low *et al.*, 2003; Mehmet *et al.*, 2003), cement manufacture (Wachira *et al.*, 2005) among others.

2.4.5 Properties of Residual Oil

Oils and fats serve as a rich source of dietary energy. They contain fatty acid components that are essential nutrients and their functional and textural characteristics contribute to the flavor and palatability of many natural and prepared foods. In the method of analysis of oils and fats, the determination entails iodine value, saponification value, unsaponifiable matter, acid value (AV), calorific value and peroxide value (PV). This analysis assists in the identification as well as test for edibility of most of the oils and fats (Aziz *et al.*, 2001).

Table 2.2: Iodine Values of some Fats and Oils

Group	Examples	Iodine value
Waxes	-	Vey small
Animals fats	Butter, lard	30-70
Non-drying oil	Olive, almond	80-110
Semi-drying	Cotton seeds oil, sesame	80-140
Drying oils	Linseed oil, sunflower oil	125-200

(Aziz *et al.*, 2001)

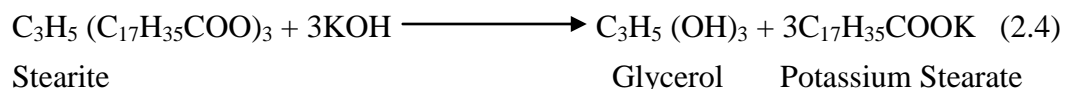
Iodine value refers to the weight of iodine absorbed by 100 parts by weight of the sample. Iodine value is a measure of the degree of unsaturation where the glycerides of the unsaturated fatty acids present unite with a definite amount of iodine. Iodine value is the most useful and easily determined figure for identifying oil or at least placing it into a particular group. The higher the iodine value, the greater the degree of unsaturation,

consequently, the greater is the liability of the oil or fat to become rancid by oxidation. Some iodine values for some fats and oil are provided in Table (2.2). Iodine value is obtained from;

$$Iodine\ value = \frac{(b-a) \times 1.269}{wt\ (in\ g)\ of\ sample} \quad (2.3)$$

Where “b” is the average titrant in millimeter (ml) of the blank titration while “a” is the titrant in ml of the sample as described by Kaimal *et al.* (2002).

Saponification value is the number of milligram of potassium hydroxide required to neutralize the fatty acids resulting from the complete hydrolysis of 1g of the sample. Soap is formed during saponification.



The esters of the fatty acids of low molecular weight require more alkali for saponification, so that the saponification value is inversely proportional to the mean of the molecular weights of the fatty acids in the glycerides present. Since many oils have somehow similar values, the saponification value is not generally useful in identification purpose as the iodine value. However, it is important in identification of the coconut oil (SV 248 to 265), palm-kernel oil (SV 230 to 254) and butterfat (SV 225), which contains a higher proportional of the lower fatty acids. Saponification value is obtained from the relation given below

$$SV = \frac{(b-a) \times 28.05}{wt\ (in\ g)\ of\ sample} \quad (2.5)$$

“b” is the average titrant in millimeter (ml) of the blank titration while “a” is the titrant in ml of the sample (Kaimal *et al.*, 2002).

Unsaponifiable matter refers to the material present in oils and fats after saponification by caustic alkali and extraction by a suitable organic solvent. These materials include hydrocarbons, higher alcohols, oil-soluble vitamins and sterols (e.g cholesterol, phytosterols). Most oils and fats of normal purity contain less than 2% of unsaponifiable matter.

Acid value also known as free fatty acids is the number of mg of alkali required to neutralize the free acidity in 1g of the sample. Acid value is a measure of the extent to which the glycerides in the oil have been decomposed by lipase or other action. Rancidity is usually accompanied by free fatty acid formation; the determination is thus used as a general indication of the condition and edibility of oils (Che Man *et al.*, 2005). Acid value is given by the relation 2.6.

$$AV = \frac{\text{titration (ml)} \times 5.61}{\text{wt of sample used}} \quad (2.6)$$

Peroxide value is another property of oils and fats which is a measure of the peroxide contained in the oil. Peroxide value is usually determined volumetrically where the method depends on the reaction of KI in acid solution with the bound oxygen followed by titration of the liberated iodine with sodium thiosulphate as presented in equation 2.7(Che Man *et al.*, 2005).

$$pv = \frac{(b-a)T}{m} \times 10^3 \text{ mEq/kg} \quad (2.7)$$

2.5 Sorption Studies

Adsorption is a process whereby materials interact by physical forces with a surface thereby causing a layer of the material to adhere to the surface. It is essentially the accumulation of materials at the chemical interfaces (Grimshaw, 1971; Van Thoor *et al.*, 1965) or generally the process in which a single or a group of ions, molecules or compounds get accumulated on the surface of another solid or liquid. The surface, typically referred to as adsorbent, in most cases will be a solid such as silica gel, alumina gel, charcoal, or sometimes a liquid such as surfactant water surface. The substances adsorbed are referred to as adsorbates which can be metal ions (Wambu *et al.*, 2009), gaseous molecular compounds such as H₂O, SO₂ etc. The relationship between the concentrations of the adsorbed material in the contacting fluid with adsorbent is called adsorption isotherm (Ruthvan, 1984; Mantell, 1951). Based on the extent of attraction between the adsorbent and adsorbates, the adsorption process can be categorized into two types: physical adsorption also known as van der Waal adsorption and chemisorption.

Adsorption which results from the van der Waal force of interaction is known as physical adsorption or van der Waal adsorption. It is a non-specific, diffuse and non-stoichiometric type, based on van der Waal (Mantell, 1951). In this type of adsorption, the process heat is of the order of 20-40 kJ/mol. This is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance and rapidly established. Thus, it is very effective particularly at a temperature close to the critical temperature of a given fluid. The process of physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, making

the process exothermic. Physical adsorption can either be monolayer or multi-layer adsorption.

Chemisorption on the other hand is the chemical interaction or electrostatic force of attraction that occurs between the adsorbent surface and adsorbate molecules. It is a process that generally occurs at the inner core specific charge site of the adsorbent and is electronic and stoichiometric in nature. The process is irreversible with high enthalpies of order 40 to 400 kJ/mol. It is associated with appreciably high activation energy and therefore termed as activated adsorption which is relatively low as compared to the former. The irreversibility of this process is ascribed to the strong electrostatic force of interaction between the adsorbent and adsorbates molecules. Chemisorption occurs usually at temperatures much higher than the critical temperature and by contrast to physical adsorption, is a specific process, which can only take place on some solid surface for a given fluid. Chemisorption leads to monolayer adsorption (Maron *et al.*, 1956). Under favorable conditions, both processes can occur simultaneously or alternately (Os'cik, 1982).

Various forms of naturally occurring physical adsorbents and materials of polymeric nature as well as chemicals adsorbents have been shown to be effective dehumidifiers (Tretiak and Abdallah, 2009). The adsorption process has many merits such as: low cost of adsorbent, easy availability of adsorbent, utilization of industrial, biological and domestic wastes as adsorbent, low operation cost, ease of operation compared to other processes, re-use of adsorbent after regeneration, environmental friendly, cost effective

and technically feasible alternative due to utilization of waste materials from the industry (Zhang *et al.*, 2003).

Due to ease of operation, adsorption techniques have been employed widely in dehumidification process. Clay, which is cheap and easily available, is used widely either as such, in treated form or mixed with hygroscopic salts such as calcium chloride to remove water moisture in air (Tretiak and Abdallah, 2009; Willium and Lu, 2002, Odigboh, 1976). Sorption studies are carried out mostly in batch scale and various adsorption parameters affecting the overall process studied. Use of silica gel and calcium impregnated in silica gel composite was reported (Jia *et al.*, 2007; Zhang *et al.*, 2005) to be effective adsorbent for dehumidification purpose due to its high performance and high sorption properties.

Silica gel desiccants are made from soda ash and sand, which are subjected to a furnace or hydrothermal process. The mixture is then milled, dissolved and granulated to form sodium silicate. Sulphuric acid is then added to form the gel which is then washed, dried and then graded. This product has constantly been used as commercial desiccant because of its large specific surface area, high adsorption capacity and special chemical properties (Zhang *et al.*, 2005). The physical properties of the silica gel depend on the pore size, pore distribution and number of surface oxygen groups. These physical and chemical properties of the silica gel have been found to be altered and improved by the impregnation of the calcium chloride which results to a composite that have sorption properties of the two ingredients as observed by Zhang *et al.* (2005) and Kontny *et al.* (1992).

2.5.1 Vapor Adsorption Equilibrium

Adsorption equilibrium is established after considerable contact of the vapors with the adsorbed surface and can be represented in the general form as shown in the equation 2.8 (Os'cik, 1982)

$$F(A, P, T) = 0 \quad (2.8)$$

$$A = F(P, T) \quad (2.9)$$

Where P is the pressure, T is the temperature and A is the adsorbed species. Since this equation depends on three parameters, we can consider adsorption equilibrium in three ways as presented in equations 2.10, 2.11 and 2.12.

$$A = f(P)_T \text{ If } T=\text{constant which is adsorption isotherm} \quad (2.10)$$

$$A = f(T)_P \text{ If } P=\text{constant which is adsorption isobar} \quad (2.11)$$

$$P = f(T)_A \text{ If } A=\text{constant which is adsorption isostore (Os'cik, 1982)} \quad (2.12)$$

In this study, experiments were carried out at constant temperature and the adsorption isotherms were studied from the sorption data obtained based on the vapour adsorption equilibrium presented in equation (2.9) above.

2.5.2 Sorption Equilibrium Analysis Models

Adsorption isotherms commonly known as equilibrium analysis models helps in determining the properties of the adsorbents such as pore volume, pore size or energy distribution and specific surface area. The isotherm curve can also be utilized to obtain information concerning the desorption mechanism strictly connected with interaction between the adsorbent and adsorbates molecules. Therefore, the efficiency of an industrial adsorbent can be assessed through this curve. The correct interpretation of

experimental adsorption isotherm can be realized in terms of some mathematical equations called adsorption isotherm model equations. Such equations are derived assuming an ideal physical model for the adsorption system. The adsorption isotherm thus developed provides useful information for estimating performance in a full scale process stream such as calculation of uptake (q_e) at equilibrium, which has a majority impact on the process economy and prediction of the relative performance of different types of adsorbents.

Before 1914, only a few theoretical interpretations of adsorption isotherms were known and used. But thereafter, a number of isotherm equations were proposed by different scholars. Some of those isotherms model equations that have been frequently adopted are: Henry law, Freundlich, Langmuir, Temkin and the Brunauer-Emmet-Teller (BET) adsorption isotherms as observed by William and Lu (2002).

2.5.2.1 Henrys Adsorption Isotherm

English chemist William Henry found experimentally that, for real solutions at low concentrations, the vapour pressure of the solute is proportional to its mole fraction. In Henry's law, the amount q , of a substance adsorbed varies directly with equilibrium concentration denoted by C_{conc} in the equation 2.13, where k_1 denotes the Henry's constant of proportionality.

$$q = k_1 C_{conc} \quad (2.13)$$

2.5.2.2 Freundlich Adsorption Isotherm

Freundlich adsorption isotherm was proposed by Boedecker in 1895 (Dabrowski, 2001) as an empirical equation. Later Freundlich made some useful modification as a result of

which, it assumed great importance (Freundlich, 1926). Freundlich isotherm assumes absolute Physical adsorption without any chemical interactions between the adsorbed particles and adsorbates. The Freundlich adsorption isotherm model can be written as given in equation 2.14 (Freundlich, 1926)

$$Q_{eq} = K_f C_{eq}^{1/n} \quad (2.14)$$

Where Q_e is equilibrium adsorption capacity (g/g), C_e is the equilibrium concentration of the adsorbates in the enclosed environment, K_f is a constant relative to the affinity for the adsorbates and value n is a constant related to the intensity of the adsorption. Introducing log to equation 2.14, we obtain linearized Freundlich equilibrium isotherm model given by equation 2.15 which is used to fit the data obtained and find whether it correlates to the model (Dabrowski, 2001).

$$\log Q_{eq} = \text{Log } K_f + 1/n \log C_{eq} \quad (2.15)$$

Where, K_f and n are Freundlich constants related to the affinity of the adsorbent for the adsorbates and the intensity of adsorption respectively (Dabrowski, 2001).

2.5.2.3 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm (Langmuir, I., 1918) is based on the following assumptions: Fixed number of adsorption sites (at equilibrium, at any temperature, a fraction of the adsorbent surface sites (θ) is occupied by adsorbed molecules and the rest ($1 - \theta$) is free), all sorption processes are homogeneous, there is only one sorbate, one sorbate molecule reacts with only one active site, no interaction between the sorbate species and monolayer surface phase is formed, and adsorption on one site does not affect other adsorption site.

The equation proposed by Langmuir is universally applicable to chemisorptions with some restrictions involving physical adsorption. This equation is applicable to the physical or chemical adsorption on solid surface with one type of adsorption active centre. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions within any given system. The Langmuir equation is given by relation 2.16.

$$\frac{x}{x_m} = \frac{BP}{1+BP} \quad (2.16)$$

The quantity adsorbed in the solid is given by x when the pressure is P , x_m represents the amount of adsorbates equivalent to complete monolayer coverage and the coefficient B is constant at constant temperature (William and Lu, 2002).

For the purpose of this study, the results were fitted in the double reciprocal Langmuir isotherm represented by the relation 2.11(William and Lu, 2002).

$$\frac{1}{Q_{eq}} = \frac{1}{K_1 Q_{max} C_{eq}} + \frac{1}{Q_{max}} \quad (2.17)$$

Where, Q_{eq} is the equilibrium concentration of adsorbates in adsorbent, C_{eq} the equilibrium concentration of saturated adsorbates, K_1 refers to Langmuir constant related to the affinity of the adsorbent and, Q_{max} is the Langmuir monolayer capacity of the adsorbent

2.5.2.4 Brunauer-Emmett-Teller (BET) Isotherm

Langmuir adsorption isotherm, although simple, has limited application. Thus, attempts have been made to generalize the Langmuir equation by taking into account lateral interaction among adsorbed molecules, their mobility and the energetic surface homogeneity of the solid. At first the BET isotherm was derived from kinetic

considerations analogous to those proposed by Langmuir while deriving the monomolecular adsorption isotherm. While the Langmuir adsorption model is valid for a single layer adsorption, the BET model represented sorption isotherm reflecting multi-layer adsorption. Both models may be deduced from either kinetic or thermodynamic consideration of adsorption (Langmuir, 1918; Brunauer, 1938).

The BET model assumes that a number of layers of adsorbates molecules form at the surface and that the Langmuir equation applies to each layer. A further assumption of BET model is that a given layer need not complete formation prior to initiation of subsequent layers. The equilibrium conditions will therefore involve several types of surfaces or number of molecular layers in each surface site, which causes the isotherm to rise indefinitely to some saturated value at high pressure lieu to leveling off as observed in Langmuir isotherms. The BET isotherm is the most widely used isotherm dealing with multilayer adsorption that follows the relation 2.18 (Brunauer, 1938).

$$\frac{V}{V_{\text{mon}}} = \frac{Cz}{(1-z)\{1-(1-C)z\}} \quad (2.18)$$

$$z = \frac{p}{p^0} \quad (2.19)$$

where p^0 is the vapour pressure above a layer of adsorbates that is more than one molecule thick and resembles a pure bulk liquid, V_{mon} is the volume corresponding to monolayer coverage and C is constant which is large when the enthalpy of desorption ($\Delta_{\text{des}} H\sigma$) from a monolayer is large compared with the enthalpy of vaporization ($\Delta_{\text{vep}} H\sigma$) of the liquid adsorbates given by relation 2.20. R is the universal gas constant and T is the temperature.

$$C = \frac{e^{(\Delta_{des} H\sigma - \Delta_{vap} H\sigma)}}{RT} \quad (2.20)$$

BET isotherm rises indefinitely as the pressure is increased because there is no limit to the amount of material that may condense when multilayer coverage may occur. Rearranging equation 2.18 above, the BET model takes the form given by equation 2.21.

$$\frac{z}{(1-z)V} = \frac{1}{CV_{mon}} + \frac{(C-1)z}{CV_{mon}} \quad (2.21)$$

BET model has been used widely in the determination of sorption behaviour of the solid desiccants. For instance, Zhang *et al.* (2005) have reported that, silica gel-calcium chloride composite sorption data fits well the fractal BET model proposed by Fripiat *et al.*, (1986) given by the relation 2.22:

$$\frac{w}{w_0} = \frac{C}{1+(C-1)\Phi^{\sum n 2-df} \Phi} \quad (2.22)$$

Where df is the fractal dimension, C is a constant, w_0 is the monomolecular equilibrium adsorptive capacity and Φ is the relative humidity. The study conducted by Zhang group established that BET theory could be used to predict the water sorption phenomena more accurately and the interpretation was found to be much simpler than using D-A equation adopted by Liu and Wang (2003). The isotherms below show the correlations between experimental data and fractal BET isotherms obtained by Zhang *et al.* (2005). For the purpose of this study, the BET analysis of the data obtained was done using the relation used by Likos and Lu, (2002) given by equation 2.23.

$$\frac{P}{X(P^0-P)} = \frac{1}{X_m c} + \frac{c-1}{X_m c} \times \frac{P}{P^0} \quad (2.23)$$

Where X is the amount of adsorbates (e.g. H_2O) adsorbed in grams per gram of adsorbent (PSBE- $CaCl_2$) at vapor pressure P and temperature T . P^0 is the saturated vapor pressure

of the adsorbates at the same temperature and X_m is the monomolecular equilibrium adsorptive capacity. The ratio P/P^0 is the relative vapor pressure or RH. The term C is a constant at any given temperature as discussed in equation 2.19.

2.5.2.5 Tempkin adsorption isotherm

Tempkin and Pyzhev suggested that due to the indirect adsorbates/ adsorbent interaction, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage (Aksu, 2005). The linear form of Tempkin isotherm can be written as shown in equation 2.24.

$$Q_e = B \ln A + B \ln C_{eq} \quad (2.24)$$

Where $B = RT/b$, T is the absolute temperature in Kelvin and R is the universal gas constant. The constant b is related to heat of adsorption. C_{eq} is the equilibrium concentration of the adsorbate.

2.5.2.6 Types of Adsorption Isotherm

Six different types of adsorption isotherm are illustrated in Figure 2.4. The six types of isotherm are characteristic of adsorbents that are microporous (type I), nonporous or macroporous (types II, III, and VI) or mesoporous (types IV and V). The type I graph depicts monolayer adsorption which is easily explained by Langmuir adsorption isotherm. With BET model, the graph arises when the value of $P/P^0 \ll 1$ and $C \gg 1$ where monolayer formation is realized (Ustinov *et al.*, 2005). Type II shows great deviation from Langmuir model and the intermediates flat region in the isotherm corresponds to monolayer formation. Type III also shows large deviation from Langmuir model and it explains the formation of multilayer. In this isotherm, there is no flattish portion which implies that monolayer formation is missing (Sing, 2001). The differences between types

II and III isotherms and between types IV and V isotherms arise from the relative strengths of the fluid-solid and fluid-fluid attractive interactions: types II and IV are associated with stronger fluid-solid interactions and types III and V are associated with weaker fluid-solid interactions. The hysteresis loops usually exhibited by types IV and V isotherms are associated with capillary condensation in the mesopores. The type VI isotherm represents adsorption on nonporous or macroporous solids where stepwise multilayer adsorption occurs (Kruk *et al.*, 2001; Barton *et al.*, 1999).

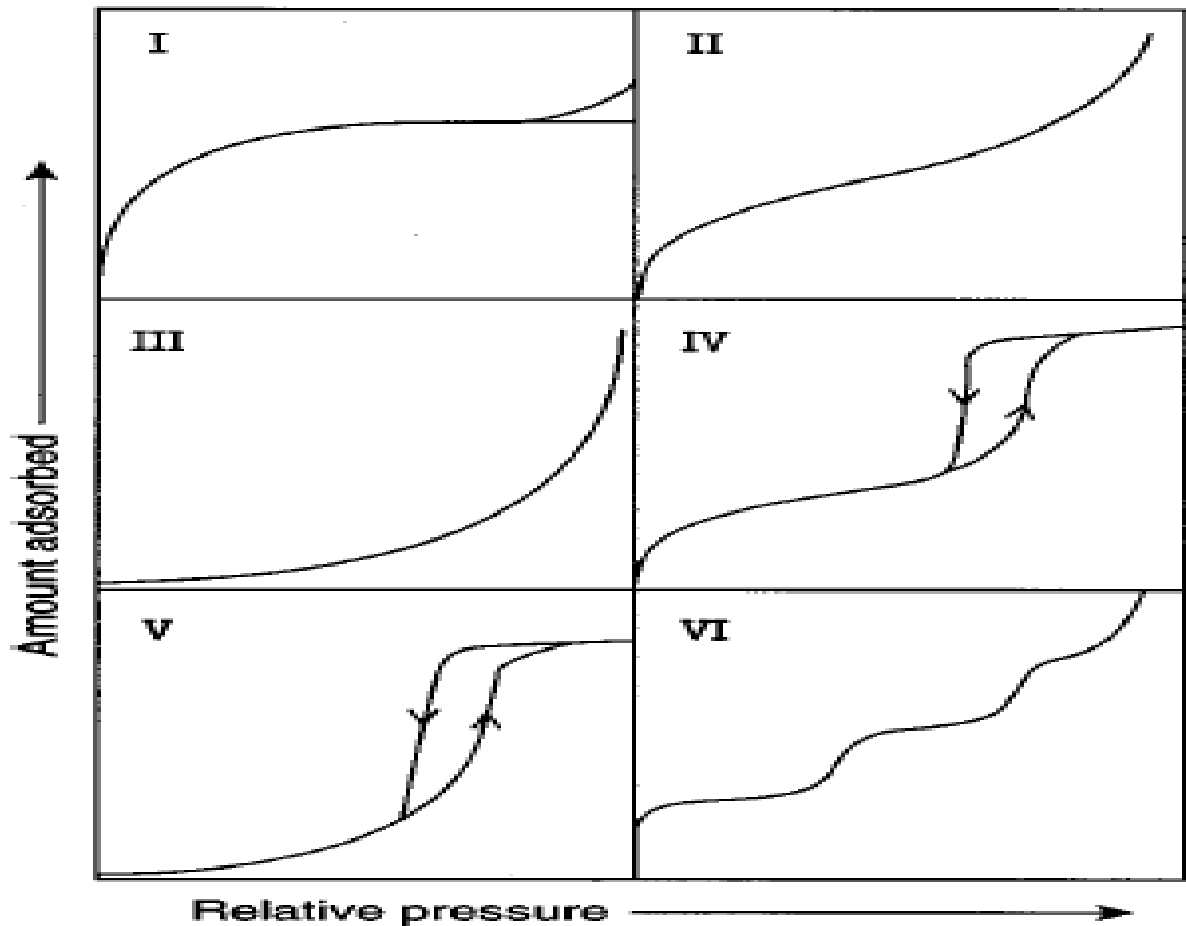


Figure 2.4: IUPAC Classifications of Adsorption Isotherms (Barton *et al.*, 1999).

2.5.3 Water Sorption Properties of the Solid Desiccant

There have been numerous studies regarding the water sorption behavior of solid desiccant and clay. The work ranges from theoretical approaches based on the consideration of molecular geometry, experimental application using a wide variety of equipment for measuring sorption isotherm (Berend *et al.*, 1995; Mooney *et al.*, 1952), experimental approaches using X-ray diffraction (Chipera *et al.*, 1997; Del Pennino *et al.*, 1981) and most recently numerical approaches using molecular dynamic computer simulation (Karaborni *et al.*, 1996). Water sorption on solid desiccant has been found to follow analytical models such as BET (Zhang *et al.*, 2005), Freundlich isotherm as well as Langmuir isotherm (Os'cik, 1982).

2.6 Thermal Physical Properties

Thermal physical properties of the adsorbent influence the performance of a dehumidifier and thus need to be investigated (Bullock and Threlkel, 1966). The properties include bulky density, particle density and equivalent diameter as observed by Thoruwa *et al.* (2000).

2.6.1 Bulky Density

Bulky density is a measure of the weight per unit volume in g/cc. This is a property of powders, granules and other divided solids which are defined as the mass of many particles of the material divided by the total volume they occupy. The total volume includes particle volume, inter-particle void volume and internal pore volume. Bulky density is not an intrinsic property of a material; it changes depending on how the material is handled. For instance, a Powder poured in a cylinder will have a particular density; if the cylinder is disturbed, the powder particles will move and settle closer

together, resulting in a higher bulk density (Grossman and Reinsch, 2002). The bulky density depends mainly on the mineral composition and the degree of compaction. The density of quartz is around 2.65 g/cm^3 but that of soil is about half that density, between 1.0 and 1.6 g/cm^3 . The bulky density of soils rich in organics and some friable clay have bulky densities well below 1 g/cm^3 . Bulky density are normally determined by a core-ring apparatus, where the apparatus is weighed when empty and when filled with dry sample and the mass difference is divided by the core volume to give the bulky density as presented in equation 2.25 (Grossman and Reinsch, 2002).

$$\phi_b = \frac{M_b}{V_m} \quad (2.25)$$

Where ϕ_b is the bulky density, M_b is the mass of the particles that constitute the adsorbent in Kg and V_m is the volume in cubic metres.

The bulky density determination is imperative in quantitative studies such as calculation of the soil moisture movement. Porosity which refers to the number of pores in an adsorbent can be calculated from the bulky density since bulky density is inversely related to the porosity. Porosity hence refers to the ratio of volume of the free space between the particles according to Hall (1979). Bed porosity for powdery and soluble materials determination is not applicable to liquid displacement, thus it is theoretically measured by the relation 2.26 (Thompson and Isaacs, 1967).

$$\epsilon = 1.0 - \frac{\text{Bulk Density } (\phi_b)}{\text{Particle Density } (\phi_p)} \quad (2.26)$$

2.6.2 Particle Density

The particle density or the true density of a particulate solid or powder, is the density of the particles that make up the powder, in contrast to the bulky density, which measures the average density of a large volume of the powder in a specific medium preferably air. The particle density is a relatively well-defined quantity, as it is not dependent on the degree of compaction of the solid, whereas it is measured in the freely settled or compacted state (tap density). The particle density is measured by Archimedes' principle or volumetric measurement.

2.6.2.1 Archimedes' Principle

In this technique, the powder or material under investigation is placed in a pycnometer of known volume, and weighed. The pycnometer is then filled with fluid of known density, in which the material is insoluble. The volume of the powder is determined by the difference between the volume as shown by the pycnometer and the volume of the fluid added (i.e. the volume of air displaced).

Slurry of the powder in a liquid of known density can also be used with hydrometer to measure particle density by buoyancy or to measure the weight of the sample in air, and in a liquid of known density.

Column of liquid with a density gradient can also be prepared: the column contains a liquid of continuously varying composition, so that the maximum density (at the bottom) is higher than that of the solid, and the minimum density is lower. If a small sample of powder is allowed to settle in this column, it will come to rest at the point where the liquid density is equal to the particle density (Bullock and Threlkel, 1966).

2.6.2.2 Volumetric Measurement

This technique utilizes a gas pycnometer in the measurement of the volume of the powder. A sample of known mass is loaded into a chamber of known volume that is connected by a closed valve to a gas reservoir of known volume, at a higher pressure than the chamber. After the valve is opened, the final pressure in the system allows the total gas volume to be determined by application of Boyle's law (Grossman and Reinsch, 2002).

2.7 Analytical Techniques

2.7.1 X-ray Fluorescence Analysis (XRFA)

Following the discovery of X-rays in 1895 by Wilhelm Roentgen, most of the early application of X-rays was in the medical field. However, in the past 50 years or so, use of techniques based on the properties of X-rays has played an increasingly important part in materials characterization and analysis. X-rays are generally electromagnetic radiation which are manifested in two forms, continuous radiation and characteristic radiation. Continuous radiation is produced when a high-energy electron beam decelerates as it approaches the electron clouds that surround the atomic nucleus. Characteristic radiation on the other hand is produced following the ejection of the inner orbital electron by high energy particles and subsequent transition of atomic orbital electrons from states of high to low energy. Moseley (1912) showed that there exist a simple relationship between the emission wavelengths and the atomic number of the excited element which is represented in equation 2.20 (Moseley, 1912)

$$\lambda^{-1/2} = a(Z - b) \quad (2.27)$$

Where, λ is the wavelength of emission, a is a constant, b is constant for all lines in a series { $b(K\alpha \text{ lines}) = 1.0$, and $b(L\alpha \text{ lines}) = 7.4$ }. Max von Laue (1912) diffraction demonstration led to two major fields of materials analysis namely; X-ray emission spectrometry and X-ray diffraction techniques. X-ray emission spectrometry is a technique for qualitative and quantitative elemental analysis by measurement of the wavelengths and intensities of X-rays from the excited elements. The second technique, X-ray diffraction, is a means of materials characterization whereby the X-ray scattering characteristics of a substance are related to the molecular arrangement of the atoms making up the scatterer.

2.7.1.1 X-ray Fluorescence spectrometry

X-ray spectrometry is a well established analytical technique and one of the most versatile methods for elemental analysis available today. X-ray fluorescence spectrometers were among the first analytical instruments to make full use of the potential of computers. The first computer-controlled spectrometers were produced as long ago as 1964 and today almost all spectrometers incorporate at least a microprocessor and in most cases include a microcomputer.

