MATHEMATICAL MODELING OF MOISTURE SORPTION CHARACTERISTICS OF DRIED TURMERIC (*Curcuma longa* L.) POWDER

Name: Abhishek Dahal

Address: Biratnagar, Morang, Nepal

Email: aabhishek.dahal12@gmail.com

Mobile No.: 9842527318

Faculty: B. Tech (Batch: 069-073)

MATHEMATICAL MODELING OF MOISTURE SORPTION CHARACTERISTICS OF DRIED TURMERIC (*Curcuma longa* L.) POWDER

by

Abhishek Dahal

Department of Food Technology

Central Campus of Technology

Institute of Science and Technology

Tribhuvan University, Nepal

2018

Mathematical Modeling of Moisture Sorption Characteristics of Dried Turmeric (*Curcuma longa* L.) Powder

A dissertation submitted to the Department of Food Technology, Central Campus of Technology, Tribhuvan University, in partial fulfillment of the requirements for the degree of B. Tech. in Food Technology

by

Abhishek Dahal

Department of Food Technology

Central Campus of Technology, Dharan

Institute of Science and Technology

Tribhuvan University, Nepal

August, 2018

Tribhuvan University

Institute of Science and Technology

Department of Food Technology

Central Campus of Technology, Dharan

Approval Letter

This *dissertation* entitled *Mathematical Modeling of Moisture Sorption Characteristics of Dried Turmeric (Curcuma longa L.) Powder* presented by Abhishek Dahal has been accepted as the partial fulfillment of the requirements for the B.Tech. degree in Food Technology.

Dissertation Committee

1. Chairperson

_____

(Mr. Basanta K. Rai, Assoc. Prof.)

2. External Examiner

_____

(Mr. Birendra K. Yadav, Asst. Prof.)

3. Supervisor

_____

(Mr. Arjun Ghimire, Asst. Prof.)

4. Internal Examiner

_____

(Mr. Kabindra Bhattarai, Teaching Asst.)

October, 2018

Acknowledgements

I would like to express my deep sense of gratitude to my respected guide Mr. Arjun Ghimire for his supervision, guidance, encouragement and instructions during the dissertation work that provided valuable insights to coordinate the sources of information and proceed to the research work.

I am eternally thankful to Prof. Dr. Dhan Bahadur Karki (Campus chief, Central Campus of Technology), Assoc. Prof. Basanta Kumar Rai (HOD, Department of Food technology) and Assoc. Prof. Geeta Bhattarai (Chairperson, Central Department of Food Technology) for their generosity and co-operation in providing opportunity and facilities to perform this work successfully.

Furthermore, I would like to thank my senior Nirat Katwal, friends Samel Pandey, Samip Khadka, Chandra Kanta Dhamala and juniors Gajendra Bhohora, Pankaj Dahal, ,Prajwal Pokharel for their co-operation to make this work successful. I am deeply indebted to all the teachers, all the technical and non-technical staffs of Central Campus of Technology and those who have directly and indirectly supported in my endeavor.

Last but not the least I am heartily thankful to my family members for their continuous support during my graduation.

Date of Submission: October, 2018

_____

Abhishek Dahal

Abstract

The mathematical modeling of moisture sorption characteristics of dried turmeric (*Curcuma longa* L) powder was carried out to fit the sorption data of different sorption models. The dried turmeric powder sample of initial moisture content 8.74% (wb)was dried in the cabinet dryer and EMC was determined by static gravimetric technique at temperatures: $20\pm1°C$, $30\pm1°C$ and $40\pm1°C$ maintaining the a_w ranging from 0.16-0.92.

Results from the experimental analysis revealed that the sorption isotherms were of sigmoid shaped type II pattern as classified by Brunauer *et al.* (1998). Statistical analysis showed that BET model gave the best fitting followed by Caurie and Hasley model over the entire range of experimental temperatures with the higher value of R^2 ranging from 0.93-0.97 and lower values of $\chi2$(0.00046-0.0209), RMSE (0.026-0.156) and SSE (0.00140-0.138) compared with other models. The monolayer moisture content decreased with increasing temperature. Such data represents a useful tool for choose appropriate storage condition and preservation techniques for the dried turmeric powder.

Keywords: Modeling, moisture sorption, temperature