2.7.1.2 Principle of X-ray Fluorescence technique

The basis of the X-ray fluorescence technique lies in the relationship between the wavelength λ (and energy E) of the X-ray photons emitted by the sample element and the atomic number Z as showed by Moseley (1912) equation 2.28.

$$\frac{E}{12.4} = \frac{1}{\lambda} = K(Z - s)^2 \quad (2.28)$$

Where; K and s are constants that depend on the spectral series of the emission line under investigation. When an atom is bombarded with the high-energy particles such as X-ray photons, an inner orbital electron may be displaced, leaving the atom in an excited state. The atom then retains stability by rearrangement of the atomic electrons, and the inner-shell vacancies may be filled with electrons from the outer shells, leading to the emission characteristic X-radiation. Not all vacancies results in the production of characteristic X-ray photons, because of the competing internal rearrangement process known as the Auger effect. The ratio of the number of the vacancies resulting in the production of the characteristics X-ray photons to the total number of vacancies created in the excitation process is referred to as fluorescent yield which takes a value of around unity to high-atomic-number elements to as little as 0.01 for the low-atomic-number elements, such as Na, Mg and Al. Most commercially available X-ray spectrometers have a range from about 0.2 to 20 Å (60-0.6 keV), which allows measurement of the K series from F ($Z = 9$) to Lu ($Z = 71$), and for the L series from Mn ($Z = 25$) to U ($Z = 92$).

2.7.1.3 Instrumentation and Techniques for X-ray Spectrometry

All conventional spectrometers comprise three basic parts- the primary source unit, the spectrometer itself, and the measuring electronics. The primary source unit consists of a very stable high-voltage generator, capable of providing up to around 3 kW of power at a potential of typically 60-80 kV, plus a sealed X-ray tube. The sealed X-ray tube consists of an anode of Cr, Rh, W, Ag, Au or Mo. It delivers an intense source of continuous radiation, which then impinges on the analyzed specimen where characteristic radiation is generated.

A portion of the characteristic fluorescence radiation is then collected by the actual spectrometer, in which the beam is passed via a collimator or slit onto the surface of analyzing crystal. The crystal diffracts individual wavelengths in accordance with Bragg's law. A single-channel, or sequential, X-ray spectrometer has one such channel, and this is generally provided with a number of crystals to select the appropriate wavelength range and dispersion conditions. A multi-channel, or simultaneous, X-ray spectrometer has many single-channel spectrometers grouped around the sample, allowing the simultaneous measurement of up to 28 elements at the same time. Although the sequential spectrometer has more versatility than the simultaneous system, it is slower.

A photon detector is typically a gas flow or a scintillation counter which converts the diffracted characteristic photons into voltage pulses, which are integrated and displayed as a measure of the characteristic line intensity. Most of the modern λ -dispersive spectrometers are controlled by a minicomputer or microprocessor, and by the use of specimen changers are capable of very high specimen throughput.

Like the λ -dispersive spectrometer, the energy-dispersive spectrometer consists of three basic parts- an excitation source, a spectrometer, and a detection system. In this system, the detector which is generally lithium-drifted silicon, Si (Li) - which is a proportional detector of high intrinsic resolution- acts as the dispersion agent itself. The detector has a resolution of 160-180 eV in comparison to 20-200 eV for the λ -dispersive system. When an X-ray photon is stopped by the detector, a cloud of ionization is generated in the form of electron-hole pairs. The number of electron-hole pairs created (the total electric charge

released) is proportional to the energy of the incident X-ray photon. The charge is swept from the diode by a high voltage applied across it. A preamplifier collects this charge and directs it to a feedback capacitor which then produces a voltage pulse that is proportional to the original X-ray photon energy. Thus, when a range of photon energies is incident upon the detector, an equivalent range of voltage pulses is produced as a detector output.

A multi-channel analyzer is useful in sorting the arriving pulses at its input to produce a histogram representation of the X-ray energy spectrum. The output from an energy-dispersive spectrometer is displayed in a manner that the operator is able to dynamically display the contents of the various channels as an energy spectrum, and provision is generally made to allow zooming in on portions of the spectrum of special interest, to overlay the spectra, subtract background in a rather interactive manner. With the modern λ -dispersive system, nearly all the energy-dispersive spectrometers will incorporate some form of minicomputer that is available for spectral stripping, peak identification, quantitative analysis and host of other useful functions.

The surface characterization of the PSBE, material that was utilized in this study has been reported by several researchers in different applications as discussed earlier. Low *et al.* (2003) and Mehmet *et al.* (2003) showed that PSBE surface property compares well with virgin bleaching earth. Wachira *et al.* (2005) working on the same material for Cement production used the X-ray technique in the determination of the composition of the material and found that with proper method of reactivation, the surface property was not altered. More recently, Wambu *et al.* (2009) pursuing a study on the possible reuse of the material on the Cu^{+2} adsorption employed the same technique and obtained similar results

as the earlier studies on the surface properties with X-ray Fluorescence technique. For certainty of the material used in this study, it was found necessary to repeat the procedure whose results are presented in chapter IV.

2.7.2 Volumetric Methods

Volumetric method is used in the determination of the amount of water sorbed in an adsorbent, determination of adsorption isotherms, surface area and pore size of the adsorbates. In the volumetric methods, the adsorbates are degassed under vacuum to remove surface contamination. Helium is next admitted into a burette of known volume and its pressure and temperature measured so that the amount at STP can be calculated. The sample tube is immersed in liquid nitrogen and helium admitted. The residual amount in the burette is determined and the amount expanded into the sample tube determined. Since helium does not adsorb on to the solid, this volume is termed the dead space volume and it is found to be linearly dependent on pressure (Sing, 2001). The helium is removed and the procedure repeated with nitrogen.

When the nitrogen expands into the sample tube, it splits into three parts, residual in the burette, dead space which can be calculated from the previously found dead space factor, and adsorbed. The process is repeated at increasing pressures and the amount adsorbed determined as a function of relative pressure. The accurate determination of the amount of gas adsorbed depends upon a precise knowledge of the dead space. Estimation of the quantity of unadsorbed gas in the dead space is complicated by the fact that part of the dead space is at room temperature and part is at liquid nitrogen temperature. Since the amount adsorbed represents the difference between the amount admitted to the burette and the amount in the dead space at equilibrium, it can only be evaluated with confidence

if the two quantities are of unlike magnitude. To achieve this, the apparatus is designed to minimize dead space volume. In practice it is found convenient to fix the volume and temperature and measure the pressure. Regardless of the particular design, the basic apparatus must provide means for removing gases and vapors which all material pick up when exposed to the atmosphere. The apparatus must also provide means for permitting re-adsorption of known quantities of vapor on the material. It should also have evacuating systems, gauges to measure vacuum, a gas storage part and an analytical part. A great variety of volumetric apparatus have been described in the literature and the earlier ones have been reviewed by Ustinov *et al.* (2005).

2.7.3 Gravimetric Technique

Vacuum microbalance techniques are normally used in the determination of physisorption and chemisorption isotherms. An example of the application of a recording microbalance for physisorption and chemisorption measurements occurred in the study of the reduction of nickel oxide, which involves the determination of argon and oxygen. Gravimetric methods have the great advantage over volumetric ones in that the volume of the adsorption system is immaterial and the amount of gas adsorbed is observed directly by measuring the increase in the weight of the solid sample upon exposure to a gas or a vapor. The tedious volume calibration and dead-space determinations are thus eliminated (Sing, 2001).

The main disadvantages of the method are: the apparatus is much less robust and correspondingly more difficult to construct and maintain than volumetric apparatus, the apparatus has to be calibrated by placing known weights in the adsorbent pan, and the method is hence subject to the errors always attached to determinations which are

dependent on the constancy of calibrations of easily fatigued and strained mechanical systems, buoyancy corrections have to be made. Thus, although many different types of gravimetric apparatus have been reported, they have not become popular due to their delicate nature and the difficulty of compensating for buoyancy effects. In gravimetric methods of surface area determination the amount of gas adsorbed is determined by weighing using an adsorption balance (Kruk *et al.*, 2001). This study employed this technique in the determination of the amount of water adsorbed to the adsorbent as well as in the determination of the isotherm model that fitted the data well. Analytical balance model AAA 160/L was used in the sorption experiments in this study.

2.8 Summary of Major Findings from Literature Review

From the literature review, clay has been observed to suppress the dissolution property of the calcium chloride. The adsorbent matrix has also been documented to have sorption capacity that is comparable to the commercially available desiccants in addition to its low cost of production. The calcium chloride on the other hand enhances the sorption ability of the host material. Literature findings have also established that regenerated spent bleaching earth posse's similar properties as virgin bleaching earth which is a member of smectite clay which was traditionally used as desiccant material. Since the disposal method of these materials has been on potential land, its disposal protocol needs an urgency address. The literature review reveals that, regenerated spent bleaching earth is a potential raw material for development of low cost adsorbent material for air dehumidification application. Thus, based on literature findings, a study was carried out to determine the feasibility of utilizing spent bleaching earth in desiccant development whose findings are reported in this work.

CHAPTER THREE

METHODOLOGY

3.1 Sample Collection and Initial Treatments

Spent bleaching earth samples were collected from the dumping site of the edible oil processing industries in Mlolongo, a peripheral town of Nairobi county, Kenya. The dumping site which is normally on potential land is given by figure 2.4 in the literature review. The sampling was done in the same site where the spent bleaching earth was collected in different heaps and mixed thoroughly using griffins chaker to give the working sample. Samples were then air-dried, and de-oiled by hexane solvent using a soxhlet extractor. De-oiled residue were then de-oxidized using hydrogen peroxide, thoroughly washed using de-ionized water and heated at 110 °C in an oven before being preserved in desiccators for experimental tests and desiccant development. The entrained oil recovered in the solvent extraction was characterized in order to determine its possible re-use in bio-diesel and soap manufacture. The surface properties of the purified spent bleaching earth (PSBE) were determined. The mixing ratio of CaCl₂ to PSBE to auxiliary in the development of the composite desiccant was determined. Activation temperature for the adsorbent was also investigated. The effect of mineral acid on the regeneration of the spent bleaching earth for dehumidification appliances was also tested. The equilibrium adsorption for samples were determined and the data obtained fitted to adsorption isotherms to determine the model which accounts for the water uptake by the sample. Two types of balance were used in weighing namely; top balance model AFP 4100 L with a resolution of 0.01g and analytical balance model AAA 160/L with a resolution of 0.0001 g.

3.2 Purification of Spent Bleaching Earth

3.2.1 Hexane Extraction

Spent bleaching earth samples, 5.00 g, were weighed and placed in eight 1000 ml conical flasks. 5 ml, 10 ml, 15 ml, 20 ml, 25 ml, 30 ml, 35 ml, and 40 ml of hexane solvent were then added to the conical flasks. The content was then stirred for 12 hrs using a magnetic stirrer, filtered and the residue dried in an oven at 80 °C for 3 hrs before cooling in a desiccator. The dry residue samples were then weighed and the results tabulated.

3.2.2 Oxidation of the Hexane Residues

Hexane residues, 30.00 g, obtained in procedure 3.2.1 were weighed in a 1000 ml beaker. 90 ml of 30% H₂O₂ solution was added and the content of the beaker warmed to 80 °C. 15 ml of 30% H₂O₂ solution were successfully added until a total of 150 ml was consumed. The oxidized samples were then washed by centrifugation (model 6000 series centrifuge at 600*10 RPM for 3 min) with two sequential wash with deionized (DI) water. The samples were then dried in an oven at 110 °C for about 6 hours, cooled in desiccators and their weight tabulated.

3.3 Initial SBE Characterization

3.3.1 Elemental Analysis of the Material by XRF

Portion of PSBE samples obtained in procedure 3.2.2 were calcined at 550 °C and cooled in desiccators for elemental analysis. Portion of these ash samples, 10.00 g, were ground to fine powder and mixed with 1.00 g of starch as binder flux in a plastic container. The mixture was moulded into pellets and analyzed for the K, Ca, Al, Mg, Fe, Mn and Si by XRFA using a sequential X-Ray Spectrophotometer (SRS) model 3000. The chemical

constituents of the sample were recorded in terms of % oxides of the constituent elements.

3.3.2 Determination of the PSBE pH

Regenerated spent bleaching earth samples, 10.00 g, were soaked for 2 hrs in 25 ml of 1M potassium chloride solutions. The pH was then measured by a Hanna Instruments pH-211-Microprocessor pH meter and results recorded.

3.3.3 Determination of the Moisture Content

Spent bleaching earth was weighed in quantity of 5.00 g and placed in a crucible. The content was then transferred in an oven and dried to constant weight at 110 °C. The dried SBE was then measured using an analytical balance and the weight difference recorded as the weight of the moisture.

3.3.4 Determination of the Ash Content

The moisture free sample obtained in the above procedure was then transferred to mantle furnace and heated for 24 hrs at 550 °C before cooling in desiccators. It was then weighed for the ash content.

3.3.5 Determination of the Organic Matter Content

The Organic matter was determined by the difference in the moisture free sample and the ash samples.

3.4 Oil Characterization

3.4.1 Peroxide Value

Peroxide value was determined using conventional methods (Che Man *et al.*, 2005). 3.32 g of fat obtained from the SBE was weighed accurately in a conical flask. 250 ml of chloroform was added and the fat was dissolved by swirling. 15 ml of glacial acetic acid and 1 ml of fresh saturated aqueous potassium iodide solution was added to the mixture. The flask was then stoppered, shaken for 1 minute and placed in the darkroom for a further 1 minute. 75 ml of distilled water was added to the mixture and stirred. The mixture was then titrated with 0.01 M sodium thiosulphate solution using soluble starch solution (1%) as an indicator. The same procedure was repeated without the fat for reagent blank determination.

3.4.2 Acid Value

25 ml of diethyl ether was mixed with 25 ml of absolute ethanol and 1ml of phenolphthalein solution (1%) and carefully titrated with 0.1 M NaOH. 7.29 g of the molten fat was dissolved in the mixture and titrated with aqueous 0.1 M NaOH shaking constantly until a pink colour persisted for 15 seconds.

3.4.3 Saponification Value

Saponification value was determined through a method reviewed by Kaimal *et al.*, (2002), where 2.00 g of fat was weighed in a conical flask and 25 ml of the alcoholic potassium hydroxide solution added. A reflux condenser was attached and the flask heated in a water bath for one hour, shaking frequently. 1 ml of phenolphthalein (1%) solution was added and the hot excess alkali was titrated with 0.5 M HCl. A blank, which

entails the reagents in the absence of the fat, was carried out at the same time and the results tabulated.

3.4.4 Unsaponifiable Value

Into a 250 ml conical flask, 2.16 g of oil was weighed. 25 ml of alcoholic KOH solution (0.5 M in 95 % ethanol) was added and the content of the flask boiled gently under reflux for 1hr. Saponifiable sample solution was transferred to a separating funnel, 50 ml of distilled water used to wash the flask, the solution was then extracted while warm three times with 50 ml of distilled water. After the last extract was added, the combined ether extracts were shaken with 20 ml of water and then vigorously with two further 20 ml quantities of water. The ether extract was washed twice with 20 ml of aqueous 0.5 M KOH solution and twice with 20 ml quantities of distilled water until the wash was no longer alkaline to phenolphthalein indicator. The ether extract was poured into the weighed flask and the solvent evaporated off. The residue was dried at 80 °C and weighed to constant weight. The unsaponifiable matter were dissolved into neutral alcohol and titrated with 0.1 M alkali (Kaimal *et al.*, (2002).

3.4.5 Determination of Impurities in Fat

A filter paper was dried in an oven at 100 °C and then cooled in desiccators. 20.00 g of fat was weighed in a 500 ml conical flask. 200 ml of diethyl ether was added and the flask stoppered, the content in the flask was then filtered with a whatman filter paper preserved in the desiccators. The residue was washed with hexane until it was free from fat. Finally, the filter paper was dried in an oven at 100 °C until a constant weight was obtained.

$$\% \text{ impurities} = \left(\frac{a}{10w} \times 100 \right) \quad (3.1)$$

Where a is the weight of the dried filter paper and w the weight of the oil sample.

3.4.6 Determination of Calorific Value

Calorific value was determined using a bomb calorimeter model CAB 101. AB1.C. Approximately 3.00g of the residual oil was weighed in a crucible and placed inside a stainless-steel container (the decomposition vessel) filled with 30 bar (435 psi) of oxygen. A cotton thread was then tied to the ignition wire and immersed in the oil on the crucible. Firing nickel wire was then stretched between the electrodes of the bomb. One milliliter of water was pipetted into the bomb and the bomb assembled. The assembled bomb was tested for the circuit completeness by a firing circuit test plug. The bomb was filled with 30 bars of oxygen gas. Water was added into the calorimeter can until a weight of 3kg was attained to submerge the bomb completely. The bomb was then placed on the three supports in the calorimeter vessel and checked for any leakage. Readjustment of the calorimeter temperature was done by the use of the balance control knob. The cover of the water jacket with thermometer and thermistors was lowered. Completeness of the circuit was re-confirmed. The temperature of the jacket and calorimeter vessel was allowed to stabilize. The initial temperature of the calorimeter was taken after stabilizing with a precision of 0.001 °C and fire switch pressed for two seconds to ignite the sample. The final temperature was taken after sequential three minutes until the readings agreed to 0.002 °C. The process was repeated three times and the temperature rise was used in calculation of the calorific value.

3.5 Development of the PSBE-CaCl₂ Adsorbent

3.5.1 Preparation of PSBE-CaCl₂ adsorbent

Industrial CaCl₂, 50.00 g, were weighed and put in five different 1000 ml conical flask labeled 1:1, 1:2, 1:3, 1:4, and 1:5. 50.00, 100.00, 150.00, 200.00 and 250.00 g of PSBE were separately added to the flasks to make the ratios of CaCl₂: PSBE as reflected in the labels. The conical flasks were then stoppered and the different ratios mixed thoroughly using Griffin Flask Shaker for about 2 hrs. The mixture was then sprayed with 20% of the net dry weight mixture amount of distilled water to form a medium hard paste. About 0.60 g of the paste formed was weighed and molded into spherical balls of approximately 1 cm in diameter. The spherical configuration of the balls was chosen to maximize the mass and heat transfer process (Gupta and Thodos, 1965; Barker, 1965). The spherical balls were then dried in air for 24 hrs; they were then transferred to an oven and dried for 12 hrs at 110 °C, followed by 8 hrs at 200 °C. They were then transferred to a furnace where different samples in each ratio were heated in batches of 50 balls for 3 hrs at 300, 400, 500, 550, 600, 650 and 700 °C respectively. Samples soaked at different temperatures were preserved in desiccators to cool for the sorption studies. Figure 3.1 below shows the solid adsorbents that were developed from the mixture of regenerated spent bleaching earth and calcium chloride.



Figure 3.1: Samples of PSBE-CaCl₂ Desiccants

3.5.2 Preliminary Sorption Studies

The sorption studies for the preliminary experiments were done in a beaker where a wire mesh was placed just above the solution of saturated potassium chromate which provides a humid environment of about 88% RH with a maximum deviation of 1% to hold the balls in position (Thoruwa *et al.*, 2000). The beaker was then carefully sealed with a clear foil after placing dry weighed adsorbents and left for 120 hrs. The sorbents observable physical properties were monitored continuously after every 12 hrs. An observable physical property here implies wetting, water dripping, colour changes, stickiness, cracking, fragmentation and solidity maintenance characteristics of the solid sorbents. Suitable sorbents were selected for further sorption studies according to the following criteria.

- i. Minimum wetness and water dripping, cracking, fragmentation and solidity maintenance characteristics.
- ii. High content of CaCl_2 salt in the sorbent mixture that indicated the least deliquescent behavior on long exposure to the high humid environment.
- iii. Lowest processing temperature to minimize production cost.

3.5.3 Optimization of the Auxiliary Starch Binder

Industrial CaCl_2 (50 g) were weighed and put in four different 1000 ml conical flask labeled 1:1, 1:2, 1:3, and 1:4. 150 g of PSBE was added into each conical flask. To the flasks, 50, 25, 12.5 and 10g of starch were added respectively. The mixture was shaken with Griffin Flask Shaker for about 2 hrs. Different adsorbents with a ratio of CaCl_2 to Starch as 1:1, 2:1, 3:1 and 4:1 were developed as presented in procedure 3.5.1 and placed in a mantle furnace where they were heated at temperatures of 550 °C. Samples were then cooled in desiccators for sorption studies. The ratio that recorded highest sorption properties was then chosen for further sorption studies as presented in 3.5.4.

3.5.4 Sorption Studies

Saturated solutions of LiCl , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, NaCl and KNO_3 were prepared by adding the salts in 500 ml distilled water contained in 1000 ml plastic beakers while stirring until no more of the solids could dissolve. The salts solutions were then placed in humidity chambers as demonstrated by Figure 3.2 in the lower compartment. Adsorbents of the ratio 3: 1: 0.20 of PSBE: CaCl_2 : starch were prepared as presented in procedure 3.5.1. Dry samples of the adsorbents were weighed and placed in humidity chambers in the upper compartment as presented in Figure 3.2, with the different saturated salt solutions; LiCl , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, NaCl and KNO_3 which created: 11.3, 32.78,

43.16, 52.89, 75.5 and 93.58% humid environment at room temperature respectively. The change in weight of the samples was monitored with time using a top balance until no more change occurred. The results were tabulated and the weight difference was used to determine the maximum water sorption in % of the dry weight of the adsorbent.



Figure 3.2: Desiccant Samples under Sorption Investigation in a Humidity Chamber

3.5.5 Comparison of the Sorption Capacity of the Adsorbent Developed with Silica Gel

Dry samples of PSBE: CaCl₂: starch adsorbents in the ratio of 3: 1: 0.20 respectively developed were weighed and placed in humidity chamber with different saturated solutions as outlined in procedure 3.5.4. Dry silica gel were also weighed and placed in the same chamber as control. The samples were left in the humidity chamber and the moisture uptake monitored after every 24 hours gravimetrically until a constant mass was obtained.

3.5.6 Test for the Effect of Acid Activation on Sorption Properties

The regenerated spent bleaching earth adsorbents in absence of the additives, that is CaCl₂ and starch, reactivated at 550 °C, were soaked in different concentrations of H₂SO₄ and HCl acidic solutions namely 0.25, 0.5, 0.75, 1, 2 and 5 M for 2 hrs. They were then washed thoroughly with distilled water until the last wash showed no significant change to blue litmus paper. The wash residues were dried for 24 hrs in an oven at 110 °C and cooled in desiccators for sorption studies. Dry samples were weighed and placed in a humidity chamber with humidity of 81 RH where the weight change was monitored with time using gravimetric technique.

3.6 Determination of Thermo Physical Properties

3.6.1 Bulk Density

The bulky densities of the samples were determined using a core-ring apparatus. The apparatus weight was recorded while empty. The apparatus was filled with dry adsorbents samples and reweighed while full and the weight recorded. This procedure

was repeated six times and the weight in each case tabulated. The bulk density was then calculated using the relation presented in equation 3.2 (Grossman and Reinsch, 2002)

$$\phi_b = \frac{M_b}{V_m} \quad (3.2)$$

Where ϕ_b is the bulky density, M_b is the mass of the particles that constitute the adsorbent in Kg and V_m is the volume in cubic metres.

3.6.2 Equivalent Diameter

The equivalent diameter was obtained from the results obtained from the procedure 3.5.1 above. In each case, the number filling the core-ring apparatus for the determination of bulky density was recorded and used to calculate the equivalent diameter using the relation 3.3 (Grossman and Reinsch, 2002)

$$d_e = 2 \left\{ \frac{3z}{4\pi} \right\}^{-3} \quad (3.3)$$

Where, d_e is the equivalent diameter and z is the volume of one spherical ball.

3.6.3 Particle Density

The particle density was determined by the water displacement method using pycnometer. Due to lack of the above equipment, the solid samples were put in air free polythene bag and water displacement method was employed in the determination of the particle density. The weight of the polythene bag was negligible and hence assumed to have insignificant effect on the particle density of the samples. The idea of using the polythene paper was to prevent the wetting of the sample while measuring the volume as well as preventing the calcium chloride from dissolving in the water. The pycnometer was weighed while empty (M_1). Then, sorbent samples in a polythene bag were placed on the pycnometer such that they occupied almost a third of its volume and weighed (M_2).

The remaining volume was filled with water and the weight recorded as M_3 . Finally, the pycnometer was filled with water and weighed as M_4 . The particle density (ϕ_p) of each trial was obtained from the relation 3.4 (Grossman and Reinsch, 2002).

$$\phi_p = \frac{M_2 - M_1}{(M_4 - M_1) - (M_3 - M_2)} \quad (3.4)$$

CHAPTER FOUR

RESULTS AND DISCUSSION

The present section reports studies on the suppression of the deliquescent behavior of CaCl_2 salt using purified spent bleaching earth (PSBE) locally available pollution prone material. The results obtained indicated that spent bleaching earth has low hygroscopic capacity and its sorption properties can be enhanced through regeneration and impregnating it with hygroscopic salts. The dissolution phenomenon of calcium chloride salt as desiccant material was found to be contained by the regenerated spent bleaching earth. The results obtained on characterization of the residual oil indicated its potential in non-food application. For the sorption mechanisms involved, BET isotherm indicated that the composite adsorbent developed involves multilayer coverage.

Results for all the experimental tests and analysis discussed in this section includes regeneration of the spent bleaching earth (SBE), characterization of both purified spent bleaching earth (PSBE) and oil recovered, optimum PSBE to CaCl_2 ratio, physical (observable) properties, sorption capacity at different temperatures and relative humidity's, effect of the acid treatment on the adsorbents, thermo physical properties of desiccants and adsorption isotherms.

4.1 Purification of Spent Bleaching Clay

The restoration of spent bleaching earth (SBE) is reported which involves three major steps: An extraction step to remove majority of entrained oil, preferably about 75% to about 95% by dry weight of SBE, an oxidation step to remove the greater part of remaining carbonaceous adsorbates which are not removed by the preceding extraction

step, and an acid wash step to restore the acidity normally associated with fresh acid-activated bleaching clays. In the present work, all the three steps were investigated but only two steps were employed in the restoration of SBE for air dehumidification appliances. The results for the best mixing ratio of hexane and spent bleaching earth in the solvent extraction step are presented in Table 4.1.

Table 4.1: The Amount of Oil Removed by Different Ratios of SBE to Hexane

Ratio of SBE: Hexane (mass in g:volume in ml)	Mass of the SBE used	Mass of the SBE after extraction	Difference in mass	% of oil removed by hexane
1:1	5.00	3.88	1.12	22.50
1:2	5.00	3.85	1.16	23.10
1:3	5.00	3.80	1.21	24.10
1:4	5.00	3.78	1.23	24.50
1:5	5.00	3.76	1.24	24.80
1:6	5.00	3.75	1.25	25.00
1:7	5.00	3.75	1.25	25.10
1:8	5.00	3.74	1.26	25.10

The results indicated an increase in the percentage of oil extracted from the SBE as the volume of hexane increased, with the ratio of 1:1 recording the least amount of oil extract, 22.5%, and the ratio of 1:8 recording the highest oil extract, 25.1%. This was attributed to the fact that, when volume of hexane is low, it got saturated by less oil content while more hexane in the mixture extracted more oil to saturation. The best ratio was found to be 1:7 which recorded 25.1% extraction but for economical reasons, ratio of 1g SBE to 5ml hexane which extracted about 24.8% of the entrained oil was chosen and used in the solvent extraction. The hexane was found to extract mainly the oil content of

the SBE which was recording a total mass of around 25% by weight of the dry SBE samples. The oil impurity after analysis recorded impurity content of 0.4% as presented in Table 4.6 which implied that hexane extracted chiefly the entrained oil. Hexane residues contained other hydrocarbons which were more adsorbed to the bleaching earth, therefore, signifying the need for the oxidation step. From the average results obtained above, the ratio of 1:5 of SBE to hexane (1 gram per 5 ml) was chosen and used in the treatment of SBE in the solvent extraction step, using a soxhlet extractor where the solvent was regenerated to minimize the regeneration cost. The solvent was replaced several times until the cloudiness disappeared from the content siphoned. Since the solvent removed primarily about 25% of the organic matter present in SBE samples, the hexane residues samples were oxidized with 30% H₂O₂ which removed about 10% of the remaining organic matter as observed in Table 4.2.

Table 4.2: The Amount of Entrained Hydrocarbons Extracted by Oxidation Process

	Wt of the SBE _{HE}	Wt of the oxidized SBE	Charge in mass	% HC
A	30.02	26.34	3.68	12.30
B	30.02	25.05	4.97	16.60
C	30.10	28.13	1.97	6.50
D	30.00	28.58	1.42	4.70
Average %HC extracted				10.00

Key:

Wt Weight in grams
SBE_{HE} SBE residuals obtained after hexane extraction
HC Hydrocarbons

For the oxidation to be realized, the temperature of hexane residues and H₂O₂ mixture was raised to 80 °C to initiate the oxidation process. This was attributed to the fact that,

the process involves bond breakage which is endothermic process thus requiring heat energy from the surrounding for activation. Once the reaction started, the energy released in the formation of the CO₂ and H₂O was enough to supply the energy required for the process and hence the heating was stopped. The two processes, hexane extraction and H₂O₂ oxidation, combined recorded an organic matter content of 35%.

Table 4.3: The Amount of Hydrocarbons in Percentage Removed by Thermal Oxidation after Hexane Extraction and Hydrogen Peroxide Oxidation Steps

	weight of SBE after Hex and HP reactivation in grams	Weight after reactivation at 550 °C in grams	Change in mass	% of HC removed by thermal oxidation
A	26.34	25.02	1.32	5.01
B	25.05	23.75	1.30	5.18
C	28.13	26.68	1.45	5.15
D	28.58	27.07	1.51	5.28
Average %HC extracted				5.16

Oxidized samples were then heat reactivated at temperatures of 550 °C. This process showed that about 5% of the hydrocarbons were entrained in the SBE even after hexane and hydrogen peroxide reactivation process as presented in Table 4.3. The 5% HCs recovered in this process was attributed to the fact that, some of the hydrocarbons are chemically bonded to the bleaching earth and thus requires energy in form of heat in order to break the bond. The results were consistent with the results obtained by Wachira *et al.*, (2005) who on a different study found the SBE to have an organic matter content of about 40%. The temperature of 550 °C was chosen since in most cases when determining the ash content, this temperature is employed implying that hydrocarbons are oxidized at lower temperatures than 550 °C.

The results for regeneration step show that the spent bleaching earth is composed of about 40% of hydrophobic material which accounts for the low water sorption by the material as presented in Table 4.5.

4.2 Properties of Heat Treated SBE

The chemical and surface properties of the regenerated spent bleaching earth were determined and the results are presented and discussed in this section. The results for elemental composition determined by X-ray fluorescence (XRF) technique are tabulated and compared with the literature values for the virgin bleaching earth (VBE) and the results of other studies. These results are important in determining whether the route followed in the activation of the spent bleaching earth (SBE) alters the composition of the unexploited bleaching earth (BE).

4.2.1 SBE chemical properties

The elemental composition of the purified spent bleaching (PSBE) was determined using XRF and results are presented in Table 4.4. The table presents the composition of alkali and alkaline earth metals, variable charged clay components and fixed charged clay components in RSBE as percentage oxides.

The sodium oxide recorded a value of 0.27% which was higher than the value (0.00) of the fullers' earth in Table 2.1 and other findings (0.17%) in literature (Wachira *et al.*, 2005), this difference was attributed to the source of the Bleaching Earth. The other oxides were observed to be lower than the literature values with MgO and CaO recording the highest differences in their percentages.

Table 4.4: Elemental Composition of PSBE

Source of data	Property	Exchangeable Alkali Ions				Variable Charge Clay Components		Fixed Charge Clay Components		Organic Matter
		K ₂ O	Na ₂ O	MgO	CaO	Al ₂ O ₃	SiO ₂	MnO ₂	Fe ₂ O ₂	OM*
Experimental values	Value in %	0.4	0.27	1.05	0.85	11.31	68.7	0.09	5.67	40±0.1
	Total in %	2.57				80.01		5.76		
Literature values of VBE Wachira <i>et al.</i> , (2005)	Value in %	0.55	0.17	3.75	2.72	11.87	67.58	-	3.60	-
	Total in %	7.19				79.45		3.60		

Key: OM* means the organic matter was not obtained by XRFA method.

The results indicated that the percentage of the elements in the RSBE increased with the decrease in the solubility of their oxides in water. Alumina and silica with the lowest solubility recorded 11.31% and 68.7% respectively where silica value was more than the literature value in Table 2.1 by 4.7% and alumina percentage by composition decreased by 4.7%. There was an increase in the content of iron determined (5.67%) as compared to VBE (1.2%) which was ascribed to the fact that iron is one of the impurity adsorbed by activated bleaching earth from oil and fats.

The exchangeable alkali ions and fixed charge clay components recorded 2.57% and 5.76% respectively by composition which agreed well with Wachira *et al.*, (2005) findings. Alumino-silicates were found to be the predominant component in the material making up to 80% of the total mass which coincides with the literature values presented in Table 2.1. The content of fixed charge metal oxides of Mn and Fe were less significant recording 6% contribution to the total mass. This implied that the adsorption on SBE is

mainly based on variable charge sites provided by aluminium ox hydroxide and the silicates or simply physical sorption on the sites created on the material after the hydrocarbons are released upon regeneration. From the results of the XRF analysis, SiO₂ recorded the highest percentage composition by mass of 68.7% which implies that it contributed mostly on the adsorption of the adsorbent due to its open structure. In general, the conduit followed was found to have no effect on the surface composition principally on the insoluble elements but the wash after the hydrogen peroxide may possibly have contributed to the low percentage of the exchangeable alkali ions as compared to the values of VBE.

4.2.2 SBE Physical properties

The Physical properties – pH, moisture content, ash content and organic matter (OM) - of the SBE was determined and results tabulated in Table 4.5 below. The values obtained compared well with the properties documented by Wambu *et al.*, (2009), the pH value was observed to be low at 3.0 with a significant difference to pH of virgin bleaching earth (VBE) 5 to 5.3 attributed to the fatty acid of the adsorbed oil.

Table 4.5: SBE Physical Properties

Property	pH	Moisture in %	Ash in %	OM in %
	3.0±0.05	6.6±0.05	53.0±0.05	40.5±0.05

The ash, moisture and OM concurred with literature values (Wachira *et al.*, 2005), but the moisture content was observed to be much lower than the moisture absorbed by virgin bleaching earth in literature. The difference in moisture between the two materials was accredited to the presence of the hydrocarbons in SBE which are hydrophobic hence

repels water molecules. With the moisture content of about 6.5%, it was clear that fresh SBE was not a good dehumidifying agent and hence required some treatment in order to improve its adsorption capability. This necessitated SBE treatment to remove most of the entrained hydrocarbons before moulding the desired desiccants adsorbents. The ash content and moisture content values obtained were used to find out the credibility of the results of organic matter (OM) presented in Table 4.1 above which confirmed the results as true findings.

4.3 Properties of Extracted Oil

The properties (calorific value, peroxide value, acid value, saponification value, unsaponifiable matter and impurities) of the oil recovered from the spent bleaching earth (SBE) are presented in this section. The results for the oil characteristic are presented in Table 4.6 and some properties compared well with results obtained by other studies (Kheang et al., 2006) provided in Table 4.7.

Table 4.6: Properties of the Extracted Oil

Property	Calorific value kJ/g	Peroxide Value in meq/kg	Acid value in %	Saponification value	Unsaponification value per in g/kg	Impurities
	12168	0.391	3.790	253.850	25.420	0.40%

The calorific value was investigated to determine whether the extracted oil could be utilized in the manufacture of the Bio-Diesel, which provided a value of 12,168 joules per gram of fuel which was extremely low as compared to 39,000- 48,000 J/g of the vegetable oils. From the results of the calorific value, it is paramount for further fuel

properties to be investigated since calorific properties indicated that the oil recovered could not be utilized as diesel substitute.

Table 4.7: Some Properties of Residual Oils of SBE from literature

Characteristic of residue oil	Solvent Extraction		SC-CO ₂ Extraction	
	Acid Activated SBE (WAC)	Neutral SBE (NC)	Acid Activated SBE (WAC)	Neutral SBE (NC)
FFA%	11.50	12.60	11.50	12.60
PV (meq/kg)	3.10	3.40	2.80	2.20
Fe (ppm)	19.30	18.70	18.10	15.80
Cu (ppm)	0.22	1.24	-	-
B-carotene(ppm)	3	6	7	7
Calorific value (kJ/kg)	38,080	39,470	-	-
Oil Recovered (%)	30	21	27	20

(Kheang *et al.*, 2006)

The acidic value which refers to the measure of the extent to which the glycerides in the oil have been decomposed by lipase or other action was determined and compared. The acid value obtained was low 3.79% compared to the results of other studies (Kheang *et al.*, 2006) of 12.6% which indicated less degradation of the oil. However, the value was high which implied that its application in food was limited. These residual oils, thus, could be used in non-food applications such as bio-lubricants, grease, plasticisers, detergents, soap, and other oleochemicals.

The saponification value recorded a value of 253.85, often used in identification of the coconut oil (SV 248-265), palm-kernel oil (SV 230-254) and butterfat (SV 225), which contains a higher proportion of the lower fatty acid. The saponification value obtained afforded a potential re-use of the oil extracted in the manufacture of soap and detergents.

The maximum Unsaponification value oil is 10 g per 1kg according to the recommended codex standards of American Oil Chemical Society (AOCS) (Chanrai and Burde, 2004),

but the extracted oil had a higher value of 25.42 g per kg which signified low level of purity, consequently the oil was concluded not fit for consumption. It was necessary to investigate the characteristics of the recovered oil in order to find out whether the oil could be utilized in other application such as biodiesel and/or soap manufacture thus ensuring maximum exploitation of the SBE components. The results obtained hence confirmed that the oil recovered from SBE could be utilized in other applications thus making maximum utilization of the components of the SBE.

4.4 Development of Solid PSBE-CaCl₂ Desiccant

4.4.1 Optimum PSBE-Calcium Chloride Ratio

Purified spent bleaching earth (PSBE) and CaCl₂ were mixed in different ratios as outlined in section 3.5.1 and 3.5.2 in order to determine the best sample ratio that can eradicate the deliquescent behaviour of the CaCl₂. The observable physical properties- cracking, water dripping and wetting phenomena- are summarized in Tables 4.8 and 4.9. phenomena and – indicates nil i.e. no water dripping and surface wetting observed.

Where extreme meant almost all the surface was wetted for all the samples tested, moderate meant at least 50% of the surface of the samples was wetted, less moderate meant at most 30% of the surface was wetted and Nil meant no wetting was observed on the surface of the samples. The results for the observed physical properties showed a decrease in all the phenomena as the activation temperatures increased. A similar general observation was observed with increasing PSBE content in the matrix.

Table 4.8: Cracking Characteristics of the Solid PSBE-CaCl₂ Desiccants in Percentages (based on the number of the balls subjected to test)

Temp °C Ratio	100	200	300	400	500	600	700
1:1	100.0	100.0	100.0	100.0	100.0	80.0	75.0
1:2	100.0	100.0	67.7	67.7	50.0	25.0	10.0
1:3	100.0	67.7	67.7	33.3	0.0	0.0	0.0
1:4	67.7	67.7	33.3	33.3	0.0	0.0	0.0
1:5	67.7	67.7	33.3	0.0	0.0	0.0	0.0
1:6	33.3	0.0	0.0	0.0	0.0	0.0	0.0
1:8	33.3	0.0	0.0	0.0	0.0	0.0	0.0

Table 4.9: Water Dripping and Surface Wetting Phenomena of the PSBE-CaCl₂ Desiccants Subjected to 88% RH for a Duration of 120 hrs.

Temp °C Ratio	100	200	300	400	500	600	700
1:1	+++	+++	+++	+++	+++	+++	+++
1:2	+++	+++	+++	+++	++	++	+
1:3	+++	+++	+++	++	++	-	-
1:4	+++	+++	+++	++	+	-	-
1:5	+++	+++	+++	+	+	-	-
1:6	+++	+++	+	+	-	-	-
1:8	+++	+++	+	+	-	-	-

Key: +++ extreme, ++ moderate, + less moderate water dripping and surface wetting

Sorbents with a mixing ratio of 1:1 and 1:2 after exposure to 88% RH environment, indicated high moisture sorption accompanied by excessive wetting, water dripping, cracking and fragmentation, and almost all the samples under test cracked and dissolved in the water absorbed forming heavy jelly like fluids almost in all temperatures of activation. The results obtained signified that a mixture of the PSBE with calcium chloride at ratio (CaCl₂: PSBE) 1:1, 1:2, and dried from 100 °C range was unable to contain the deliquescent behavior of the salt at all. The results compared with Thoruwa *et al.*, (2000) finding who observed the same trend on clay-CaCl₂ adsorbent. The

phenomena was attributed to a high smectite content in the bleaching earth which possess high colloidal properties (Grim, 1968), as well as high content of CaCl_2 which is deliquescent in nature. However, increasing the amount of clay to calcium chloride salt ratio to 1:3 and above reduced the excessive wetting and water dripping especially to the adsorbents regenerated at temperatures above 500 °C.

The excessive wetting on the surface as well as cracking and spalling of the balls processed at 100 °C to 400 °C upon exposure to high RH was associated to incomplete combustion of the hydrocarbons in these adsorbents which could have sealed the pores, in addition to incomplete reactivation of the samples. A mixture of CaCl_2 with PSBE at ratios of 1:3 and above, processed at temperatures above 500 °C suppressed the deliquescent behavior of the CaCl_2 salt, thus maintaining solidity integrity. The adsorbents processed at temperatures beyond 500 °C recorded minimum wetting and water dripping as well as high solidity maintenance as they did not crack or spall. This was ascribed to the complete combustion of the hydrocarbons from the host material, hence opening the adsorption sites and ameliorated the adsorption of water molecules on the adsorbent as well as observed physical properties.

The results for sorption of different samples tested at different temperatures are summarized in Table 4.10, Figures 4.1 and 4.2. The balls regenerated at 100 °C to 400 °C were observed to be dark in colour which was attributed to the incomplete combustion of hydrocarbons. After H_2O_2 oxidation step the results outlined a decrease in moisture sorption as temperature increased and a peak was observed at 400 °C as outlined by Figure 4.2.

Table 4.10: Amount of water absorbed by samples of different CaCl₂ to PSBE mixing ratios at different temperatures in percentages

Temp in °C	Amount of water absorbed in % per dry weight of the sample in different duration of exposure to different RH environment				
	300	400	500	600	700
Adsorbent					
Pure PSBE	13.15	13.23	6.30	3.37	2.53
1:1	Excess wetness	Excess wetness	Excess wetness	Excess wetness	Excess wetness
1:2	30.97	42.56	39.3	27.22	18.31
1:3	36.20	38.77	38.4	26.35	16.44
1:4	47.45	41.55	29.7	21.79	13.2
1:5	44.97	41.15	20.4	16.03	12.45
1.6	42.77	32.37	21.2	14.28	13.1
1.8	40.47	34.13	20.3	13.36	9.27

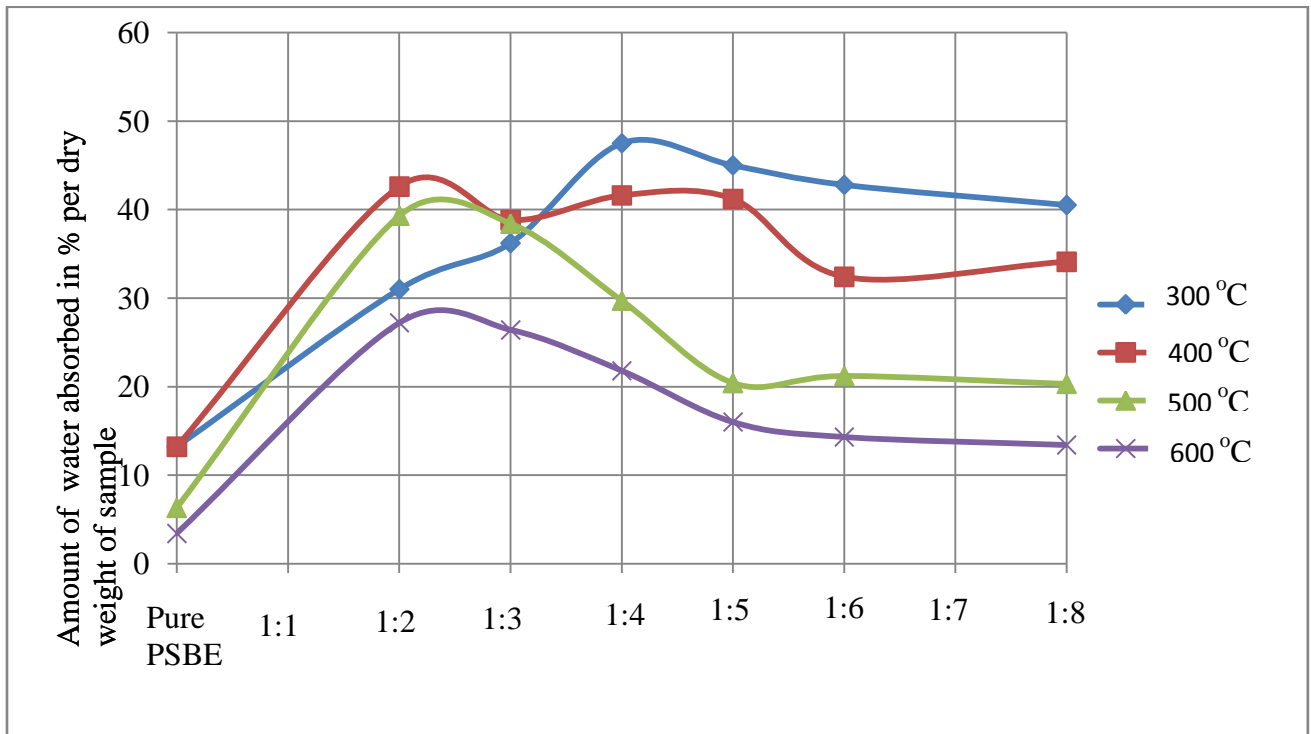


Figure 4.1: Amount of Water Absorbed by Different Ratios of CaCl₂ to PSBE (1:1 to 1:8) Processed at Different Temperatures Subjected to 88% Relative Humidity (RH) for 120 hrs.

The results of Figure 4.1 illustrates that, at low temperatures of activation, all the samples recorded high water content due to excessive wetting of the samples as observed in Table 4.9 . Samples processed at temperatures of 500 °C and above showed a gradual decline of water uptake as the CaCl₂ content reduced and the activation temperature increased.

The ratio of 1:3 indicated highest water uptake in percentage per dry weight of the sample in activation temperatures of 550 °C and above as represented in Figure 4.2, followed by 1:4 and 1:5 respectively with better observed physical properties, which necessitated further studies on these ratios at different temperatures as presented in section 4.4.3 in order to establish the best activation temperature. Figure 4.2 shows the water uptake of different solid desiccant samples, series 1 represents RSBE blank sample while series 2 to 7 represents sample ratios of 1:2 to 1:8 respectively. The ratio is based on the mixing ratio of calcium chloride to PSBE.

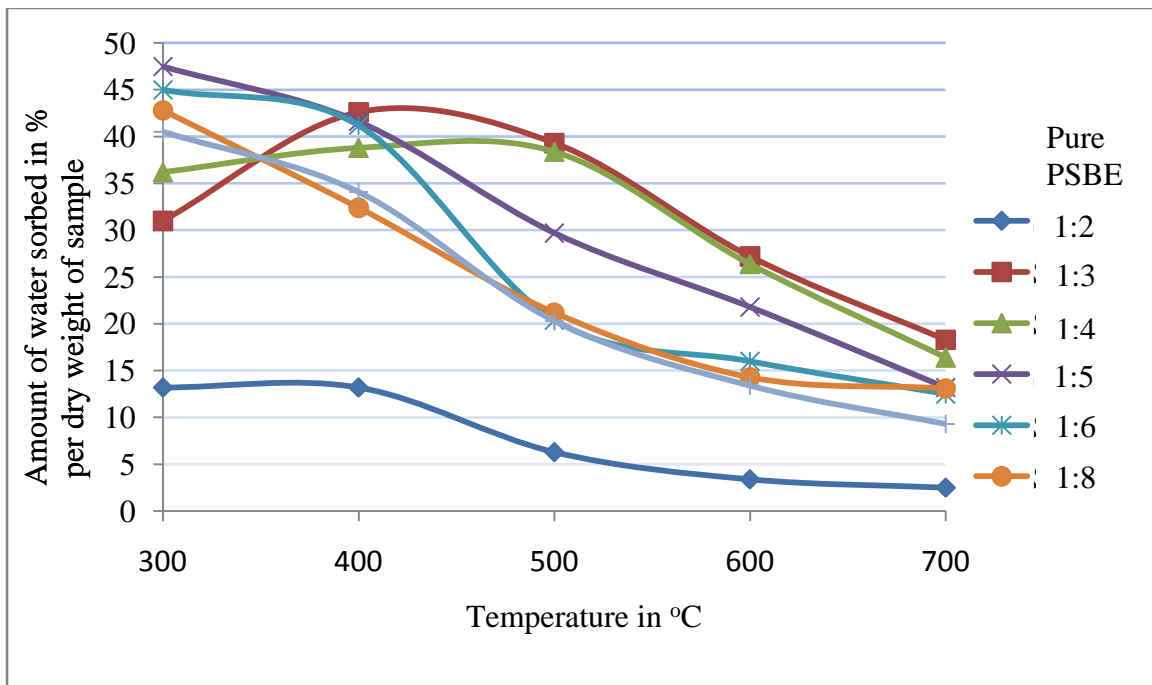


Figure 4.2: Effect of Processing Temperature on Water Uptake for Different PSBE-CaCl₂ Desiccant Samples Exposed to 88%RH for 120 hrs.

4.4.2 Selected PSBE-CaCl₂ Ratio

Suitable sorbents for further tests were selected using the following criteria: Minimum wetness and water dripping, cracking, fragmentation and solidity maintenance characteristics, high content of CaCl₂ salt in the sorbent mixture that indicated the least deliquescent behavior on long exposure to a high humid environment, lowest processing temperature to minimize production costs, high moisture content. Based on the stipulated criteria, a mixture of PSBE with calcium chloride sorbent of ratio (CaCl₂: PSBE), 1:3, 1:4, 1:5 were selected and tested for the effect of processing temperature ranging from 300 °C to 700 °C on moisture sorption.

4.4.3 Effect of Processing Temperature on PSBE-CaCl₂ Sorbent Solidity Maintenances

The results obtained in procedure 3.4.1 indicated that the solvent extraction and H₂O₂ oxidation process did not remove the entire entrained hydrocarbons from the SBE. Thermal processing was hence paramount in order to remove approximately 5% of the entrained HC after the two regeneration steps as well as reactivating the sorption sites of the adsorbent. Moisture sorption at various processing temperature are summarized graphically by Figure 4.3 and in the appendix I by table B. The sorbents indicated increased moisture sorption when processed at 300 °C and 400 °C, a decrease at 500 °C, an increase at 550 °C and a gradual decline in absorbed moisture when processed beyond 550 °C. The least moisture sorption occurred when processed at 700 °C. The peak observed at 400 °C was ignored on the basis of the phenomena of excessive wetting to the sample as discussed earlier in section 4.4.1. The water sorption results indicated two moisture sorption peaks at 550 °C and 650 °C for all the samples tested.

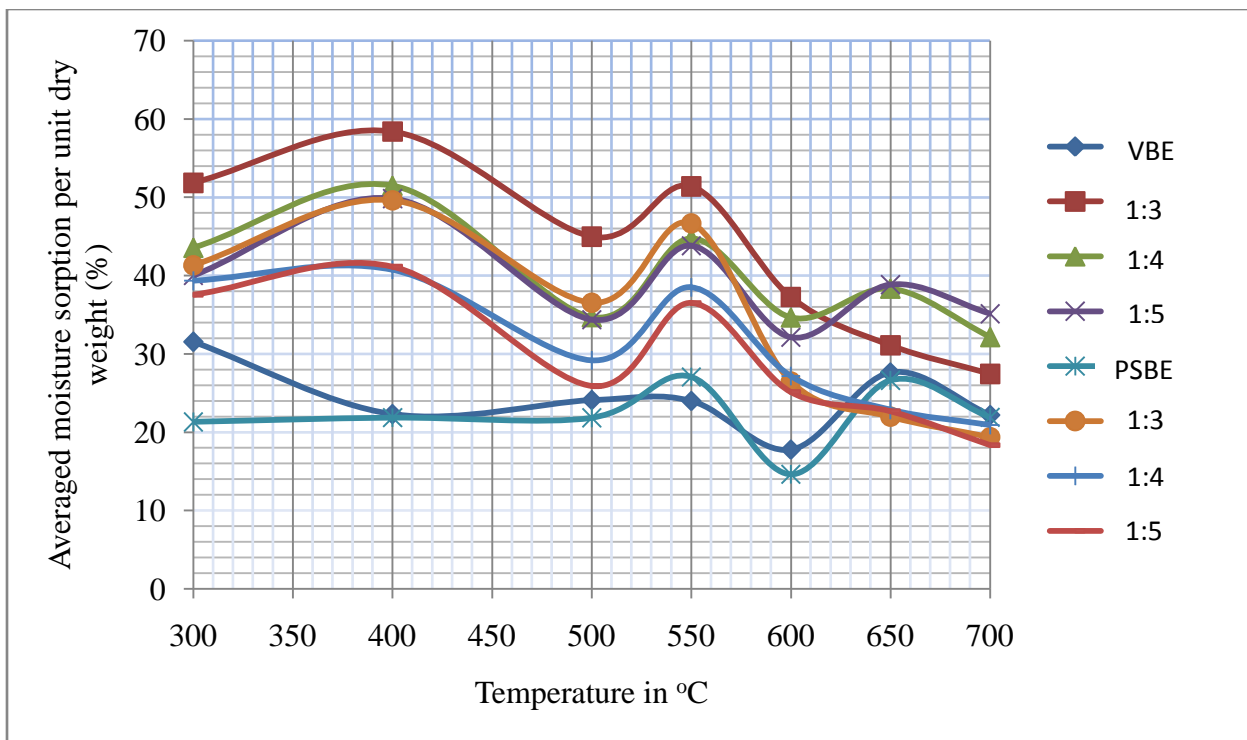


Figure 4.3: Effect of Processing Temperature on PSBE-CaCl₂ Adsorbents on Water Adsorption.

Key: VBE is the virgin bleaching earth and PSBE is the purified spent bleaching earth

The increased moisture sorption when processed between the temperatures of 300 °C to 400 °C was imputed to the excessive surface wetting of the samples due to incomplete combustion of the hydrocarbons which sealed the adsorption sites. The decline from 400 °C to 500 °C was attributed to combustion of most of the remaining hydrocarbons which decreased the wetting phenomena. The adsorption peak observed on the adsorbents reactivated at 550 °C was also observed by Tretiak and Abdallah (2009) when studying the sorption properties of clay-CaCl₂ adsorbent, however the peak at 650 °C was not in literature for solid desiccants but was observed by Wambu *et al.*, (2009), who reported a peak on the same material on copper adsorption when reactivated at 700 °C. The peak at 550 °C was accredited to the de-hydroxylation of γ -aluminium trihydroxides to γ -alumina

which is a more porous matrix structure upon calcinations, in addition to the complete combustion of the hydrocarbons which results in a large moisture exchange surface area (Low *et al.*, 1998). The peak at 650 °C in Figure 4.3 accounted for the formation of ρ -alumina (Wambu *et al.*, 2009), another product of calcinations of trihydroxides of aluminium which is characterized by high surface area that upgrades the sorption. The conversion of the aluminium trihydroxides to alumina on calcinations proceeds via partial dehydroxylation that begins at temperatures of 225 °C converting gibbsite to Boehmite with a loss of water followed by conversion of Boehmite to alumina from 525 °C as indicated in equations 4.1 and 4.2.



This explains the increase on adsorption from 300 °C. The lower moisture sorption at 700 °C was as a result of the conversion of the active alumina to relatively inert α -alumina in the range of 700 °C - 1000 °C (Wambu *et al.*, 2009, Thoruwa *et al.*, 2000). It can also be attributed to a decreased hygroscopic behaviour of the impregnated salt as it approaches its melting point of 782 °C.

4.4.4 PSBE-CaCl₂ Sorbents for Binder Additives treatments

Based on the experimental investigations conducted in sections 3.5.1 and 3.5.2, suitable solid PSBE-CaCl₂ sorbents for air dehumidification were selected and subjected to further tests on porosity additives impregnation to eliminate the undesired physical characteristics and increase the moisture sorption based on the following criteria: Optimum moisture sorption, Maintenance of solid integrity and mechanical stability.

Therefore, CaCl₂-PSBE sorbent mixture at a ratio of 1:3 and processed at 550 °C were selected using the stipulated criteria.

4.4.5 Optimum Binder Additives Ratio

Major problems faced in the selected sorbents included surface wetting, water dripping and cracking for the sorbents processed between 300 °C to 700 °C. Due to pronounced spalling and cracking of the balls, it was found necessary to include binders in the matrix to reinforce the stability of the adsorbent and starch was proposed as the binder due to its availability at low cost. Selection of the starch was dictated by the presence of the –OH functional group (Zhou *et al.*, 2004). It was projected that -OH could coordinate a bond with oxygen atoms in the SiO₂ and alumina hence stabilizing the matrix. Samples of different mixing ratio of starch based on the amount of CaCl₂ were developed to a mixing ratio of 1:1 to 1:5 as presented in table C appendix I. The PSBE and CaCl₂ amount were held constant and starch was varied in the matrix to develop above ratios as outlined in procedure 3.4.3.

The moisture sorption tests to investigate the effect of starch content on CaCl₂-PSBE for the above sorbent mixture, regenerated at 550 °C are presented in Figure 4.4 and Table C Appendix I. The table provides the amount of water absorbed both in grams and percentages for samples impregnated with starch. The optimization of starch was based on the amount of calcium chloride in the adsorbent.

The starch additives were found to be auspicious in improving the physical characteristics of the adsorbent especially on water dripping and cracking, however, the additive reduced

the sorption property by almost 1-3% as observed from the difference in the blank and the sample ratios of table C appendix I.

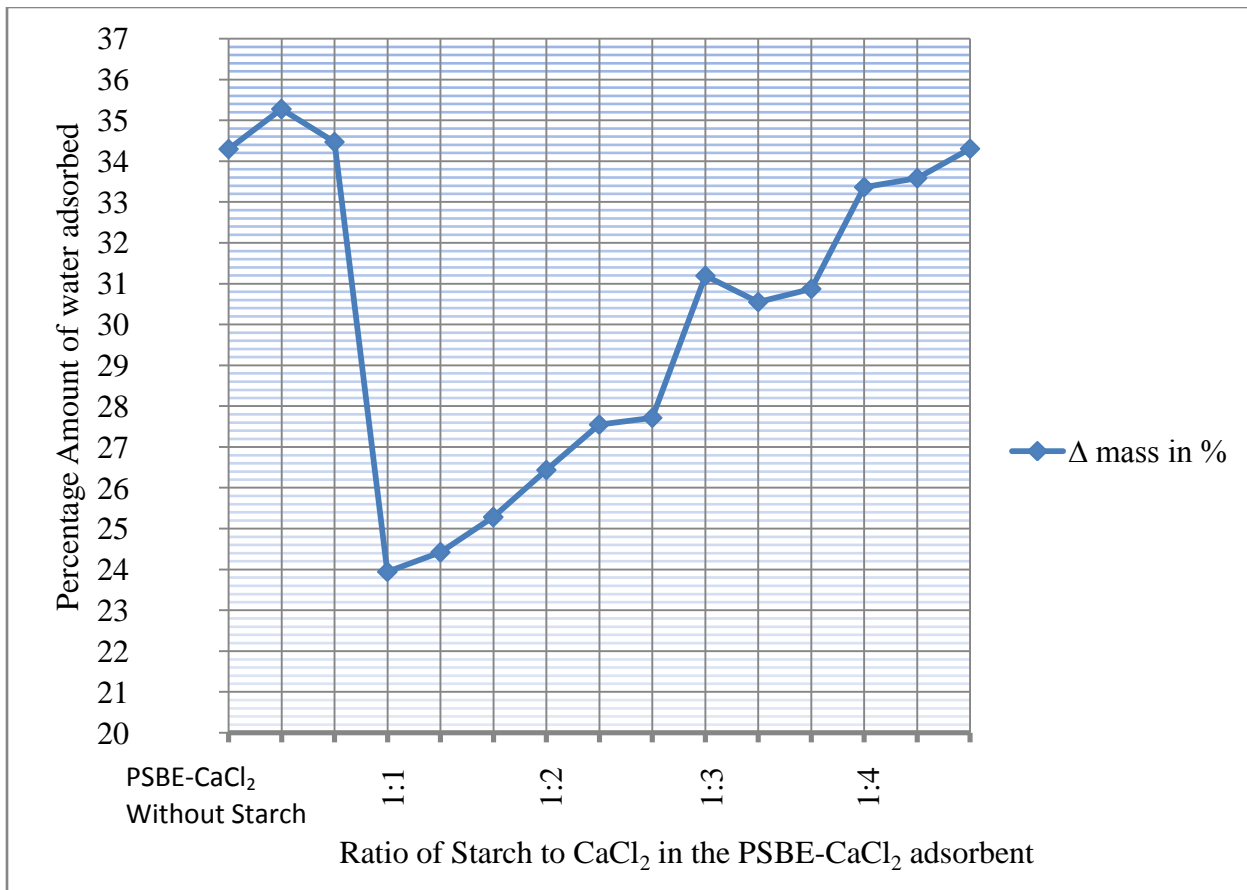


Figure 4.4: Effect of Binder Additives on the Sorption Properties of Sorbents.

From Figure 4.4, the blank sample absorbed about 35% of the water which dropped to 24% when starch was added to the matrix with a ratio of 1:1 starch to CaCl₂ ratio. However, the amount adsorbed was found to increase with a decrease in the amount of starch added to the adsorbent as presented above and observed in Figure 4.4. The ratio of 1:1 (starch to calcium chloride) recorded the least amount of water uptake of about 24% per dry weight of the sample as depicted in Figure 4.4. This was attributed to the fact that starch are hydrocarbons and hence hydrophobic, thus the more the starch in the matrix the less the hygroscopic the samples was. The sorbents with 1:4 and 1:5 ratio (starch:

CaCl₂) recorded almost equal amount of water adsorbed to that of the blank (blank implied to samples with no starch additives). It was generally observed that, the starch stabilizer was a necessity as it curbed the heinous cracking, water dripping and surface wetting phenomena observed in non bided samples, however, the amount should be limited in the adsorbent sample owing to its hydrophobic property in order to augment water uptake.

4.4.6 Effect of Thermal Treatment on Starch Impregnated Samples.

Observed physical properties for samples of starch to calcium chloride in the ratios 1:1, 1:2, 1:3, 1:4 and 1:5 for the sorbents selected in procedure 3.5.3 were determined upon thermal treatment and the results are presented in Table 4.11

Table 4.11: Cracking Characteristics of the Adsorbents Samples Impregnated with Starch and Processed at 550 °C

Ratio of Starch to CaCl ₂ in the PSBE-CaCl ₂ adsorbent	Extent of cracking observed on the surface of the samples
1:1	At least 80% of the surface cracked and 80% of the samples tested showed the same results
1:2	At most 60% of the surface cracked and 60% of the samples tested showed the same results
1:3	At most 30% of the surface cracked and 30% of the samples tested showed the same results
1:4	At most 5% of the surface cracked and 5% of the samples tested showed the same results
1:5	No cracks were observed on the surface for most of the samples tested

The adsorbents were observed to have profound cracks on the surface when heated at high temperatures where the phenomena were more pronounced to those sorbents with high starch content (Zhou *et al.*, 2004). The results indicated that, at least 80% of the surface of the samples and the samples thermally treated for the adsorbent with the ratio

of 1:1 starch to CaCl₂ ratio cracked. The magnitude of surface cracking was found to diminish as the ratio reduced- the amount of starch in the adsorbent reduced- with the sample ratio of 1:5 recording the least surface cracking phenomena. The cracking was ascribed to the fact that, starch is oxidized to water and carbon (IV) oxide which forms cracks on the surface as they are expelled from the medium. Thus, the more the starch, the more the number of gaseous molecules expelled, hence the more pronounced the cracks. Starch was found necessary if applied in small quantities since the starch bided samples were stable in comparison to the non bided balls. 5% starch additives was selected since it suppressed the water dripping, cracking and bolstered the sorbents.

4.4.7 Effect of Starch Additive on the PSBE-CaCl₂ Physical Properties on Exposure to 81% Relative Humidity

The starch additive was found to suppress the water dripping, spalling and cracking of the adsorbent upon subjecting them at high RH environment as outlined in Table 4.12.

Table 4.12: Observed Water Dripping, Surface Wetting and Fragmentation Phenomena for PSBE-CaCl₂ Desiccant Samples Impregnated with Starch Additive

Properties Ratio	Fragmentation	Surface wetting	Water dripping
1:1	Nil	Nil	Nil
1:2	Nil	Nil	Nil
1:3	Nil	Nil	Nil
1:4	Nil	At most 5% (Limited)	Nil
1:5	Nil	At most 10% (Limited)	Nil
Blank	Nil	At most 50% (Excessive)	Moderately

The more the starch additive impregnated the more static the samples were and enhanced the physical properties for the adsorbent were. The 1:1 (CaCl₂: Starch) recorded no surface wetting, water dripping and cracking, but on contrary, it recorded the least water

uptake as observed in Figure 4.4. The 1:5 (CaCl₂: Starch) recorded the highest water uptake which was slightly less than the blank but marked surface wetting of at most 10% of its entire surface. The results of observed physical properties depicted pronounced improvement to the physical properties of the sorbents with an increase in the amount of impregnated starch to the matrix adsorbent. Due to the necessity of a strong static adsorbent material, it was found necessary to include a binder, hence samples with a ratio of 1:5 (Starch: CaCl₂) were selected and subjected for further sorption properties tests.

4.4.8 Effect of Acid Treatment on Spent Bleaching Earth.

From the literature, acid treatment has been found to restore the acidic nature of the spent bleaching earth by introducing the hydrogen ions on the material which are good leaving groups and can easily be exchanged with other substances. This in turn enhances the sorption properties of the holding matrix. Since the acid treatment improves the sorption properties of the holding matrix but not the additives, tests were carried out on the PSBE without the additives. Two acids that are commonly used in reactivating the bleaching earth for oil manufacturing were used at concentrations of 0.25, 0.5, 0.75, 1, 2 and 5M respectively where solid desiccants reactivated at 550 °C were soaked for 2 hours in the above concentrations, oven dried and tests on water uptake carried out in a humidity chamber with 81% RH. The tests on acid activation were carried out in order to verify whether the step was obligatory in the regeneration of SBE for air dehumidification applications.

4.4.8.1 Effect of Sulphuric Acid Treatment

Effervescences were observed when the sorbents were added in the acidic solution which intensified with increased concentration. The reaction subsided gradually and bubbles

ceased after around 30 minutes of exposure. The samples treated with H_2SO_4 were found to sprout (sprout implied to formation of protuberant on the surface of the desiccant samples) after exposing them to a high humid environment. The protuberance phenomena were observed to increase with increase in concentration which busted into fragments after long exposure. Fragmentation of the sorbents was due to the fact that, sulphate ions from the acid combined with the cations present in the PSBE such as Ca^{2+} and Mg^{2+} to form sulphate salts which were efflorescent in nature. As the efflorescence process took place, the water given out to the atmosphere carried soluble salts on its way out of the matrix causing the protuberance and fragmentation of the sorbent. Due to excessive sprouting and fragmentation of the samples reactivated with sulphuric acid, the sorption properties could not be monitored to equilibrium. Hence, sulphuric acid was found not to be practical in the reactivation of the SBE for desiccant development.

4.4.8.2 Effect of the Hydrochloric Acid Treatment

The results for the amounts of water adsorbed by samples soaked in hydrochloric acid in percentage per dry weight of the sample are presented on Table 4.13. The equilibrium for the acid treated samples was attained after exposing the desiccants for around 54 hours to a relative humidity of 81%. It was observed that the acid treatment had insignificant contribution to the adsorption of water by the PSBE since the solvent regenerated SBE absorbed 16% of water per dry weight while acid treated PSBE sample absorbed about 18% per dry weight of the sample that was almost 2% more at equilibrium. The concentration of the acid did not alter the sorption properties of the SBE, since there was no significant difference in the adsorption capacity of 0.25M and 5M treated SBE

samples, however, sorption capacity indicated a decline with increase in molarity of the acid.

Table 4.13: Amount of Water Adsorbed for HCl Treated Adsorbent Samples in Percentage per Dry Weight of the Sample in Different Hours of Exposure to 81% RH

Concentration in Molarity	Amount of water absorbed in % per dry weight of the sample in different duration of exposure to 81% RH environment				
	2 hrs	22 hrs	54 hrs	102 hrs	144 hrs
0.25M	7.00	17.20	18.40	18.40	18.60
0.50M	7.10	17.40	18.40	18.35	18.55
0.75M	6.87	16.90	18.10	18.30	18.00
1.00M	6.63	16.57	17.77	17.83	17.50
2.00M	6.63	16.90	17.70	18.00	17.57
5.00M	6.83	16.90	17.77	18.00	17.50

These results correlated well with Wambu *et al.*, (2009) findings which showed PSBE adsorption efficiency is a function of the presence of silica rather than the acid reactivation. However, the 2% increase agrees with results obtained by Low *et al.*, (1998) and Kheok and Lim (1982) who indicated that acid-treatment increases sorptive ability of SBE. The increase is attributed to the coordination between the H⁺ in the SBE after the treatment and the oxygen atom in the water molecule leading to the formation of a hydronium ion. The increase in adsorption after the acid treatment can also be qualified to the acidic nature of the surface which causes the material to be more hygroscopic. Owing to almost equivalent sorption capacity of the acid treated samples and untreated

sample, the acid step was found to be of no consequence in SBE activation for the dehumidification purpose.

4.5 Water Adsorption Characteristics

4.5.1 Introduction

This section reports results for air dehumidification experiments where moist air at room temperature and different RH were created in a closed chamber (Figure 3.2) by saturated salt solutions (procedure 3.5.4). Dry weighed solid Samples of PSBE supported CaCl_2 were then placed in the humidity chamber. Measurements were made gravimetrically to obtain the moisture absorbed by the samples over time. The equilibrium moisture sorption's for the selected sorbents as a function of time in percentages per unit dry weight of the sample are presented in Table 4.14(a) and in Figure 4.5.

Table 4.14 (a): Moisture Sorption Capacity of the Samples per Dry Weight Desiccant at Different RH Environment

		Amount of water absorbed in % per dry weight of the sample in different duration of exposure to different RH environment							
% RH	Time (Hrs)	24	48	72	96	120	144	168	192
	11.3		1.94	2.67	2.87	3.07	3.16	3.2	3.2
32.78		16.21	18.59	19.07	19.55	20.02	20.02	20.02	20.02
43.16		17.63	19.57	20.29	20.53	21.5	21.74	21.74	21.74
52.89		18.01	20.34	21.97	23.09	22.76	24.01	24.27	24.28
75.5		19.22	33.1	38.3	40.52	42.25	43.22	44.32	44.32
93.58		29.45	40.14	45.51	47.78	47.94	48.19	48.19	48.19

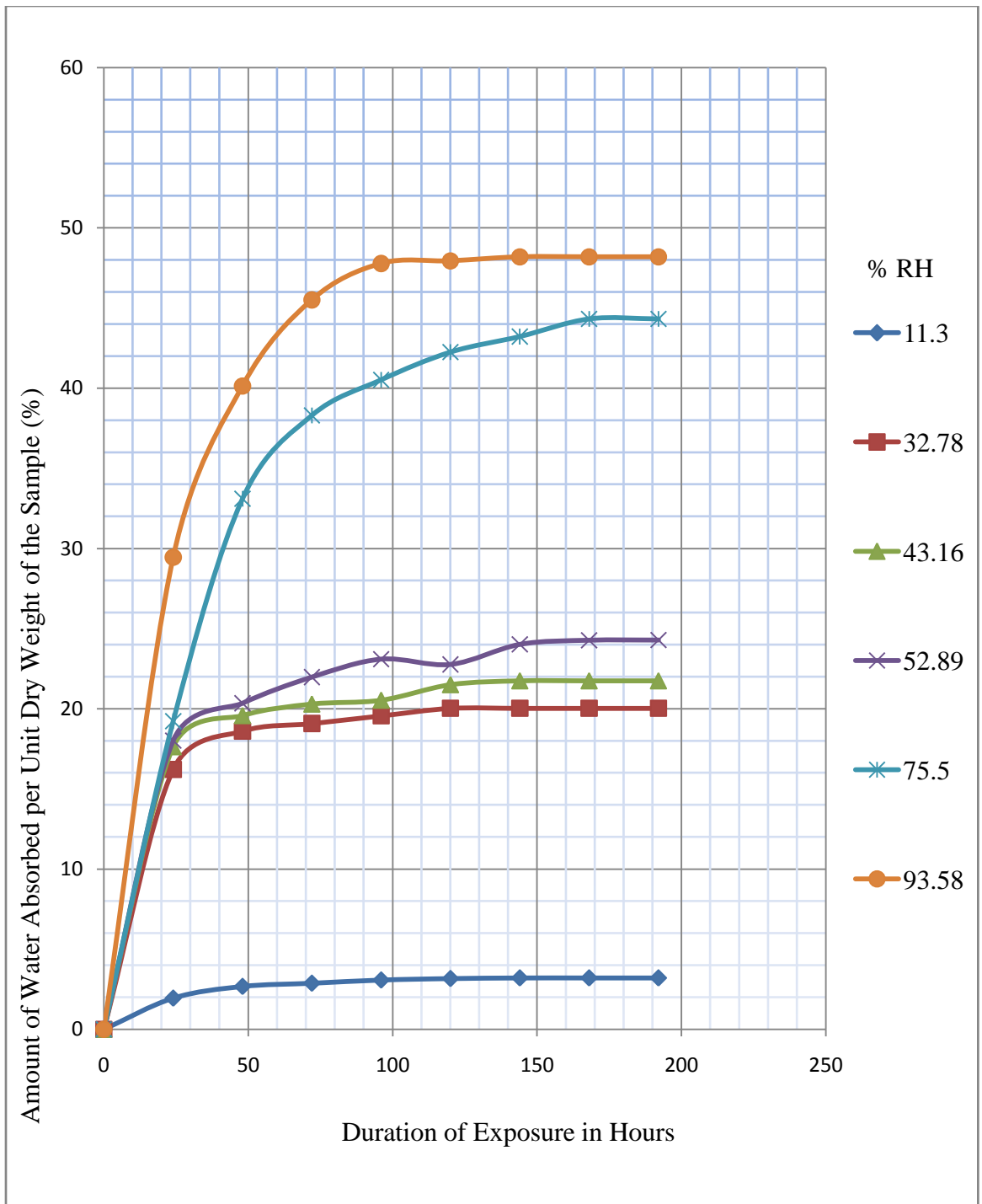


Figure 4.5: Amount of Water Absorbed against time in Hours for CaCl₂-PSBE Samples in Different Relative Humidity.

Key: 11.3 to 93.58 on the legend represent the relative humidity in percentage.

The results indicated high rate of adsorption for the first 24 hours of exposure followed by a gradual increase in water uptake in all the relative humidity tested to an equilibration time of 144 hours for both low and high relative humidities. For all the tests conducted, duration of 144 hours was selected as the upper limit when the samples recorded constant change in mass and just before the sorbents were excessively wetted for the sorbents in high relative humidities. The high water uptake at the beginning was as a result of enormous adsorption sites on the outer core of the adsorbent. With time, the outer core became saturated and the decline in the rate of adsorption after 24 hours of exposure is associated to the slow rate of diffusion of the water molecules to the inner core of the desiccant. The results obtained were similar to those of other desiccants (Jia *et al.*, 2007, Thoruwa *et al.*, 2000). The equilibrium moisture sorptions for sorbents at 550 °C were observed to amount to 3.2, 20.02, 21.74, 24.28, 44.32 and 48.19% of the moisture adsorbed by dry weight of the adsorbent at 11.3, 32.78, 43.16, 52.89, 75.5 and 93.58% RH respectively. This indicated that adsorption of water molecules from the air is directly proportional to the relative humidity as outlined in Figure 4.6.

The sorption capability was enhanced with increase in relative humidity and a maximum of 48% water uptake per unit dry sample was recorded at relative humidity of about 90%. This was attributed to the high concentration of water molecules at high relative humidity that interacted with the surface of the sample hence increasing the sorption capacity (Ustinov *et al.*, 2005) as a result of increased condensation. Similarly, at low relative humidity, the water molecules have high thermal energy and thus are desorbed easily due to their high tendency of escape. The thermal energy and tendency to escape from the

adsorbent surface of molecules decreases with increase in the rate of collision of the molecules to the surface.

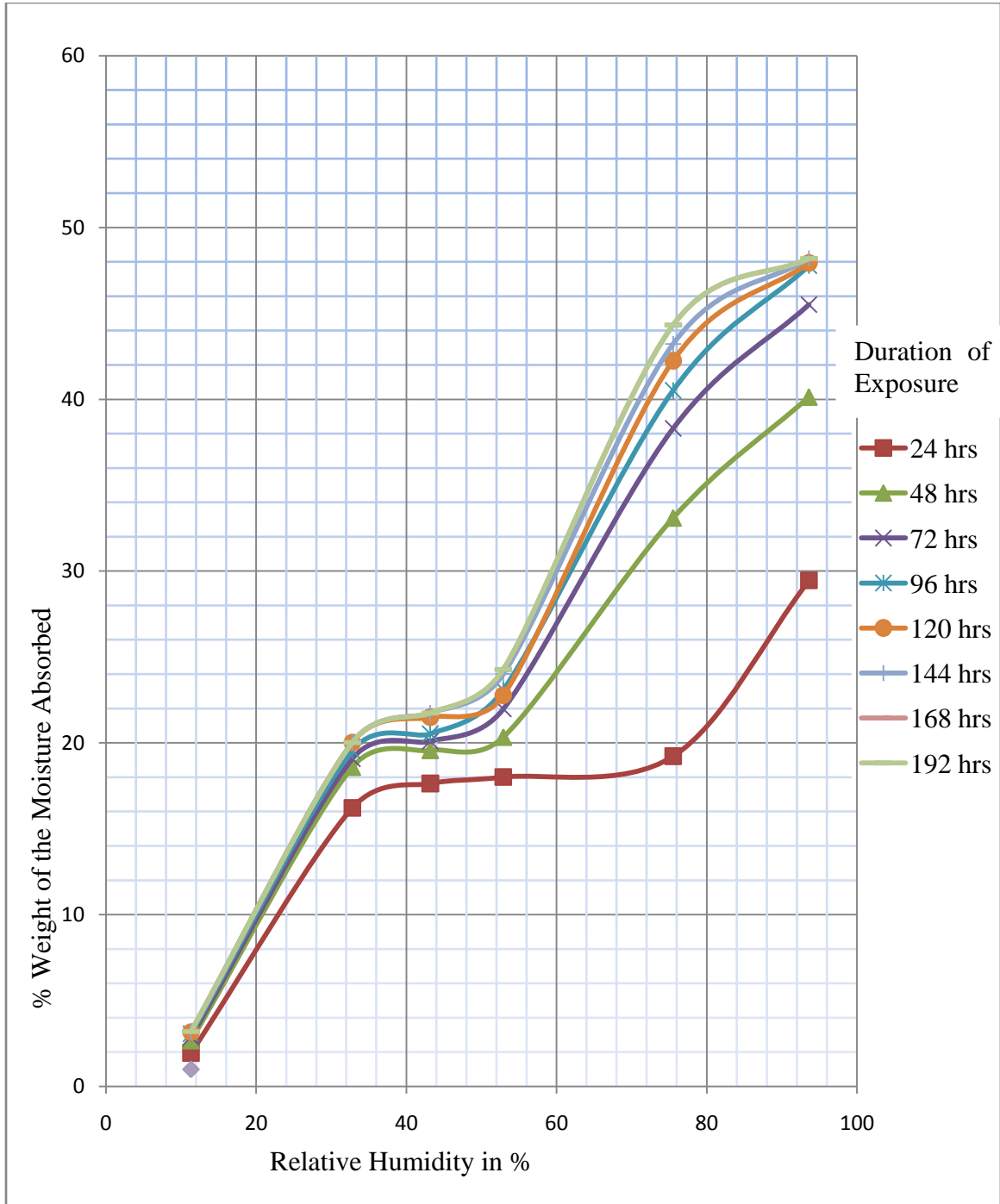


Figure 4.6: Amount of Water Absorbed against Percentage Relative Humidity per unit Dry Weight PSBE-CaCl₂ Desiccant Samples.

The rate of collision is directly proportional to the relative humidity which accounts for the increased sorption with increase in relative humidity as indicated in Figure 4.6. Figure 4.6 resembles the Langmuir isotherm type II which indicates that, the adsorbent developed is a macroporous adsorbent. Also, the isotherm shows a great deviation of the sorption characteristic of the PSBE-CaCl₂ adsorbent from Langmuir model.

The current desiccant proved to be more practical in high relative humidity ranging from 70% RH where it recorded equivalent moisture uptake as the available commercial desiccants such as silica gel. It was observed that, unlike the adsorbent developed by Thoruwa *et al.*, (2000), the current desiccant recorded minimal fragmentation characteristics after 192 hours. However, the excessive wetness at high humidities was in agreement with his findings. Therefore, it was concluded that the equilibrium moisture sorption at 550 °C for the desiccant developed was 48%. Figure 4.7 below represents a cross-sectional photograph of the area and instruments used in water sorption determination in the study.

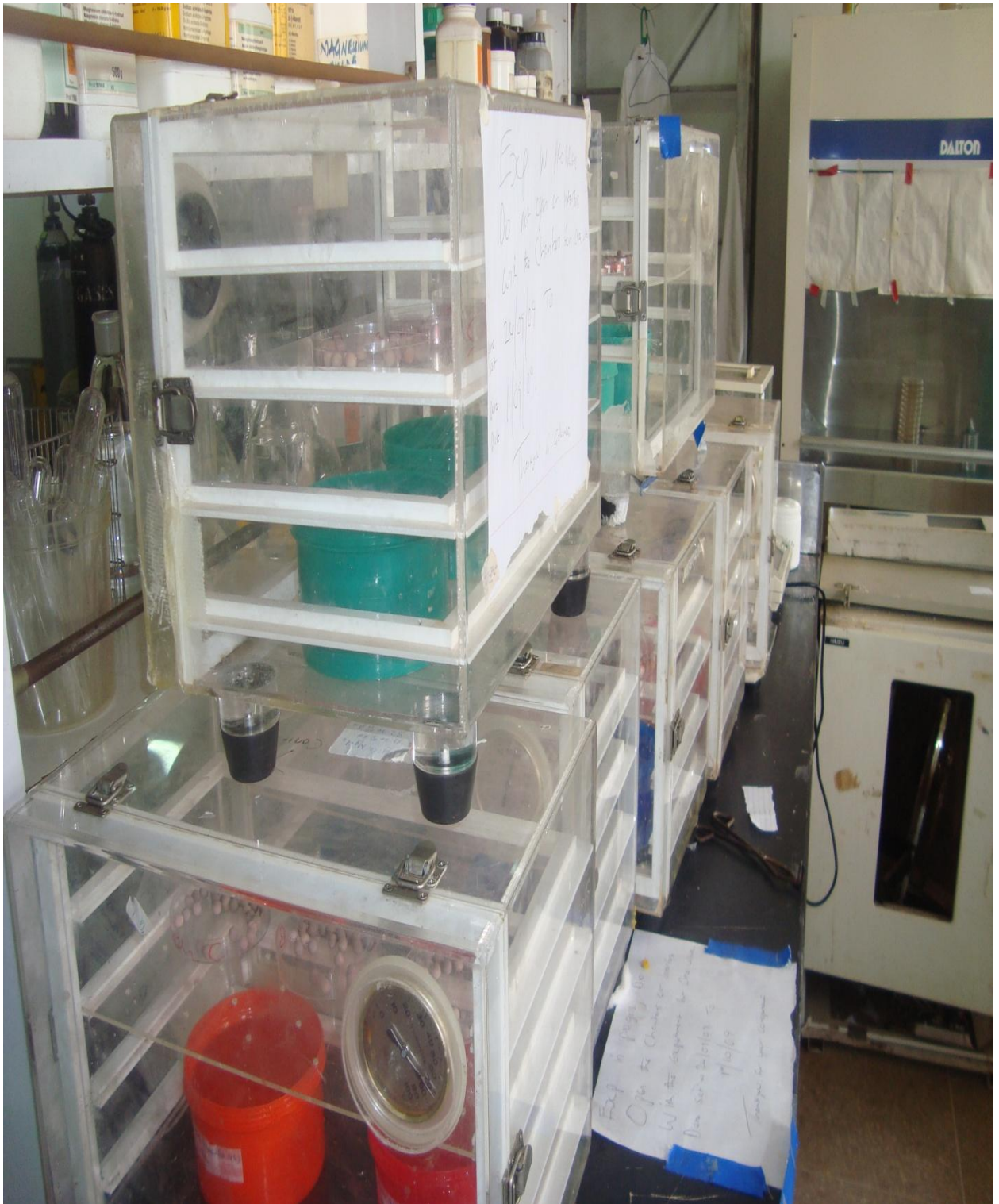


Figure 4.7: Cross-Sectional Photography for Water Sorption Determination Experimental Set-up.

4.5.2 Comparison of Water Sorption Capacity of PSBE-CaCl₂ Adsorbent with Silica Gel

The water sorption capacity of the developed desiccant was compared with commercially available silica gel desiccant as outlined in procedure 3.5.5 and the results are presented in table 4.14 (b).

Table: 4.14 (b): Comparison of Water Sorption Capacity of PSBE-CaCl₂ Adsorbent with Silica Gel

Time (hrs) \ % RH	Amount of water absorbed by PSBE - CaCl ₂ samples in % per dry unit sample					Amount of water absorbed by Silica gel in % per dry unit sample				
	11.3	32.78	43.16	75.5	93.58	11.3	32.78	43.16	75.5	93.58
24	1.94	16.21	17.63	19.22	29.45	2.02	16.63	18.1	22.78	33.89
48	2.67	18.59	19.57	33.1	40.14	2.8	19.32	20.43	35.97	45.35
72	2.87	19.07	20.29	38.3	45.51	3.02	21.37	22.95	42.66	45.58
96	3.07	19.55	20.53	40.52	47.78	3.02	22.45	24.57	43.65	45.88
120	3.16	20.02	21.5	42.25	47.94	3.02	24.35	26	43.66	46.58
144	3.2	20.02	21.74	43.22	48.19	3.02	25.54	27.43	43.71	46.58
168	3.2	20.02	21.74	44.32	48.19	3.02	25.21	27.43	43.76	46.58
192	3.2	20.02	21.74	44.32	48.19	3.02	25.22	27.43	43.76	46.58

The result of table 4.14 (b) indicates that at low relative humidity, both silica gel and the PSBE-CaCl₂ adsorbent developed absorbed very low water from the atmosphere. This is attributed to the fact that, the adsorption is a reversible process where the adsorbed water molecules are also desorbed. When the concentration of water molecules is low in air, 11.3% RH, few molecules interact with the adsorbent surface thus few molecules of the water are adsorbed. Similarly, with low concentration of the adsorbate, the molecules have high thermal energy as explained earlier, thus more molecules escape from the adsorbents once they are adsorbed which accounts for the low sorption capacity for %RH below 60% (Likos and Lu, 2002). However, it was noted that PSBE-CaCl₂ adsorbent was

less effective at low relative humid environment as it absorbed less water as compared to silica gel as observed in figure 4.11.

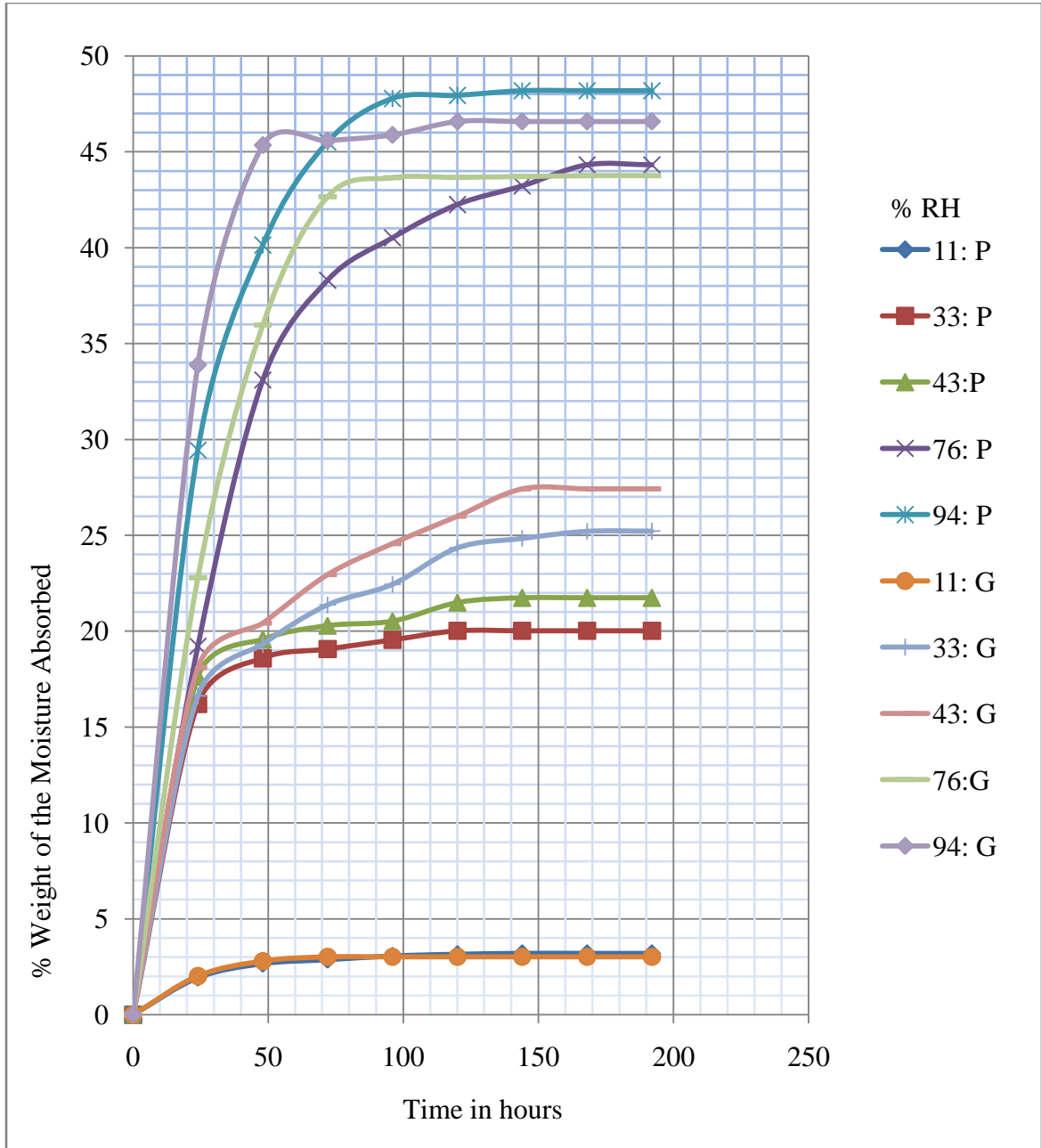


Figure 4.8: Correlations between Experimental Data and BET Isotherms for Silica Gel Adsorbents .

Key: P- refers to PSBE-CaCl₂ adsorbent samples under the specified %RH
 G- refers to silica gel samples under the specified %RH

The sorption properties were observed to improve as the relative humidity increased as observed in figure 4.8. This was qualified to the fact that, more water molecules interact with the surface of the adsorbent hence increasing the adsorption. Also, when the humidity increases, the thermal energy of the water molecules decreases, thus few molecules escape from the surface accounting for the high water uptake at high relative humidity (Likos and Lu, 2002). For all the trials made, PSBE-CaCl₂ was found to be more efficient at high relative humidity as compared to the silica gel. This was ascribed to the fact that, the impregnated CaCl₂ dissolves in the water absorbed to form solutions in the adsorbent pores which also absorbs more water. In actual fact, the desiccant developed is characterized by solid adsorption by the host material PSBE, solid calcium chloride and chemisorptions by calcium chloride solution after dissolution in the pores as observed by Thoruwa *et al.*(2000).

4.5.3 Langmuir and Freundlich Isotherms

The adsorption results for the SBE reactivated at 550 °C were fitted to Freundlich equilibrium isotherms (equation 2.10) and the double reciprocal Langmuir isotherm (equation 2.12). The data for SBE samples fitted well the Freundlich isotherm than the Langmuir Isotherms as indicated by the regression analysis values presented in table 4.15 (a) and (b) respectively. In the comparison, the low relative humidity was excluded in Langmuir Isotherms because the Q_{max} for the isotherms when 11.3% RH was included gave a negative value. From the values obtained, the regression analysis recorded low values at very low RH (RH < 30%) and very high relative humidities (RH > 70), which conformed with the BET isotherm. R^2 value in both models improved considerably with an increase in the relative humidities due to increase in the vapour pressure as the

concentration of the water molecules increased as observed in table 4.15 (a) and (b). This led to an enhanced interaction of the water molecules with the adsorbent surface hence increasing the rate of adsorption as well as equilibration.

Table 4.15 (a): Freundlich Constants

Freundlich constants for PSBE sorbent at different relative humidity			
%RH	R^2	K_f	n
11.3	0.929	1.150	3.650
32.78	9.929	11.480	8.700
43.16	0.978	12.390	8.850
52.89	0.971	11.090	6.450
75.5	0.899	5.330	2.280
93.58	0.903	13.030	3.620

Table 4.15 (b): Langmuir Constants

Langmuir constants for PSBE sorbent at different time of exposure at constant temperature but different relative humidity					
All the RH humidity included			11.3% RH not inclusive		
Time of exposure	R^2		R^2	Qmax	K_1
24 hrs	0.955		0.667	8064	0.000130
48hrs	0.969		0.823	20,833	0.000032
72hrs	0.972		0.828	31,250	0.000020
96hrs	0.970		0.857	31,667	0.000019
120hrs	0.974		0.837	35,714	0.000018

The goodness of fit for curves were found to improve with an increase in time of exposure which was attributed to the approach of equilibration which has been

documented to occur between 30 to 150 hrs (Zhang *et al.*, 2005). The Q_{\max} values were found to increase as the equilibration is approached with 35,714 as the maximum at 120hrs. Similarly, the Langmuir constant K_1 which is the affinity of the adsorbate to the adsorbent was found to approach zero as the equilibrium is approached. The trend was consistent with the literature values obtained for SBE in the adsorption of other adsorbates such as metal ions as reported by Wambu *et al.*, (2009), (Q_{\max} 10,000 at 370 °C in the adsorption of copper from solution). The rise in the Q_{\max} as the exposure time increases is ascribed to the shift of the sorption from monolayer to multilayer surfaces, which also explains why the curves are not compliance with the Langmuir model which assumes monolayer coverage. The values for the Freundlich constant n indicative of binding efficiency of the material for water molecules were within recommended limits in accordance to Tryball (1980) who indicated that value of n between 1 and 10 are indicative of effective adsorption.

4.5.4 BET Isotherms for the CaCl₂ Supported on PSBE Desiccant

In order to have a good understanding on the water sorption, the BET model proposed by Brunauer *et al.*, (1938) was employed to fit the experimental data. According to BET theory, physical sorption involves the formation of many molecular layers of adsorbates on the adsorbent surface. Water sorption was modeled by the linear equation 2.23 given in chapter 2. According to the equation, a plot of $P/X(P^0-P)$ versus P/P^0 gives yield to linear curves whose slope and the y-intercept is equal to $(C-1)/X_m C$ and $1/X_m C$ respectively. The values of X_m and C were obtained from the graphs of experimental sorption data represented by figure 4.9 and used to back calculate the mass of H₂O at monolayer coverage for each period of exposure.

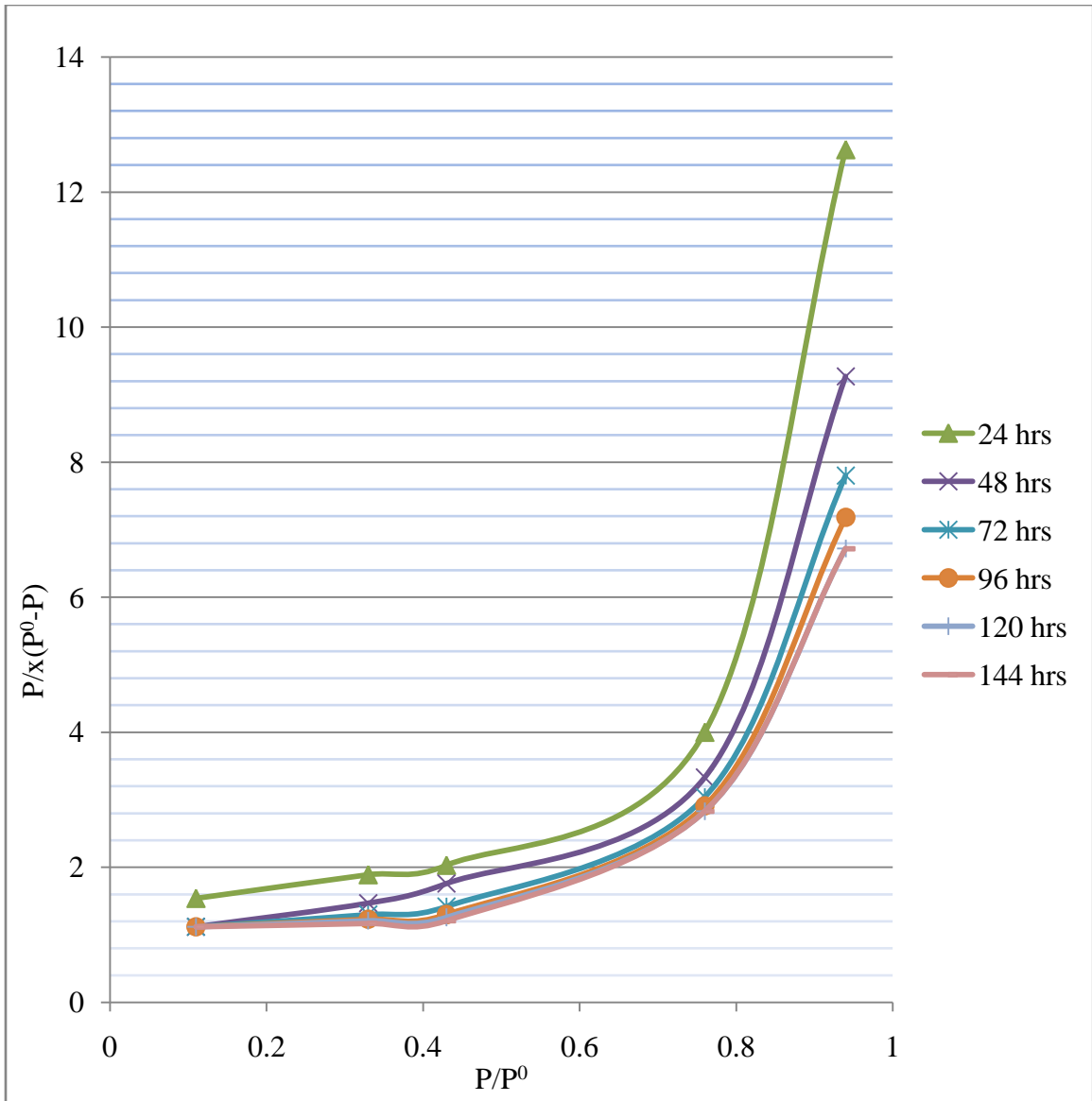


Figure 4.9: Correlations between Experimental Data and BET Isotherms for PSBE-CaCl₂ Adsorbents.

Brunauer-Emmett-Teller (BET) plots for the PSBE-CaCl₂ adsorbent at different period of exposure are presented in Figure 4.9. It was apparent that the plots indeed yielded linear relations for RH values less than 60% ($P/P^0 < 0.6$) as indicated by figures 4.10 and 4.11. The results were satisfactory with the observation made by Likos and Lu, (2002), while determining sorption behaviour of Smectite-Kaolinite adsorbent who established that a linear relation occurred at low relative humidity.

Table 4.16 (a): Parameter Values and Goodness of Fit for BET Model on Experimental Data

Hours of Exposure	R ²	C	X _m mg H ₂ O/g desi	E _I -E _L (j/mol)
24	0.999	1.12	162	12,487.23
48	0.974	3.16	88.5	35,233.2
72	0.990	1.9	123.5	21,184.52
96	0.992	1.52	156.25	16,947.63
120	0.997	1.4	166	15,609.65

Table 4.16 (b): Literature Values of some Constants in the BET Analysis Model

Adsorbent	R ²	X _m mg H ₂ O/g desi	E _I -E _L (j/mol)	Literature
Kaolinite		5.91	7,366	Likos and Lu (2002)
Smectite		58.4	6,159	
CAI	0.976	180		Zhang <i>et al.</i> , (2005)
MSG	0.946	670		
CaCl ₂	0.999	1260		

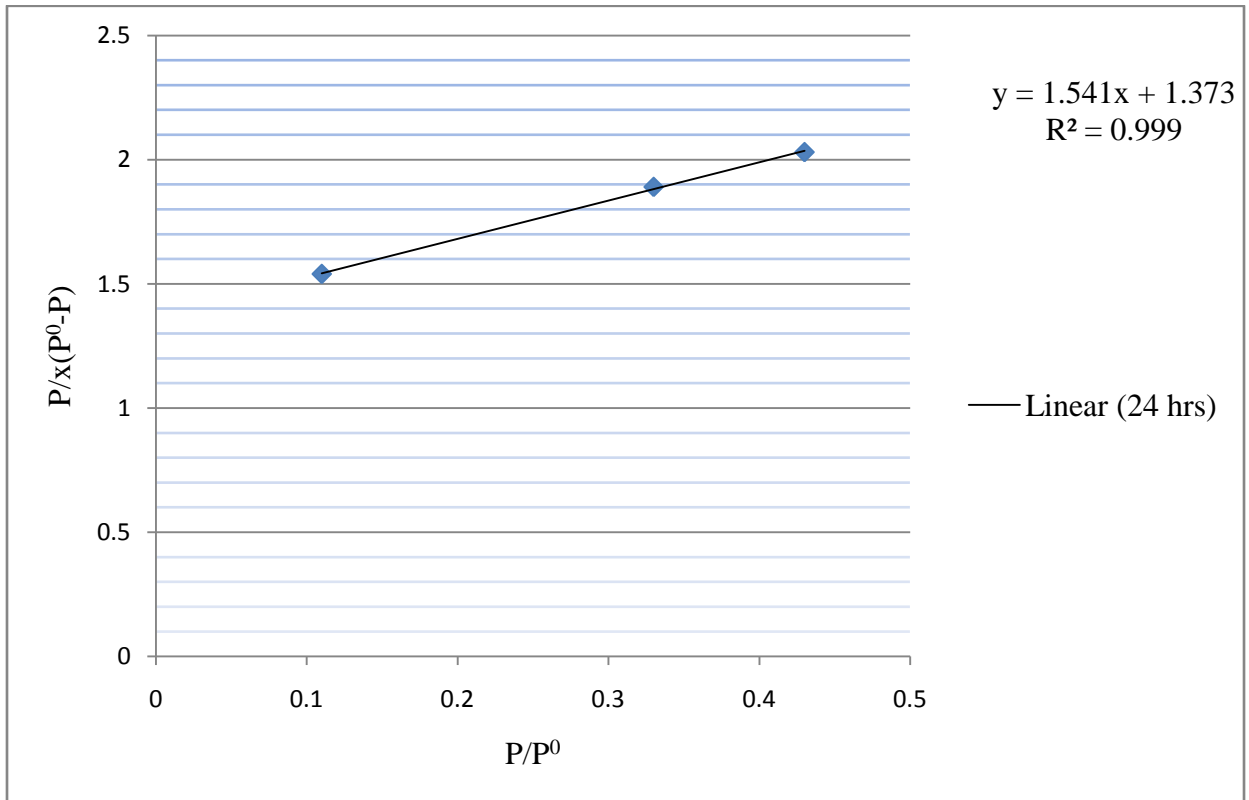


Figure 4.10: Linear Graph for BET Model at Low Relative Humidity ($P/P^0 < 0.6$) for 24 Hours of Exposure.

The linearity was observed to improve with long exposure of the solids to testing environment as observed in table 4.16 (a) with 120 hours of exposure recording regression analysis value of 0.997 which was an indication of experimental data adhering to Langmuir model at low relative humidity. The R^2 value of 0.999 observed at 24 hours of exposure is ascribed to the high water uptake for the first few hours of exposure.

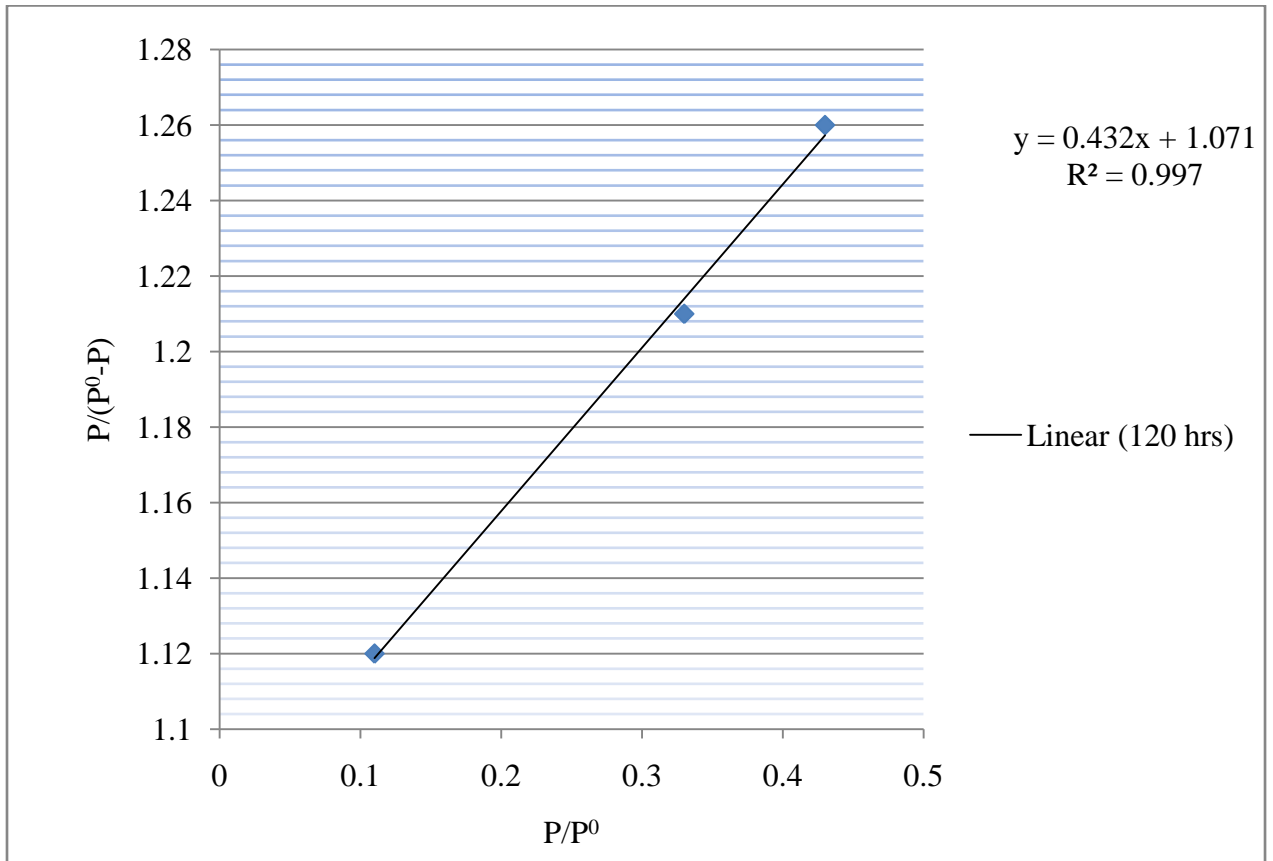


Figure 4.11: Linear Graph for BET Model at Low Relative Humidity ($P/P^0 < 0.6$) for 120 Hours of Exposure.

The linearity at low pressure is associated to basic assumption of Langmuir adsorption isotherm that adsorption is monolayer in nature. Under these conditions, water molecules were assumed to possess high thermal energy and high escape velocity which resulted to less number of molecules near the surface of the desiccant. Under high pressure and low

temperature, thermal energy of water molecules decreases and more molecules accumulates on the surface of the adsorbent causing multilayer adsorption to occur. This in turn leads to the breakage of linearity as observed in figure 4.9 for RH beyond 0.6 (Likos and Lu, 2002). The adsorption isotherm represented by figure 4.9 resembled type III isotherm (Ustinov *et al.*, 2005) which was a characteristic of nonporous or macroporous adsorbent with a weaker fluid-solid interaction.

Table 4.16 (a) presented mass of water at monolayer coverage as 166 mg per gram of the desiccant. The value was observed to be almost triple of the value documented for smectite but very low as compared to the value for CaCl_2 . This implied that, CaCl_2 indeed enhanced the sorption capacity of the PSBE (Thoruwa *et al.*, 2000). The sorption isotherms discussed showed that the BET model was more convenient in fitting and interpreting the results obtained especially if the high humidity were included. The isotherm type III figure 4.9 indicated a large deviation from Langmuir model which confirmed the results obtained in table 4.15 (b). The results for water sorption were found to be practically interpreted by BET model at high relative humidity and to fit Langmuir model at low relative humidity where linearity was established.

4.6 Determination of Thermo physical Properties of Solid PSBE Supported CaCl_2 Sorbent

Evaluation of air dehumidification and regeneration performance of RSBE supported CaCl_2 in a packed bed requires the knowledge of the thermo physical properties. Thermo physical referred to here include: equivalent diameter, bulky density, particle density, specific heat capacity, thermal diffusivity, thermal conductivity, porosity and heat of hydration. The knowledge of porosity is essential in determining pressure drop and flow rate characteristics of packed beds while specific heat, thermal conductivity and heat of

hydration are important in determining the heat and mass transfer characteristics of desiccant bed. Since most of the thermo physical properties outlined above are determined theoretically in literature (Tretiak and Abdallah, 2009), the present work reports only the results for thermo physical properties that could be determined experimentally namely; bulky density, particle density and equivalent diameter which were reported for the purpose of comparison of the present sorbent with the clay-CaCl₂ desiccant.

4.6.1 Bulky Density and Equivalent Diameter

The bulky density obtained from a core ring apparatus are provided in Table 4.17. The volume of the apparatus was calculated from the dimensions provided in appendix IV B and the relation 4.3 which amounted to 98.1748cm³.

$$v = \pi r^2 h \quad (4.3)$$

$$v = \pi 5^2 5$$

$$= 98.1748 \text{ cm}^3$$

Table 4.17: Bulky Density and Equivalent Diameter of PSBE Supported CaCl₂ of One Particle Size

Trial Number	Mass of sorbent (grams)	Number of balls that fills the core-ring	Bulky Density in kgm ⁻³	Equivalent Diameter in cm
1	71.30	203	726.26	0.97
2	70.80	207	721.16	0.97
3	72.00	206	733.39	0.97
4	71.10	204	724.21	0.97
5	70.20	210	715.05	0.96
Mean	71.08	206	724.01	0.97
Standard Deviation	0.66	2.74	4.49	0.9700

The calculated volume was used to calculate the bulky densities of different samples of PSBE supported CaCl_2 using the relation given in equation 2.25 and sample calculation 4.4.

$$\begin{aligned}\phi_b &= \frac{0.0713}{0.0000981748} & (4.4) \\ &= 726.2557 \text{ kgm}^{-3}\end{aligned}$$

The calculation of the bulky density is also represented in appendix (IV A). The mean bulky density obtained was $724.0147 \text{ kgm}^{-3}$ with a standard deviation (STDEV) of 4.4886 as indicated in Table 4.17. The value obtained indicated low degree of compaction of the spherical balls in a unit volume. Therefore, the adsorbent developed can be utilized in the design of desiccant wheels or packed bed for air dehumidification in large scale, because of its low bulky density which indicates high porosity of the material hence the air to be dehumidified can easily penetrate the adsorbent bed. In addition, most isotherm data are published as loading per unit mass, which is fine for determining total adsorbent cost, since prices are quoted per unit mass. The less the bulky density the lower the production cost. Conversely, the bulky density assists in determining the vessel dimension from the necessary amount of adsorbent.

Sample calculation for the equivalent diameter is given by equation 4.5.

$$\begin{aligned}\text{Volume of 1 ball} &= \frac{98.1748 \text{ cm}^3}{206} & (4.5) \\ &= 0.4766 \text{ cm}^3 \\ \frac{4}{3}\pi r^3 &= 0.4766.\end{aligned}$$

$$r = \sqrt[3]{\frac{0.4766 \times 3}{4\pi}}$$

$$= 0.4846 \text{ cm}$$

$$\text{Equivalent diameter } d_e = 0.4846 \times 2 = 0.9692 \text{ cm}$$

The equivalent diameter was obtained as 0.9692 cm with a standard deviation of 0.97 as observed from the table which was slightly lower than value used in development of about 1cm in procedure 3.5.1. The reduction was attributed to the loss of water and compaction of the desiccant balls during thermal treatment. However, the results for equivalent diameter indicated that, thermal treatment did not alter significantly the compaction of the solid adsorbent which accounts for the low bulky density obtained in relation 4.4.

4.6.2 Particle Density

Table 4.18: The Particle Densities in kgm^{-3} of the Solid Samples

Trials	Particle density in kgm^{-3}
1	2363.50
2	2363.30
3	2365.10
Mean	2363.97
Standard deviation	0.9866

The average particle density obtained was 2363.97 kgm^{-3} with a deviation of (0.9866), which differed with a value of 106.73 kgm^{-3} from the particle density obtained by Thoruwa *et al.*, (2000), while working on calcium chloride supported on clay sorbent. The difference was associated with the use of the polythene paper which could have resulted to some errors in the measurement of the volume for the samples. The use of the

polythene paper to prevent the wetting of the samples thus led to the difference observed from literature values. The calculation of the particle density is represented in the Appendix (IV, C). The results for the particle density are significant since particle density determines the inner porosity of the adsorbent particle, but excludes void fraction of the bed. The value of 2363.97 kgm^{-3} indicates that the particle size is small implying that the adsorption rate of the water molecules diffusing into the intra particle structure is increased. The increased rate of adsorption afforded by the high value of particle density obtained in Table 4.19 leads to less adsorbent requirement for the bed depth as well as contact time for the region in which the adsorbate is being removed, thus reducing the production cost. Moreover, the particle density assists in determining how fast heat can be moved in the bed based on porosity. The greater the value of particle density compared to the bulky density, the more the porosity of the packed bed and the faster the heat transfer which is important in air dehumidification for air-conditioning application. Table 4.19 gives a summary of the average of thermo-physical determined.

Table 4.19: Summary of the Average Values Obtained for the Thermo-Physical Properties

Bulky Density	Equivalent Diameter	Particle Density	Pore Space	Porosity
724.00 kgm^{-3}	0.97 cm	2363.97 kgm^{-3}	70%	0.70

From the three thermo physical properties determined experimentally, the PSBE was shown to portray both physical and chemical properties almost similar to properties portrayed by the virgin bleaching earth after solvent and thermal treatment since PSBE- CaCl_2 desiccant possessed almost similar properties as Clay- CaCl_2 desiccant developed by Tretiak and Abdallah (2009). Furthermore, the adsorbent developed was found to

posses a porosity of 0.7 and pore space of 70% as presented in Table 4.19, which indicates that it can be utilized in developing desiccant wheels or packed bed for air dehumidification applications.

4.7 Summary of Major Findings of This Study

From this study, it was apparent that SBE could be used as a host material for CaCl_2 in desiccant development as it contained the deliquescence behaviour of the salt. The purification for the SBE in desiccant development application was found to be a three step procedure which was unique from other uses for the residue. The purification step was found to restore the properties of the virgin bleaching earth and the acid activation step was found not vital in the activation process. Purified spent bleaching earth was found to adsorb about 15% of water by weight which was identical to water sorption capacity of pure clay such as smectite family. With this sorption capacity and availability, PSBE was found necessary to be the host material for suppressing the deliquescent behaviour of calcium chloride.

In order to prepare the adsorbent, the mixing ratio of the components was established and a mixture of PSBE, CaCl_2 and starch in the ratio of 3: 1: 0.20 was established to give the best adsorbent in terms of thermal physical and sorption characteristics. The starch was included in the matrix as an auxiliary binder which strengthened the matrix and curbed the disintegration of the adsorbent on prolonged exposure to high relative humidity. The best processing temperature was established to be 550 °C. The solid matrix developed was found to be effective in removing 40 to 48% of water from air especially in high humidity environments and thus could be used in packaging and preservation of goods in tropic regions such as Mombasa and other areas with high relative humidity. The amount

of water adsorbed by the adsorbent developed was comparable to commercially available desiccants as discussed earlier thus justifying the findings.

The results of the isotherms indicated that Freundlich model fitted the experimental data well than Langmuir model though the later was well defined at low temperatures. The BET isotherm which characterizes multilayer adsorption showed that the water adsorption followed type III isotherm as discussed which was an indicative that water sorption on desiccant matrix involved multilayer rather than monolayer adsorption. The multilayer is a characteristic of physical adsorption which implied that desiccants primarily attract water by physical adsorption. This means that water molecule attracted in the adsorbent forms the first layer which also attract water from the air, that is, the layer of water formed becomes adsorbent. The finding of this study hence gives an alternative disposal protocol for spent bleaching earth and a low cost adsorbent for air dehumidification applications in tropical regions. From the comparison study with silica gel, it was observed that the adsorbent developed was more efficient at high relative humidity with equilibrium adsorption capacity of 48%.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the findings of this study, the following conclusions were drawn;

- i. Reactivation efficacy of different reactivation conditions investigated showed that solvent oil extraction followed by 30% H₂O₂ oxidation and heat treatment at 550 °C are the most effective in SBE reactivation for desiccant development
- ii. Hexane was found to be the best choice in extraction as it yielded almost pure oil hence maximizing on the re-use of the SBE components on non-food oleo chemical applications
- iii. It was evident that acid treatment did not improve the sorption properties of the SBE as acid treated samples recorded almost similar adsorption capacity as the acid-untreated samples thus the step concluded not necessary
- iv. The regeneration process followed did not alter the composition of bleaching earth
- v. The best mixing ratio: CaCl₂ : PSBE : Starch = 1: 3: 0.2
- vi. For large scale production of solid PSBE-CaCl₂, samples should be dried at 110 °C for 6 hours, 6 hours at 200 °C and finally fired in a furnace for duration of 3 hours at 550 °C
- vii. PSBE-CaCl₂ mixed in the ratio of CaCl₂: PSBE: starch = 1: 3: 0.2 developed exhibited maximum moisture sorption of about 33-48% under 75-93% RH, comparable to other commercial available desiccants such as silica gel. Therefore the desiccant material is suitable for air dehumidification applications at high humid environs.

- viii. PSBE was able to suppress the dissolution phenomenon of CaCl_2 salt
- ix. Experimental data indicated a good fit to Freundlich Isotherm than Langmuir Isotherm
- x. In all cases however, water sorption onto PSBE- CaCl_2 was better described by BET isotherm which conformed to other studies, which implies adsorption involves multilayer coverage rather than monolayer proposed by Langmuir, the sorption followed Langmuir type III isotherm.
- xi. From the thermo physical properties, the solid developed can be applied in desiccant wheel or packed beds for air dehumidification
- xii. From the results of comparison, PSBE- CaCl_2 adsorbent developed was found to have almost equivalent moisture capacity as commercially available silica gel at all relative humidities.
- xiii. The objective and all specific objectives of this study were successfully achieved

5.2 Recommendations

The findings of this study indicated that SBE when regenerated has a high potential for dehumidifying air; however, the study makes the following recommendations for future work:

- i. Further work on the SBE adsorptive properties for air dehumidification using other hygroscopic salts that are not deliquescent in nature is important
- ii. The virgin bleaching earth as the host material for CaCl_2 salt in the development of desiccants to be investigated.
- iii. Other auxiliary binders which are non hydrophobic to be tested such of vermiculite.

- iv. The feasibility re-use of the oil extracted in soap making and bio-diesel manufacture to be investigated in order to ensure maximum utilization of the SBE waste.
- v. More tests to be carried out on the thermo physical properties of the PSBE-CaCl₂ solid samples.
- vi. From the results obtained, it is recommended that the oil manufacturing industries should utilize the spent bleaching earth (SBE) in developing other adsorptive materials such as desiccants which they utilize or sell to other industries rather than disposing the material in the potential land.

REFERENCES

- Ahmed, M.H. (2005). Experimental Investigation on the Adsorption/Desorption Processes using Solid Desiccant in an Inclined-Fluidized Bed. *Journal of Renewable Energy*; **30**: 1913-1921.
- Aksu, Z. (2005). Application of Biosorption for the Removal of Organic Pollutants: A Review, *Process Biochemistry*; **40**: 997-1026.
- Albright, L.D. and Behler, M.L. (1984). An Air-Liquid Heat Exchanger for Greenhouse Humidity Control. *Transactions of the American Society of Applied Engineering*; **27**: 1524-1530.
- Al-Zahrani, A.A. and Daous, M.A. (2000). Recycling of Spent Bleaching Clay and Oil Recovery, *Press Safety and Environment Protection*; **78** (B3): 224-228.
- Aristov, Y., Cacciola G. and Parmon V.N. (2002). A Family of New Working Materials for Solid Sorption Air Conditioning Systems. *Applied Thermal Engineering*; **22**: 191-204.
- Aristov, Y., Tokarev, M.M. and Cacciola G. (1996a). Selective Water Sorbents for Multiple Applications, 1. CaCl_2 Confined in Mesopores of Silica Gel: Sorption Properties. *Reaction Kinetics and Catalysis Letters*; **59** (2): 325-333.
- Aristov, Y., Tokarev, M.M. and Cacciola G. (1996b). Selective Water Sorbents for Multiple Applications, 2. CaCl_2 Confined in Mesopores of Silica Gel: Sorption Properties. *Reaction Kinetics and Catalysis Letters*; **59** (2): 335-342.
- Armstrong, P.R. and Brusewitz, G.H. (1984). Design and Testing of a Liquid Desiccant Dehumidifier. *Transactions of the American Society of Applied Engineering*; **27** (1):169-172.
- ASHRAE. (1983). Sorption Dehumidification and Pressure Drying Equipment. In: American Society of Heating and Refrigerating and Air-Conditioning Engineers, New York.
- Aziz, A.R., Harcharan, S., Elkanzi, E.M., Lam, L.S. and Liew, S.H. (2001). Feasibility Study of Oil Recovery from Used Bleaching Earth Using Waste Solvents. Porim International Palm Oil Congress. Proc. PP. 126-133.
- Barker, J.J. (1965). Heat Transfer in Packed Beds. *Journal of Industrial Engineer and Chemical Society*; **57**: 43-51.
- Barton, T.J., Klemperer, L.M. and Yaghi, O.M. (1999). Tailored Porous Materials. *Journal of chemical materials*; **11**: 2633-2656.
- Berend, I., Cases, J., Francos, M., Uriot, J., Michot, L., Maison, A. and Thomas, F. (1995). Mechanism of Adsorption and Desorption of Water Vapour by Homoinic Montmorillonites. *Clays and Clay Minerals*; **43**: 324-336.

- Bharathan, D., Parsons, J.R. and Maclaine-cross, I.L. (1986); Experimental Study of an Advanced Silica gel Dehumidifier. SERI, TR-252-2983, Golden, Co: Solar Energy Research Institute. Proceedings of the Third Symposium on Improving Building Systems in Hot and Humid Climates, Arlington, TX, November 18-19.
- Blair, R., Gagnon, J., Salmon, R.E. and Pickard M.D. (1986) Evaluation of Spent Bleaching Clay as Feed Supplement in Broilers Diets. *Journal of poultry Science*; **59**: 74-79.
- Boukerroui, A. and Ouali, M.S. (2000). Regeneration of spent Bleaching Earth and its Re-use in the Refining of Edible Oil. *Journal of chemical Technology and Biotechnology*; **75** (9): 773-776.
- Brindley, G.W. and Nakahira M. (1957). Kinetics of Dehydroxylation of Kaolinites and Halloysites. *Journal of American Ceramics Society*; **40**: 346-350.
- Brunauer, S., Emmett, P.H. and Teller, E. (1938). "Absorption of Gases in Multimolecular Layers," *Journal of American Chemical Society*; **60**: 309.
- Brusewitz, G.H. and Sharma A.D. (1983). Variable-Depth Sorption Bed for Dehumidification. *Transactions of the American Society of Applied Engineering*; **26** (1): 228-232.
- Brusewitz, G.H. and Stone M.L. (1987). Microcomputer Controlled Desiccant Dehumidifier. *Transactions of the American Society of Applied Engineering*; **30** (2): 459-46.
- Bullock, C.E. and Threlkel J.L. (1966). "Dehumidification of Moist Air by Adiabatic Adsorption". *Transaction of American Society of Heat Refrigeration and Air Conditioning Engineers*; **72**: 301-313.
- Chang, T.W., Wang, M.K. and Lin, C. (2002), `Adsorption of Copper in Different Sorbent/Water Ratios of Soil Systems. ` *Water, Air and Soil Pollution*; **138**: 199-209.
- Chanrai, N.G. and Burde, S.G. (2004). Recovery of Oil from Spent Bleaching Earth. US Patent No. 6,780,321 B2.
- Che Man, Y.B., Tan, C.P., Nor Aini, I., Nazimah, S.A.H. and Gan, H.L. (2005). Characterization of Vegetable Oil by Surface Acoustic Wave Spending Electric Nose. *Journal of Food Chemistry*; **89**: 507-518.
- Cheah, K.Y. and Lion, S.W. (2002) "Regeneration of Spent Bleaching Clay." Malaysia Palm Oil Board, Kaula Lumpur, Malaysia.
- Chipera, S.J. Caley, J.W. and Bish, D.L. (1997) Controlled-Humidity XRD Analyses: Application to the Study of Smectite Expansion/Contraction. *Advances in X-ray Analysis*; **39**: 713-721.
- Collier, R.K., Cale, T.S. and Lavan, Z. (1986). Advanced Desiccant Material Assessment. *Gas Research Institute Report GRI-86/0182*.

- Croome-Gale, D.J. and Roberts, B.M. (1975). Air Conditioning and Ventilation of Buildings. Pergamon Press Ltd., Oxford.
- Dabrowski, A. (2001). Adsorption and its Application in Industry and Environmental Protection. Elsevier Science publishers, Amsterdam. pp. 1-69.
- Dabrowski, A. (2001). Adsorption from Theory to Practice. *Colloid interface science*; **93**: 135-224.
- Dai, Y.J., Wang, R.Z. and Zhang, H.F. (2001). Parameter Analysis to Improve Rotatory Desiccant Dehumidification Using Mathematical Model. *International Journal of Thermal Sciences*; **40**: 400-408.
- Daido, M. (1987). A Recovery and Re-Use System for Fatty Oils from By-Products & Waste Materials of Vegetable Oil Production. *Conservation and Recycling*; **10**: 273-278.
- Del Pennino, U., Mezzega, E., Valeri, S., Alietti, A., Franca-Brigatti, M. and Poppi, L. (1981). Interlayer Water and Swelling Properties of Monoionic Montmollironite. *Journal of Colloid and Interface Science*; **84**, 301.
- DeVries, D.A. (1966). Thermal Conductivity of Soils, In: W.R. VanWijk (Ed.), physics of plant Environment, North Holland publishing Co., Amsterdam.
- Dubinin, M.M. (1975). "Physical Adsorption of Gases and Vapours in Micropores." Progress in Surface and Membrane Science. Academia publishers, New York. PP. 105-134.
- Dupont M., Celestine, B. and Beighin, B. (1994). Desiccant Solar Air Conditioning in Tropical Climates: II-Field Testing in Guadeloupe. *Solar Energy*; **52**(6): 519-524.
- Factor, M.F. and Grossman G. (1980). A Packed Bed Dehumidifier/ Regenerator for Solar Air Conditioning with Liquid Desiccant. *Solar Energy*; **24**: 541-550.
- Fletcher, J.W. (1980). Performance of an Experimental Annual Solar Regenerated Desiccant Crop Dryer. In: American Society of Applied Engineering, National Energy Symposium. **1**: 95-99.
- Florides, G.A., Kalogirou, S.A., Tassou, S.A. and Wrobel, L.C. (2003) Design and Construction of LiBr-water Absorption Machine. *Energy Conservation Management*; **44**: 2483-2508.
- Folletto, E.L., Alves, C.A., Sganzrla, L.R. and Porto, M.L. (2002). 'Regeneration and Utilization of Spent Bleaching Clay.' *Latin American Applied Research*; **32**: 205-208.
- Freundlich, H. (1922). Colloidals and Capillary Chemistry E.P. Daltons and Company, New York. pp. 1-124.
- Fripiat J.J., Gatineau, L. and Van Damme, H. (1986). Multilayer Physical Adsorption of Fractal Surfaces. *Langmuir* **2** (5): 562-567.

- Gastuche, M.C., Toussant, F., Fripiant, J.J., Toulleaux, R. and Van Meesche, M. (1962). Study of Intermediate Stages in Kaolin-Metakaolin Transformation. *Clay Miner. Bull.* **5** (29): 227-236.
- Grim, R.E. (1986). *Clay Mineralogy*. McGraw-Hill Book Company, New York.
- Grimshaw R.W. (1971). *The Chemistry and Physics of Clays and Allied Ceramic Materials*; Ernest Benn Ltd. London. pp. 286, 300.
- Grossman R.B. and Reinsch T.G. (2002). SSSA Book Series: Five methods of soil analysis ch2, Ed. Soil Science Society of America.
- Gupta, A.S. and Thodos. (1963). Direct Analogy Between Mass and Heat Transfer of Bed of Spheres. *Transaction of American Society of Heat Refrigeration and Air Conditioning Engineers*; **9** (6): 751-754.
- Hall, C.W. (1979). *Dictionary of Drying*. Marcel Decker Inc, New York.
- Hamed, A.M. (2002). Theoretical and Experimental Study on the Transient Adsorption Characteristics of Vertical Packed Porous Bed. *Journal of Renewable Energy*; **27**: 525-541.
- Hamed, A.M. (2003). Desorption Characteristics of Desiccant Bed for Solar Dehumidification/ Humidifier Air Conditioning System. *Journal of renewable Energy*; **28**: 2099-2111.
- Haresh K., (2009). Psychometric process: Cooling and Dehumidification and Heating and Dehumidification. HVACR.
- Jia, C.X., Dai, Y.J., Wu, J.Y. and Wang, R.Z. (2007). Use of compound desiccant to develop high performance desiccant cooling system; *International Journal of Refrigeration*; **30**: 345-353.
- Jurinak J.J. and Banks (1982), "A Numerical Evaluation of two Analogy Solutions for a Rotatory Silica gel Dehumidifier," *Heat Transfer in Porous Media*, ASME pub, HTD-vol **22**.
- Kaimal, T.N.B., Vijayalakshmi, P., Laximi, A.A. and Ramakinga, B. (2002). Process for Simultaneous Conversion of Adsorbed Oil to Alkyl Esters and Regeneration of Commercial Spent Bleaching Earth for Reuse. US Patent 0115875 A1.
- Karaborni, S., Smith, B., Heidug, W. and Van Oort, E. (1996). The Swelling of Clays: Molecular Simulations of the Hydration of Montmorillonite. *Journal of Science*; **271**: 1102-1106.
- Kenneth, E.M., Vassilios, G. and Wain-sun, H. (1992). *Adsorption Technology for Air and Water pollution Control*. Lewis Publishers, INC, U.S.A. pp. 1-169.

- Kheang, L.S., Cheng, S.F., Choo, Y.M. and Ngan, M.A. (2006). A Study of Residual Oils Recovered from Spent Bleaching Earth: Their Characteristics and Applications. *American Journal of Applied Sciences*; **3** (10): 2063-2067.
- Kontny, M.J. and Mulski, C.A. (1992). Gelatin Capsule Brittleness as a Function of Relative Humidity at Room Temperature. *International Journal of Pharmacy*; **54**: 79-85.
- Kruk, M. and Jaroniek, M. (2001). Characterization of Modified Mesoporous Silica using Argon and Nitrogen Adsorption. *Journal of Microporous and Mesoporous Matter*; **44-45** : 725-732.
- Langmuir, I.J. (1918). The Adsorption of Gases on Plane Surface of Glass, Mica and Platinum. *Journal of American Chemical Society*; **40**: 1361.
- Lepoidevin, R.E. and Roberts, W.J. (1981). A Prototype Heat Exchanger for Humidity Control in Greenhouses. Paper no. 81-4525.
- Likos, W.J. and Lu, N. (2002). Automated Measurements of Total Suction Characteristics in the High Suction Range: Application to the Assessment of Swelling Potential. *Journal of the Transportation Research Board*, **1755**, 119- 128.
- Liu, Y.F. and Wang, R.Z. (2003). Pore Structure of New Composite Adsorbent $\text{SiO}_2 \cdot x\text{H}_2\text{O} \cdot y\text{CaCl}_2$ with High Uptake of Water from Air. *Journal of Science in China Series; E* **46**(5): 551-559.
- Low, K.S., Lee, C.K. and Lee, T.S. (2003), 'Acid Activated Spent Bleaching Earth as a Sorbent for Chromium (IV) in Aqueous Solution.' *Journal of Colloid Interface Science*, **307** (1): 9-16
- Low, K.S., Lee, C.K. and Lee, Y.K. (1998). Decoloration of Crude Palm Oil by Acid Activated Spent Bleaching Earth. *Journal of Chemical Technology and Biotechnology*; **72**: 67-73.
- Mana M., Ouali M.S. and De Menorval L.C. (2007). Removal of Basic Dyes from Aqueous Solutions with a Treated Spent Bleaching Earth. *J of Colloid Interface Science* **307** (1): 9-16.
- Mana M., Ouali, M.S., Lindheimer, M. and Menorval, L.C. (2008). Removal of Lead from Aqueous Solutions with a Treated Spent Bleaching Earth. *Journal of Hazard Mater*; **159** (2-3): 358-364.
- Mantell, C.L. (1951). Adsorption. McGraw-Hill Book Company New York. pp :349-467
- Maron, S.H., Bobalek, E.G. and Fok, S.M. (1956). Determination of Surface Areas of Carbon Blacks by Soap Adsorption. *Journal of colloid science*; **11**: 21-33.
- Matsuki, K. and Saito, Y. (1988). Desiccant Cooling R & D in Japan. *Transaction of American Society of Heat Refrigeration and Air Conditioning Engineers*; **94** (1): 537-551.

- McDermott, G.N. (1982). Environmental Aspects of Animal and Vegetable Oil Processing. In Bailey's Industry Oil and Fat Products: Vol 2, 4th edition. D. Swern. John Wiley and Sons, New York; 527 & Ndasn; 86.
- Mehmet, M., Kizilcikli, I., Bicer, O. and Tuncay, M. (2003). 'Removal of MCPA from Aqueous Solutions by Acid Activated Spent Bleaching Earth.' *Journal of Environmental Science*; **38** (6): 813-827.
- Mei V., Ghezlagh, H., Gidaspow, D. and Lavan, Z. (1979). Development of Solar Desiccant Dehumidifier. *American Chemical Society, Paper No 799056*.
- Miller, M.W. (1985). Solar Drying Coupled with Solid Desiccant Energy Storage. *Transactions of the American Society of Applied Engineering*; **28** (2): 649-656.
- Mokaya R Jones W Davies, M.E and Whittle, M.E. (1993) Chlorophyll Adsorption by Alumina Pillared Acid Activated Clay. *Journal of American Oil Chemical Society*; **70**: 241-244.
- Mooney, R.W., Keenan, A.G. and Wood, L.A. (1952) Adsorption of Water Vapour by Montmorillonite. II. Effect of Exchangeable Ions and Lattice Swelling as Measured by X-Ray Diffraction. *Journal of the American Chemical Society*; **74**: 1371-1374.
- Ng, K.F., Nair, N.K., Liew, K.Y. and Noor, A.M. (1997) "Surface and Pore Structure of Deoiled Acid- and Heat- treated Spent Bleaching Clays", *Journal of American Oil Chemical Society*; **74** (8): 963-970.
- Odigboh, E.U. (1976). Dehumidified air from Sorbents Beds for Aeration of Food Grains. *Journal of Agricultural Engineering*; **21** (2): 73-280.
- Os'cik, J. (1982). Adsorption. PWM-Polish Scientific Publishers, Warszawa, Warsaw. pp. 28-29.
- Patterson, H.B.W. (1992). Bleaching and Purifying Fats and Oil: theory and Practice. American Oil Chemists' Society Press.
- Patterson, J.W. (1989). Industrial Waste Reduction. *Environ Science technology*; **23**: 1032-1038.
- Pesaran A.A, Penny, T.R. and Chanderna, A.W. (1992). Desiccant Cooling: State of art Assessment, NREL/TP-4147.
- Pollard, S.J.T., Sollars, J.C. and Perry R. (1993). The Reuse of Spent Bleaching Earth: A Feasibility Study in Waste Minimization for the Edible Oil Industry. *Journal of Science Direct*; **45**: 53-58.
- Ruthvan, D.M. (1984). Principles of Adsorption and Desorption process. A Willey Inter science Publication, New York, pp. 116-153.
- Sing, K. (2001). The use of Nitrogen Adsorption for the Characterization of Porous Materials. *Journal of Colloid and Surface*; **157-188**: 3-9.

- Srikhirin, P., Aphornratana, S. and Chungpaibulpatana, S. (2001). Review of Absorption Technologies. *Renewable and Sustainable Energy Reviews*; **5**: 343-372.
- Sumathy K., Yeung, K.H. and Li Yong (2003). Technology Development in the Solar Adsorption Refrigeration Systems. *Progress in Energy and Combustion Science*; **29**: 301-327.
- Taylor, D.R. and Jenkins, D.B. (1987) "Acid-Activated Clays", Society of Mining Engineering of the American Institute of Mechanical Engineers, *Transactions*; **282**: 1901-1910.
- Thompson, R.A. and Isaacs, G.W. (1967). Porosity Determination of Grains and Seeds with Air-Comparison Pycnometer. *Transactions of the American Society of Applied Engineering*, **10** (5): 693-696.
- Thoruwa, T.F.N. and Ben-Abdullah, N. (1988). Moisture Sorption Characteristics of Solid Clay Supported CaCl₂ CSAE paper No. 88-407.
- Thoruwa, T.F.N., Johnstone, C.M., Grant, A.D. and Smith, J.E. (2000). Novel, Low Cost CaCl₂ Based Desiccant for Solar Crop Drying Applications. *Journal of Renewable Energy*; **19** (4): 513-520
- Tretiak and Abdallah (2009). Sorption and Desorption Characteristic of Packed Bed of Clay-CaCl₂ Desiccant Particles. *Journal of Solar Energy*; 1861-1870.
- Ustinov, E.A., Do, D.D. and Jaroniek, M. (2005). Adsorption of Argon and Nitrogen in Cylindrical Pores of MCM-41 materials. Application of Density Functional Theory. *Applied Surface Science*. **252** (4): 1013-1028
- Van der Marel, H.W. and Beutelspacher, H. (1976). Atlas of Infrared Spectroscopy of Minerals and Their Admixtures. Elsevier scientific publishing co. Amsterdam. pp. 190-193.
- Van Thoor, T.J.W., Dijkhoff, K., Codd, L.W., Fearon, H.J., van Oss, C.L., Roebersa, H.G. and Stanford, E.G. (eds.) (1965); *Chemical Technology: An Encyclopedic Treatment (Vol .2) – Nonmetallic Ores, Silicate Industries and Solid Mineral Fuels*. pp. 185-212.
- Wachira, J.M., wa Thiong'o J.K. and Muthakia, G.K. (2005). Low Cost Pozzolana Based Cement from Industrial and Agricultural Waste Materials, *Journal of civil Engineering Research and Practice*; **2** (1): 15-21.
- Wambu, E., Muthakia, G.K., Wa-Thiongo, J.K. and Shiundu, P.K. (2009). "Regeneration of Spent Bleaching Earth and its Adsorption of Copper (II) ions from aqueous solution." *Journal of Applied Clay Science*; **46**: 176-180.
- Wang, G., M. Liu and Claridge, D. (2007). Decouple Modeling of Chilled Water Cooling Coils, *ASHRAE Transactions*, Vol.113, Part 1. p 484-493

- Wang, I. H. and Lin C.I. (2000) "Kinetics of Heat Regeneration of Spent Bleaching Clay", *Journal of Chemical Engineering, Japan*; **33** (3): 522-525.
- Watts, K.C, Bilanski, W.K. and Menzies, D.R. (1986) Comparison of Drying Corn Using Sodium Bentonite and calcium Bentonite. *Canadian Agricultural Engineering*; **28**: 35-41.
- Wilkinson, W.H., Landstrom, G.W. and Novosel, D. (1988). Dublsorb-A Universal Desiccant Hybrid Approach. *Transaction of American Society of Heat Refrigeration and Air Conditioning Engineers*; **94** (1): 563-567.
- William, J.L. and Lu, N. (2002). Water Vapor Sorption Behavior of Smectite-Kaolinite Mixtures. *Clay and Clay Minerals*, vol **50**, No 5, 553-561.
- Young, J.R. (1967). Humidity Control in Laboratory using Salt Solutions- A Review. *Journal of applied Chemistry*; **17**: 241-245.
- Zhang, X.J., Dai, Y.J. and Wang, R.Z. (2003). A simulation Study of Heat and Mass Transfer in a Honeycombed Rotatory Desiccant Dehumidifier. *Applied Thermal Engineering*; **23** (8): 989-1003.
- Zhang, X.J., Sumathy, Y.J. and Wang, R.Z. (2005). Parametric Study on the Silica-Gel Calcium Chloride Composite Desiccant Rotatory Wheel Employing Fractal BET Adsorption Isotherm, *Journal of Energy*; **29**: 37-51.
- Zhou, X., Yang, J. and Guohui, Q. (2004). Adhesive Building and Self-curing Characteristics of α -Starch Based Composite Binder for Green Sand Mould/Core. *Journal of Matter Science and Technology*, vol **20**, No 5, 234-247.

APPENDICES

Appendix I

Raw Data used to generate the Graphs and Isotherms for Water Sorption on the Solid PSBE-CaCl₂ Desiccant in This Study

Table A: Amount of Water Absorbed by Samples of Different CaCl₂ to PSBE Mixing Ratios at Different Temperatures in Percentages.

Temp in °C	300	400	500	600	700
Pure PSBE	13.15	13.23	6.30	3.37	2.53
1:1	-	-	-	-	-
1:2	30.97	42.56	39.3	27.22	18.31
1:3	36.20	38.77	38.4	26.35	16.44
1:4	47.45	41.55	29.7	21.79	13.2
1:5	44.97	41.15	20.4	16.03	12.45
1.6	42.77	32.37	21.2	14.28	13.1
1.8	40.47	34.13	20.3	13.36	9.27

Table B: Effect of Processing Temperature on Water Uptake of Different PSBE-CaCl₂ Samples in % per Dry Weight of the Sample

Temp °C		300	400	500	550	600	650	700
OBE (Virgin Bleaching Earth)	Blank	31.54	22.32	24.11	24.01	17.79	27.64	22.19
	1:3	51.85	58.41	44.98	51.40	37.27	41.12	27.45
	1:4	43.55	51.5	34.72	44.75	34.67	38.35	32.15
	1:5	40.03	49.85	34.38	43.83	32.12	38.86	35.14
PSBE	Blank	21.32	21.87	21.85	27.07	14.64	26.63	21.91
	1:3	41.33	49.63	36.54	46.67	26.48	21.99	19.38
	1:4	39.34	40.75	29.18	38.52	27.18	22.88	20.93
	1:5	37.57	41.15	25.93	36.51	25.13	22.68	18.36

Table C: Effect of Binder Additives on the Sorption Properties of Sorbents

Ratio	00hrs	120hrs	Δ mass in g	Δ mass in %
PSBE-CaCl ₂ without starch	0.3694	0.4961	0.1267	34.29886
	0.3711	0.502	0.1309	35.27351
	0.3580	0.4814	0.1234	34.46927
1:1	0.2752	0.3411	0.0659	23.94622
	0.2756	0.3429	0.0673	24.41945
	0.2666	0.334	0.0674	25.28132
1:2	0.3109	0.3931	0.0822	26.43937
	0.3118	0.3977	0.0859	27.54971
	0.3280	0.4189	0.0909	27.71341
1:3	0.3209	0.4210	0.1001	31.19352
	0.3358	0.4384	0.1026	30.5539
	0.3268	0.4277	0.1009	30.87515
1:4	0.3144	0.4193	0.1049	33.36514
	0.3088	0.4125	0.1037	33.58161
	0.2871	0.3856	0.0985	34.3086
1:5	0.3056	0.4092	0.1036	33.9052
	0.2938	0.3944	0.1006	34.2523
	0.3139	0.4208	0.1069	34.0457

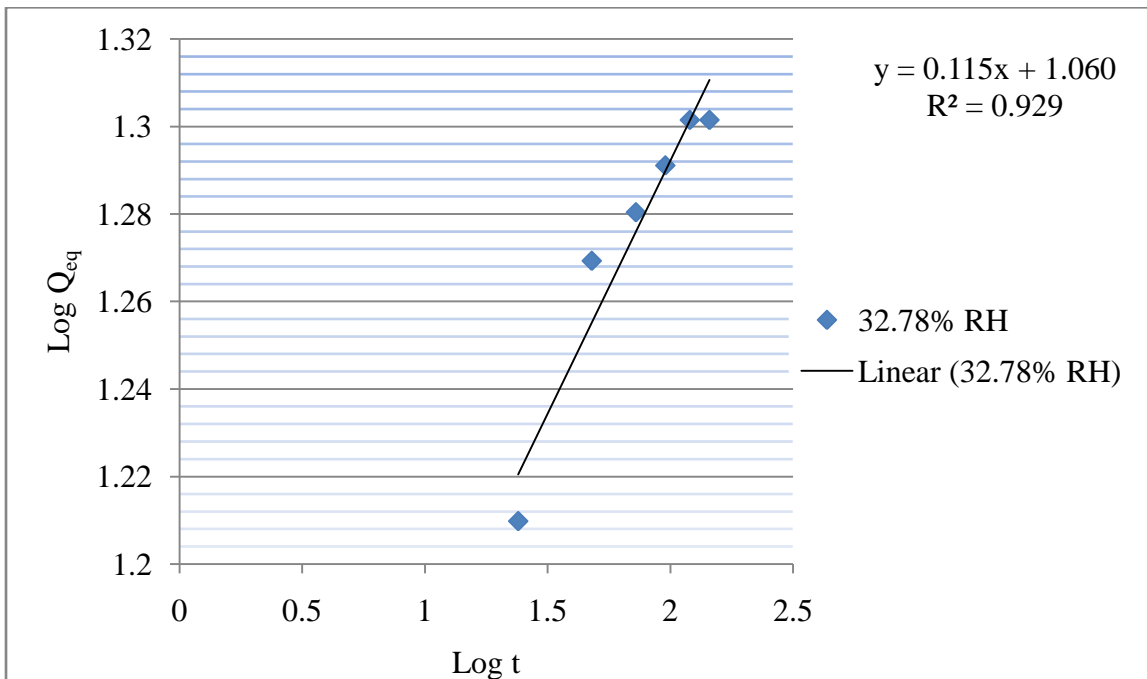
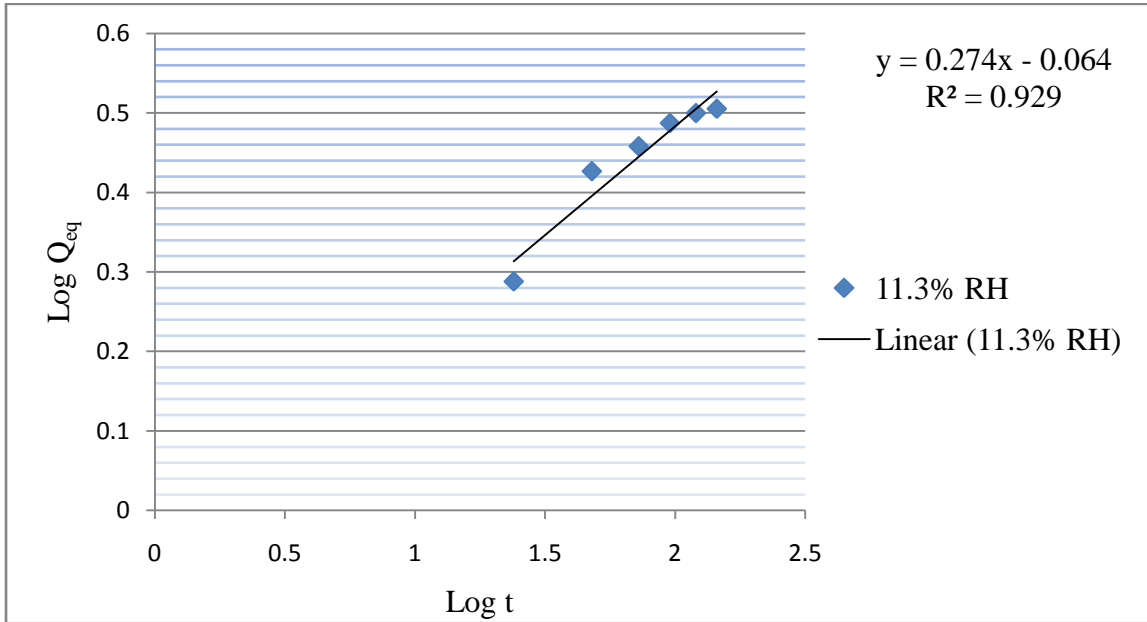
Table D: Moisture Sorption Capacity of the Samples per Dry Weight Desiccant at Different RH Environment

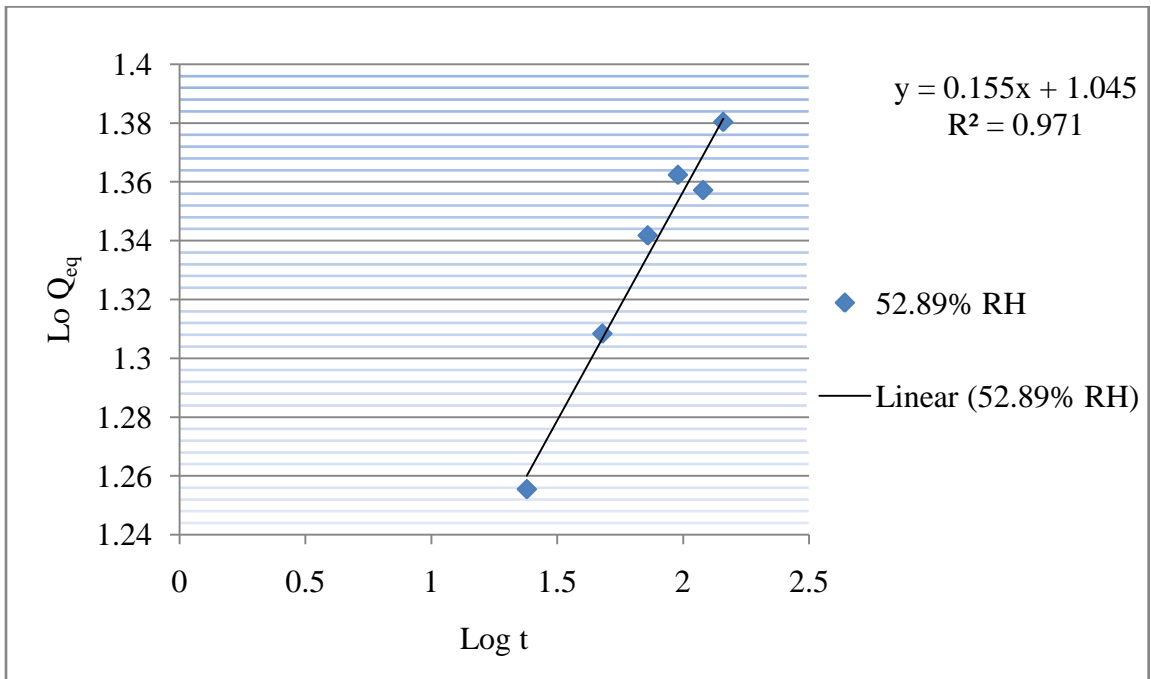
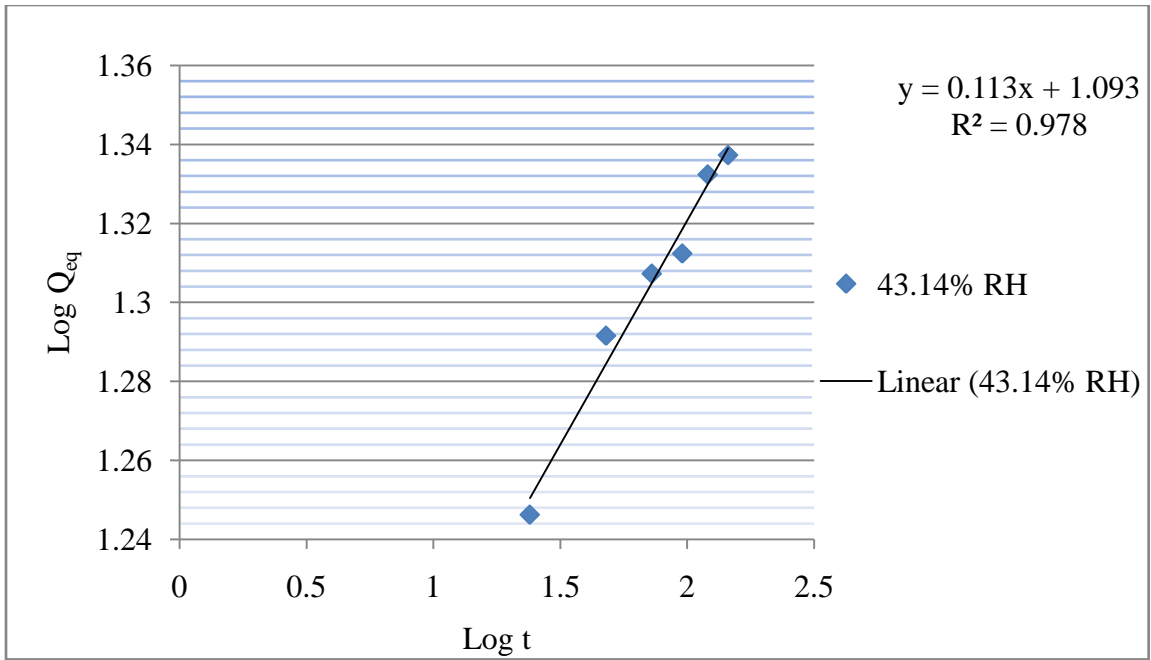
		Amount of water absorbed in % per dry weight of the sample in different duration of exposure to 81% RH environment								
% RH	Time (Hrs)	0	24	48	72	96	120	144	168	192
	11.3	0	1.94	2.67	2.87	3.07	3.16	3.2	3.2	3.2
32.78	0	16.21	18.59	19.07	19.55	20.02	20.02	20.02	20.02	20.02
43.16	0	17.63	19.57	20.29	20.53	21.5	21.74	21.74	21.74	21.74
52.89	0	18.01	20.34	21.97	23.09	22.76	24.01	24.27	24.27	24.28
75.5	0	19.22	33.1	38.3	40.52	42.25	43.22	44.32	44.32	44.32
93.58	0	29.45	40.14	45.51	47.78	47.94	48.19	48.19	48.19	48.19

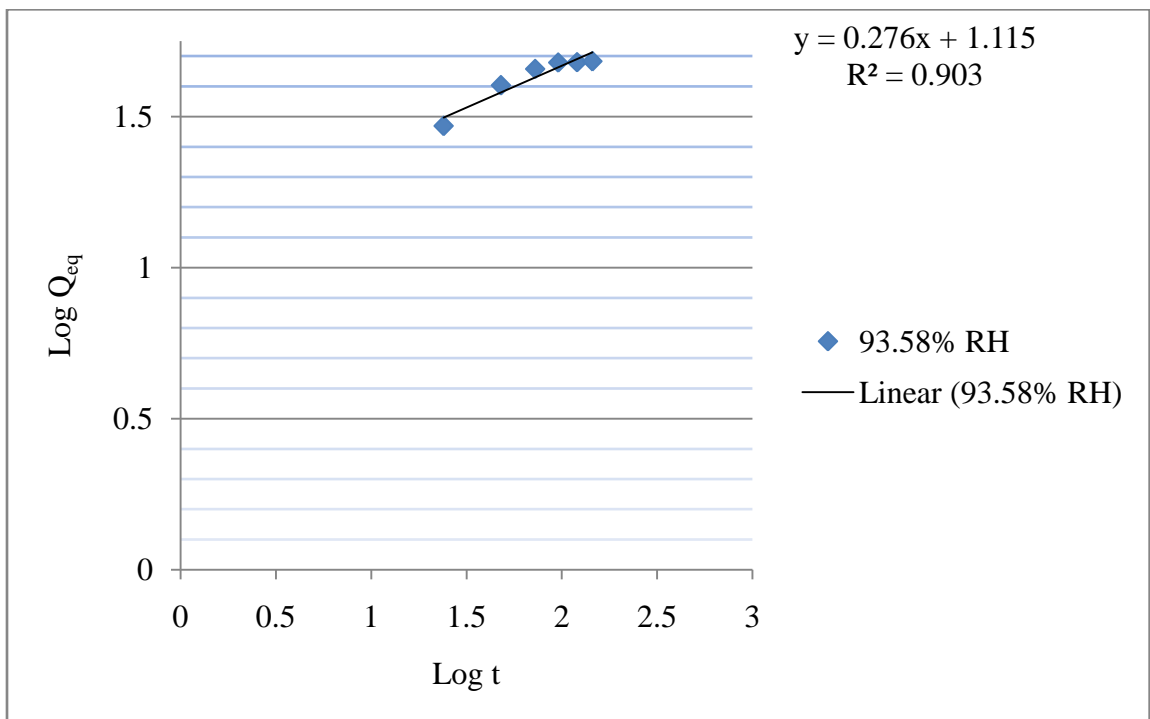
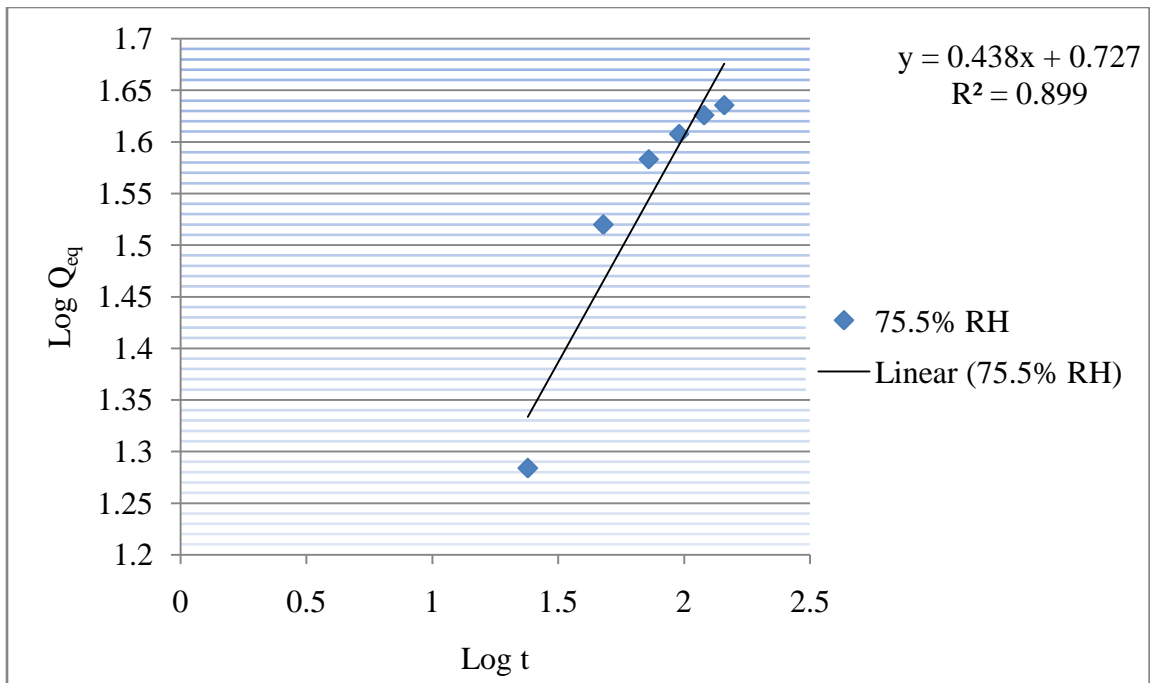
Appendix II

Linear Freundlich and Langmuir Isotherms for the PSBE-CaCl₂ Desiccants Sorption at Different Time Intervals.

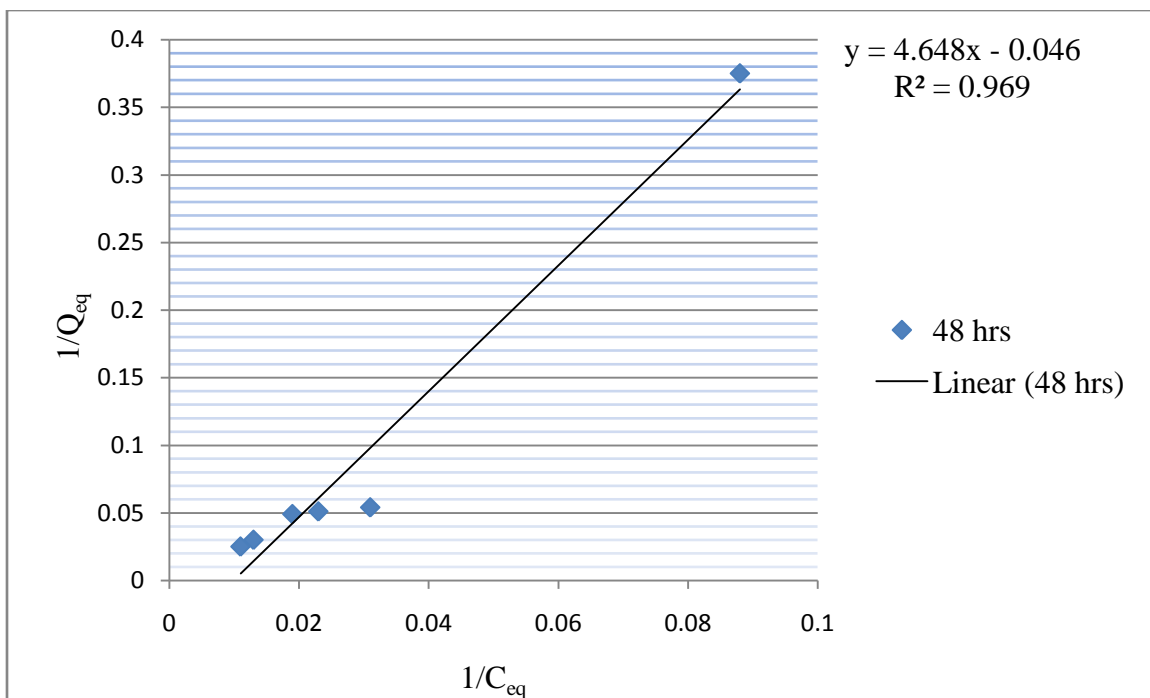
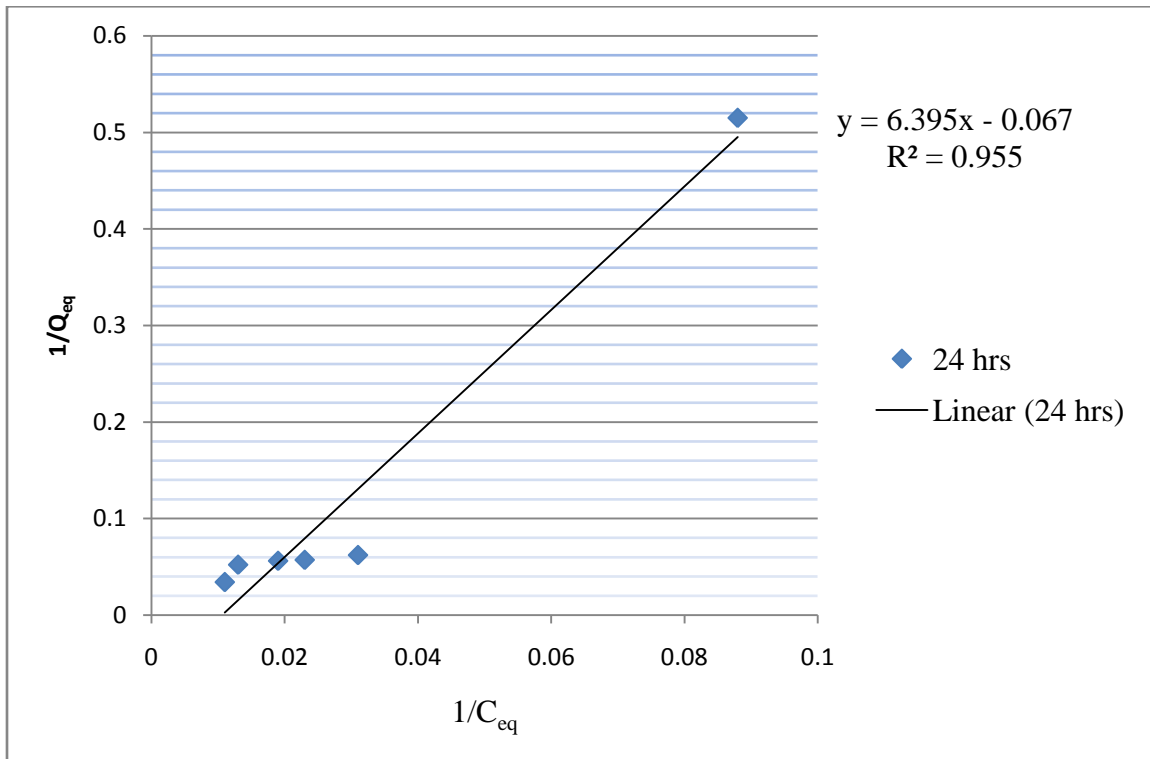
Appendix II (a): Freundlich Isotherms for Solid PSBE-CaCl₂ Desiccants at Different RH.

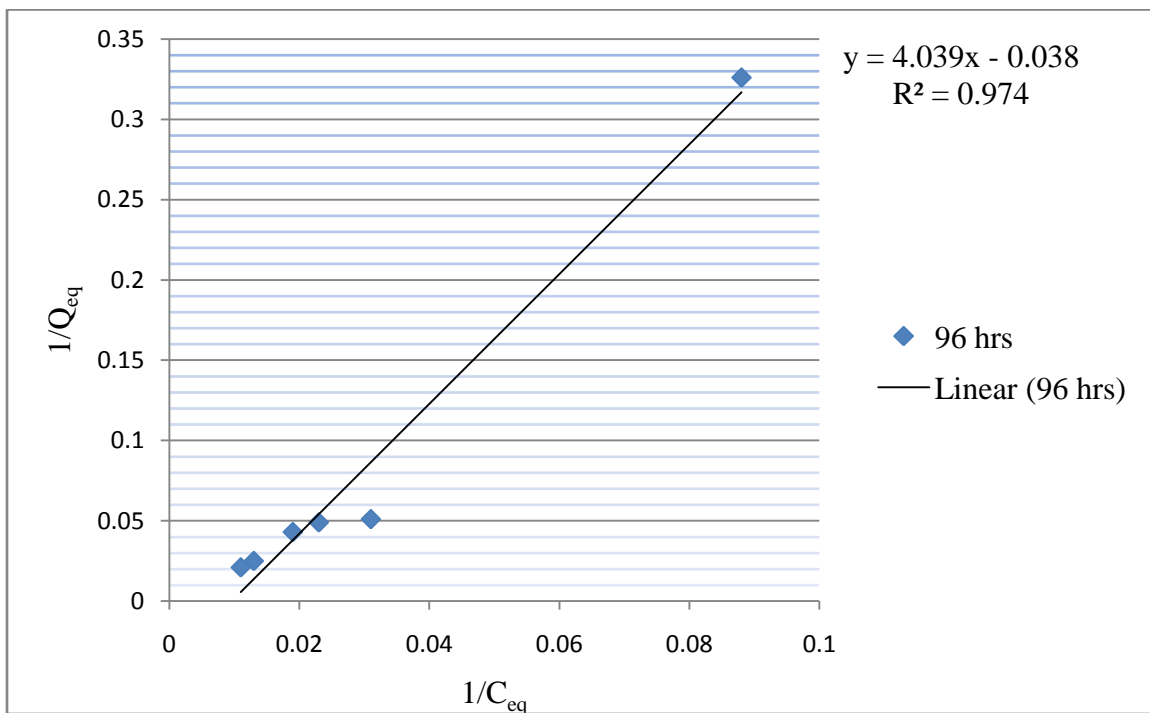
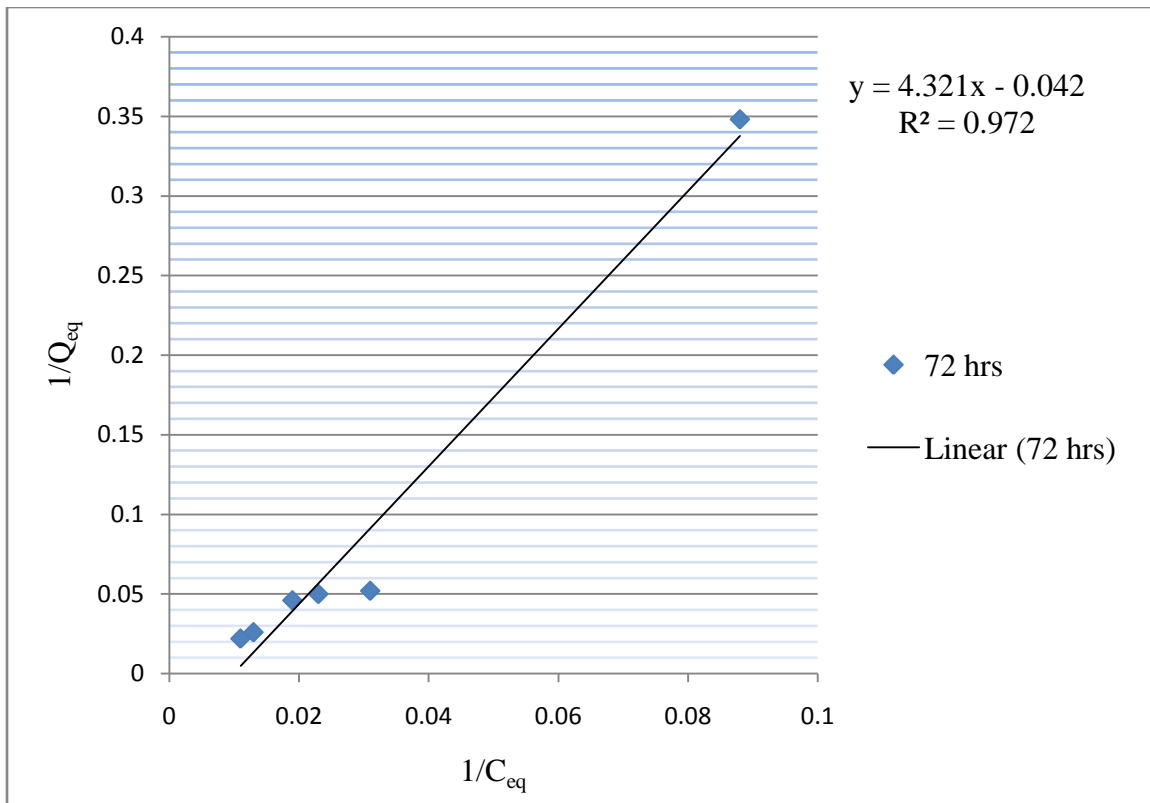


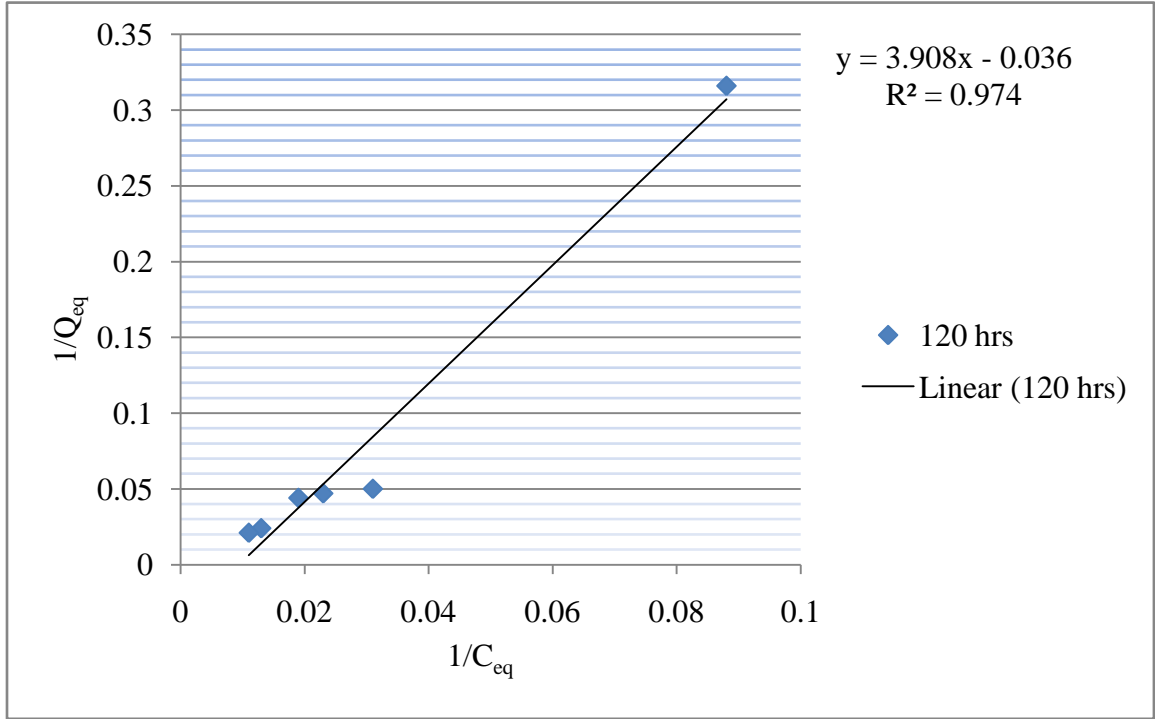




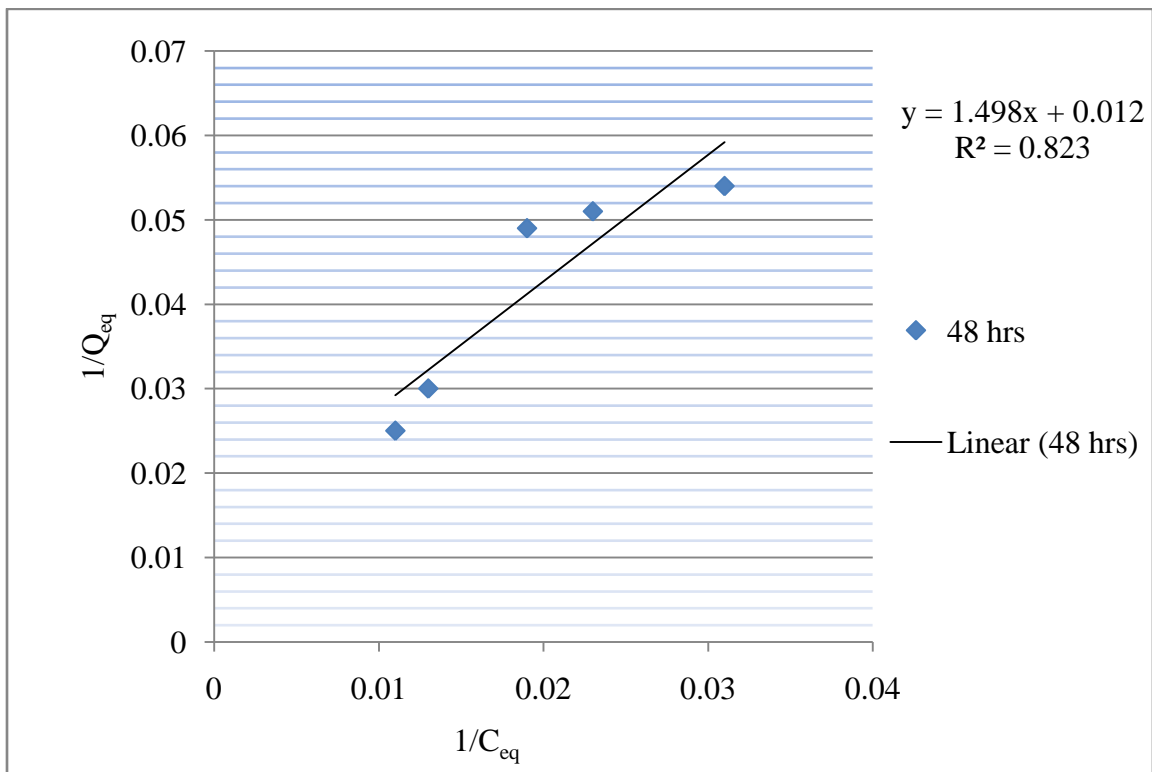
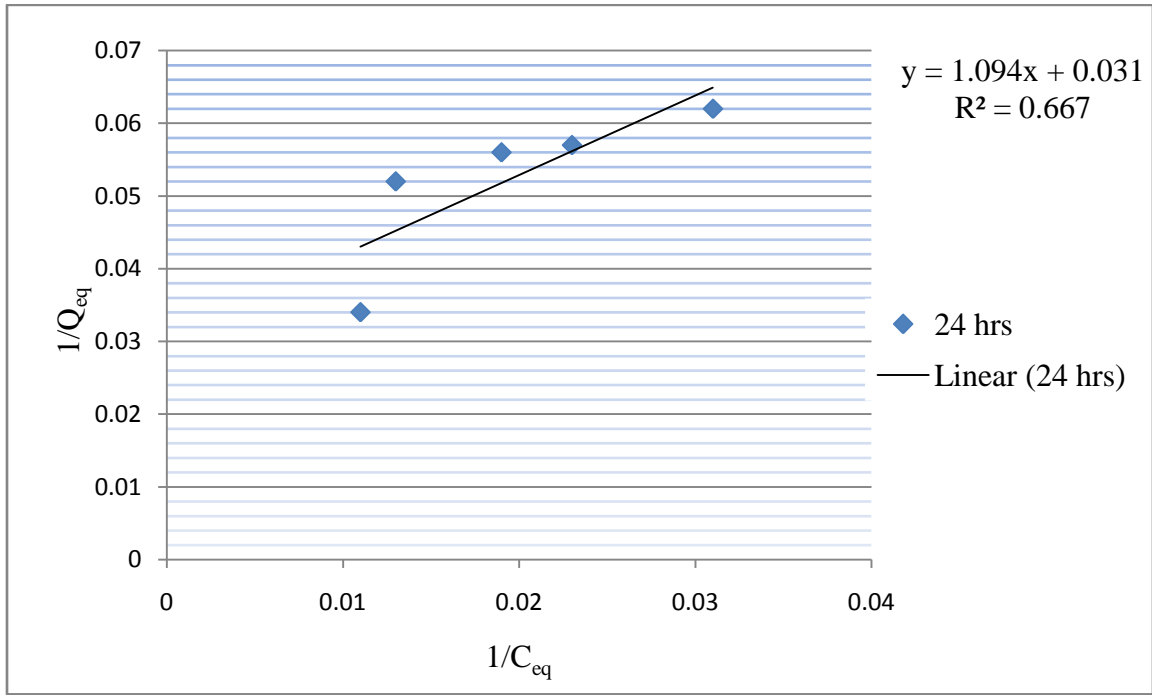
Appendix II (b): Langmuir Isotherms for Solid PSBE-CaCl₂ Desiccants at Different RH.

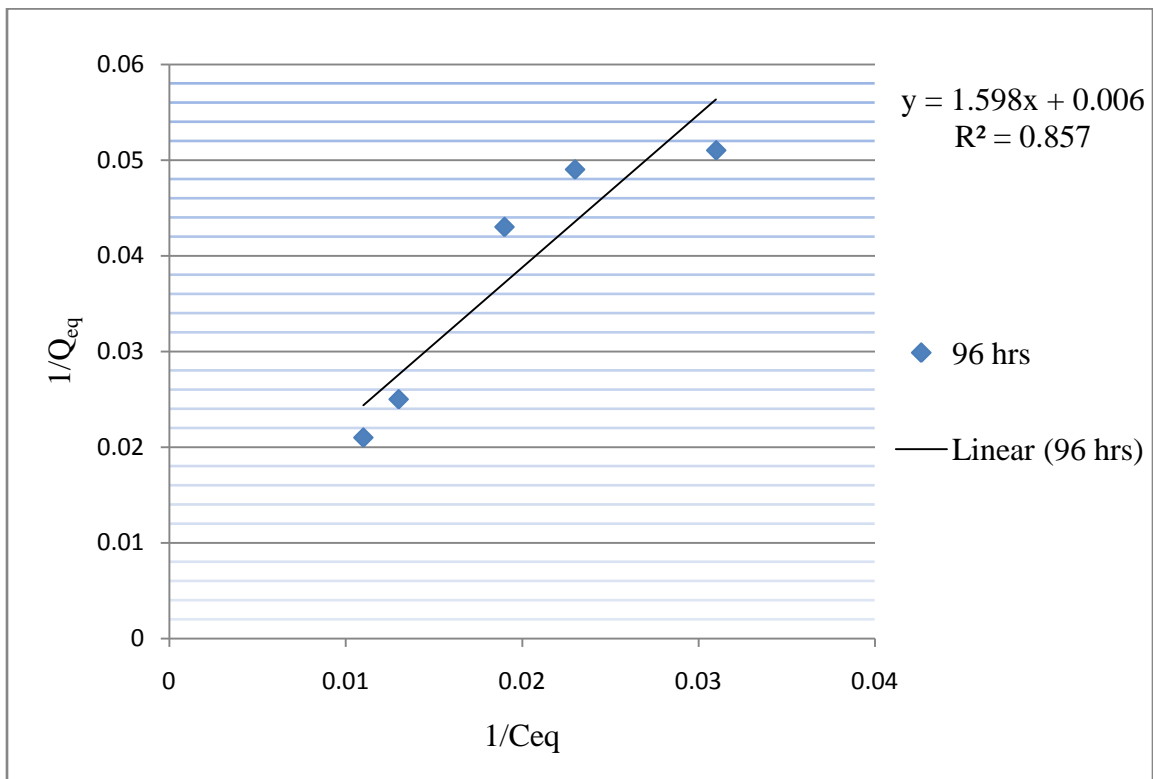
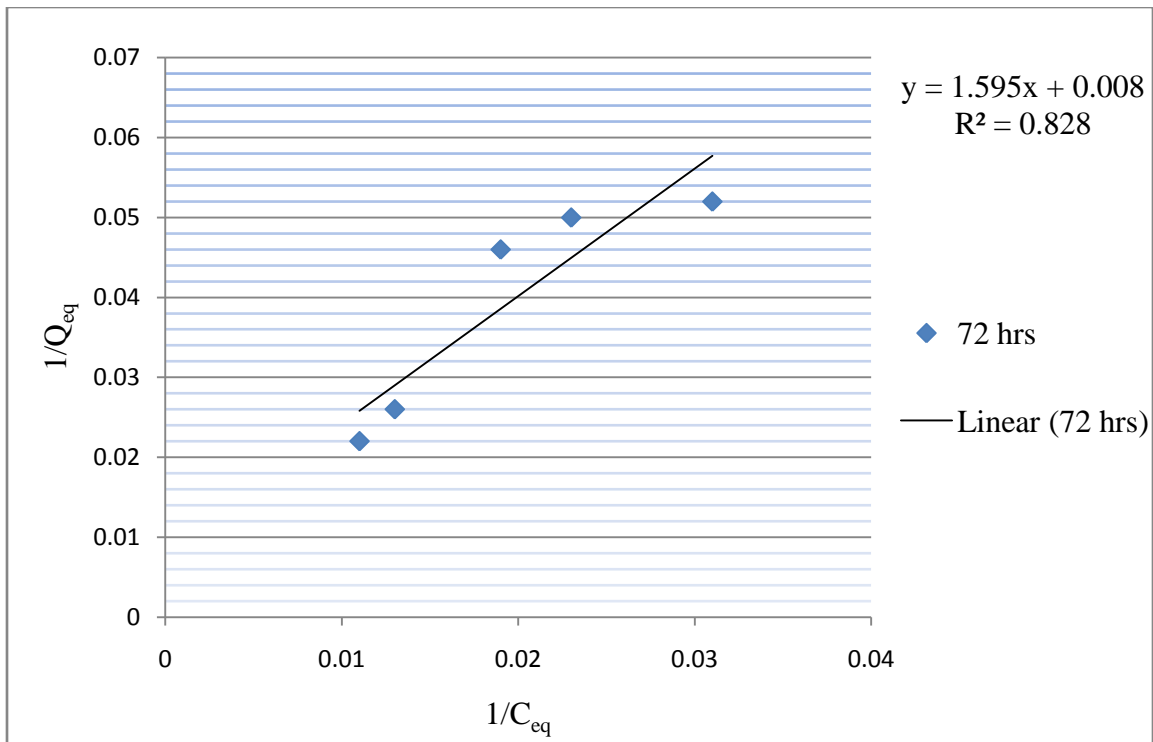


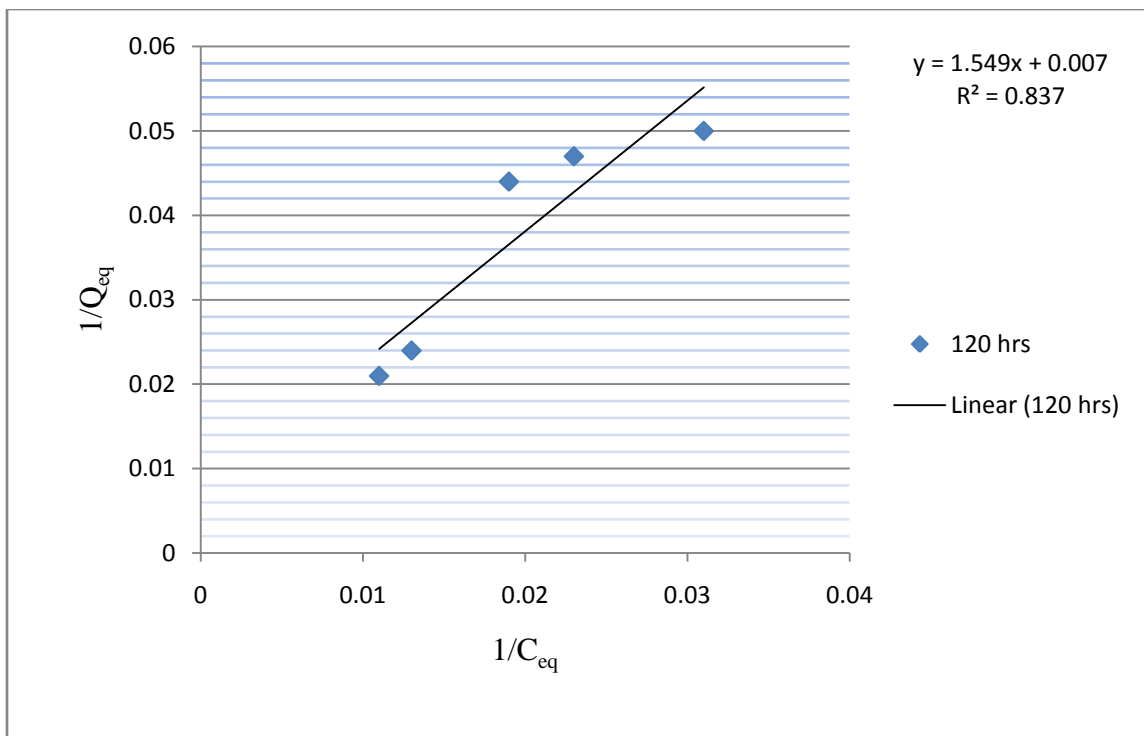




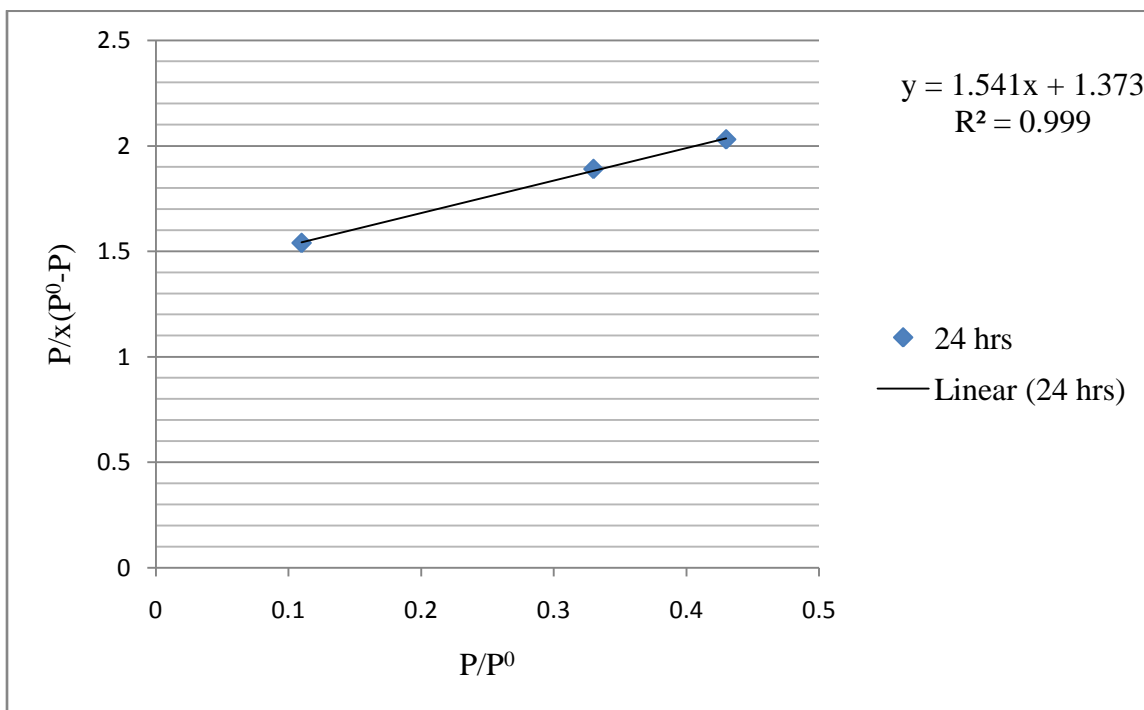
Langmuir Isotherm for Different hours of Exposure 11.3% Relative Humidity not Inclusive

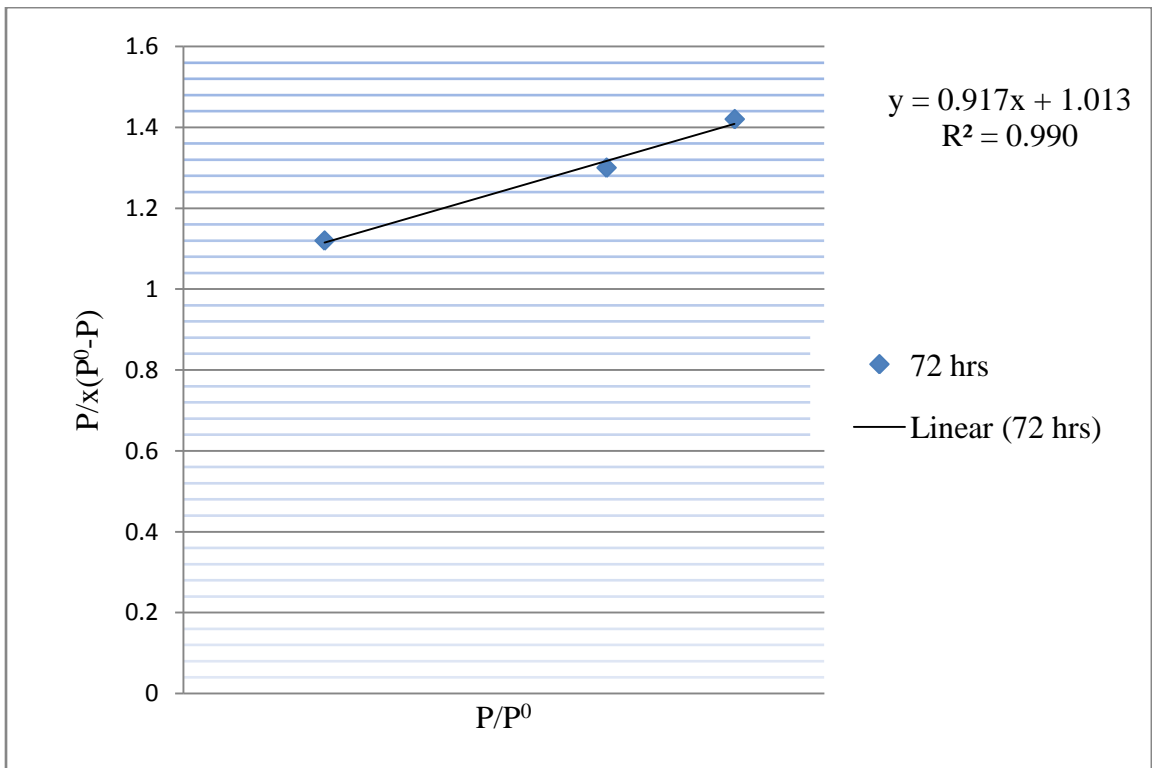
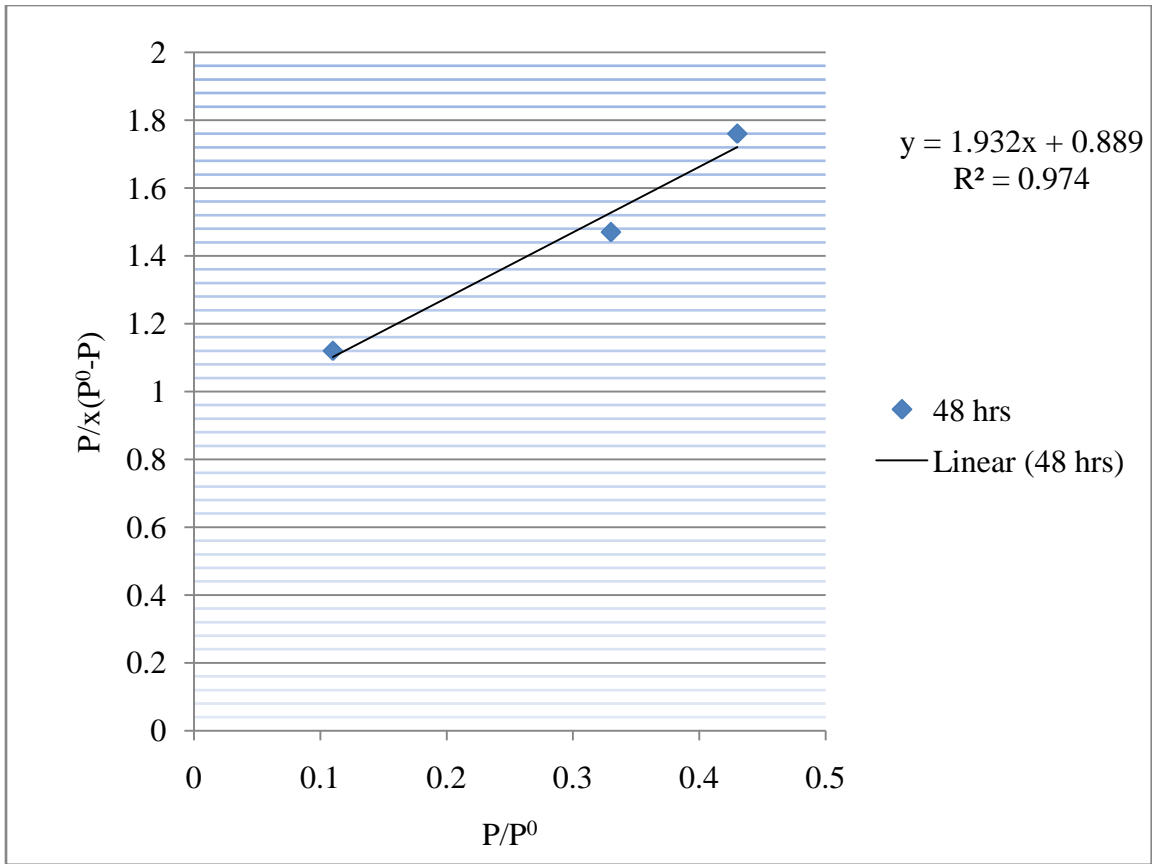


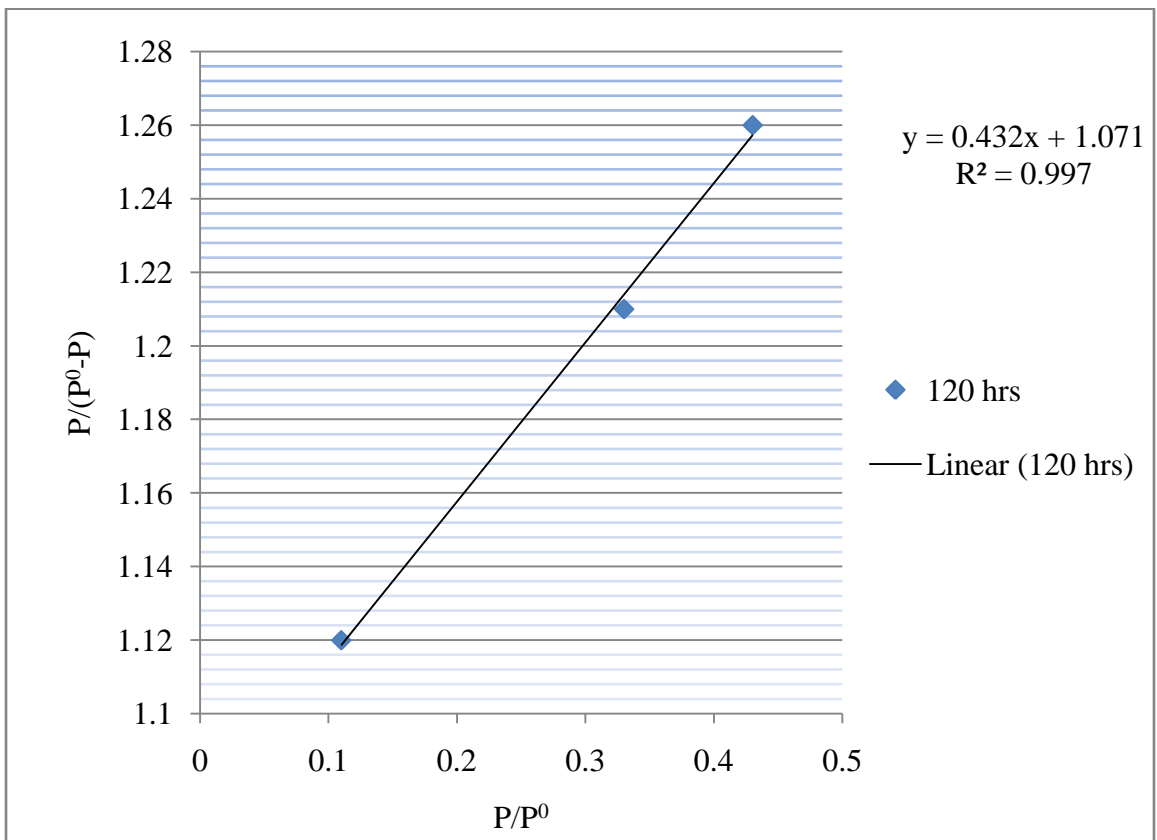
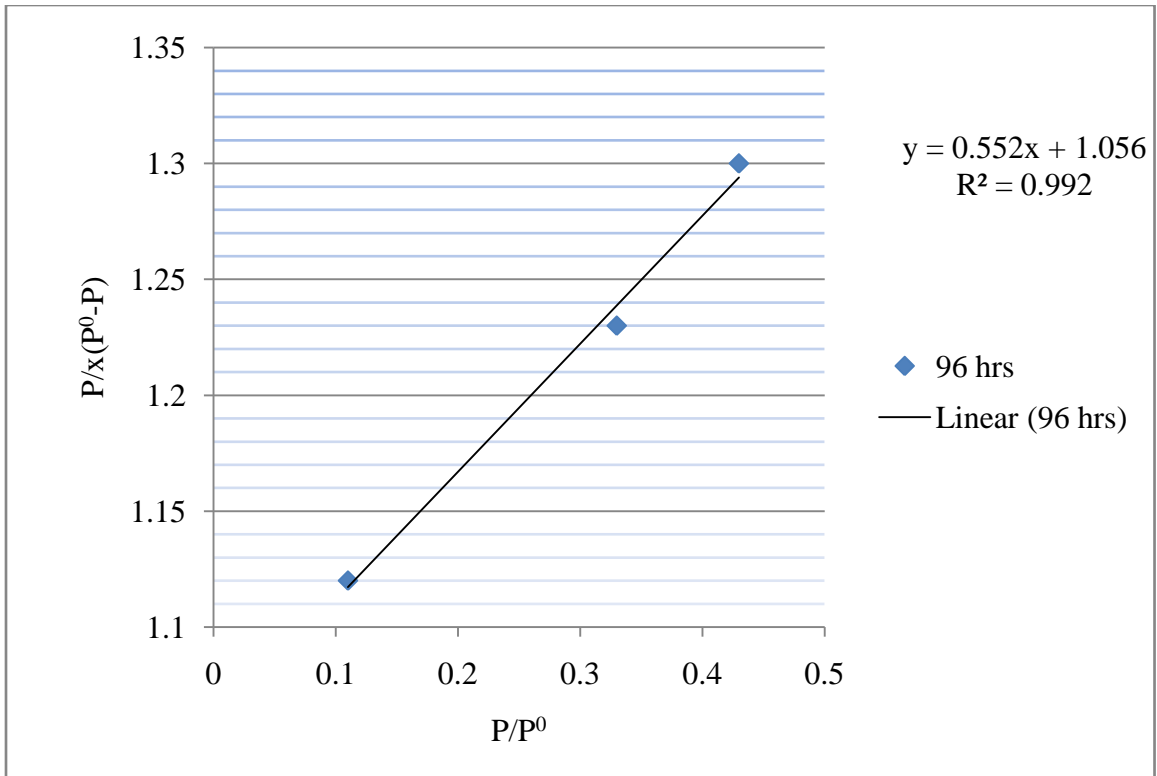




Appendix II (c): BET Isotherms for Solid PSBE-CaCl₂ Desiccants at Different Equilibration Time.







Appendix III

Mathematical samples on the calculation of the thermo physical properties of the PSBE-CaCl₂ sorbents

A: Bulky Density Determination

Weight of Pycnometer = 85.6g

Weight of pycnometer and solid samples = 156.9g

Weight of the solid samples only = 71.3g

Trial	1	2	3	4	5
Weight of the core-ring	85.6g	85.8g	85.8g	85.6g	85.8g
Weight of the core-ring + SS	156.9g	156.6g	157.8g	156.7g	156.0g
Weight of SS	71.3g	70.8g	72g	71.1g	70.2g
Bulky Density	726.2557	721.1627	733.3858	724.2184	715.0511

The diameter and the height of the core-ring apparatus was known and provided by the lab technician as 5cm and 5cm respectively, which assisted in the calculation of the volume of the apparatus as shown below.

$$v = \pi r^2 h.$$

$$v = \pi 5^2 5$$

$$= 98.1748 \text{ cm}^3$$

$$\phi_b = \frac{0.0713}{0.0000981748}.$$

$$= 726.2557 \text{ kg m}^{-3}$$

B: Equivalent Diameter Determination

The average number of balls in the core-ring apparatus were 206 as indicated in table () of chapter 4.

$$\text{Volume of 1 ball} = \frac{98.1748 \text{ cm}^3}{206}$$

$$= 0.4766 \text{ cm}^3$$

$$\frac{4}{3}\pi r^3 = 0.4766.$$

$$r = \sqrt[3]{\frac{0.4766 \times 3}{4\pi}}.$$

$$= 0.4846 \text{ cm}$$

$$\text{Equivalent diameter} = 0.4846 \times 2 = 0.9692 \text{ cm}$$

C: Particle Density Determination

Trials	1	2	3
M ₁	557.5 g	557.6 g	557.9 g
M ₂	689.2 g	689.0 g	689.4 g
M ₃	1491.7 g	1491.5 g	1491.2 g
M ₄	1415.3 g	1415.7 g	1415.3 g
ϕ _p	2363.5 Kgm ⁻³	2363.3 kgm ⁻³	2363.97 kgm ⁻³

Trial 1, M₁ = 557.5g, M₂ = 689.2g, M₃ = 1491.7g, M₄ = 1415.3g

$$\phi_p = \frac{M_2 - M_1}{(M_4 - M_1) - (M_3 - M_2)}.$$

$$= \frac{689.2 - 557.5}{(1415.3 - 557.5) - (1491.7 - 689.2)}.$$

$$= 2363.5 \text{ kgm}^{-3}.$$

Appendix V

Isotherm Constants Determination (Sample Calculations based at 120 hrs only)

A: Freundlich Constants

$$\log k_f = 1.115$$

$$k_f = 10^{1.115}$$

$$= 13.03$$

$$\frac{1}{n} = 0.276$$

$$n = \frac{1}{0.276}$$

$$= 3.62$$

B: BET Constants

$$\frac{1}{x_m c} = 1.071$$

$$x_m c = \frac{1}{1.071}$$

$$= 0.93$$

$$\frac{c - 1}{0.93} = 0.432$$

$$c - 1 = 0.4$$

$$c = 1.4$$

$$1.4x_m = 0.93$$

$$x_m = \frac{0.93}{1.4}$$

$$= 0.664$$

0.664g of H₂O are adsorbed in 4g

Therefore 166 mg of H₂O are adsorbed in one gram of the adsorbent.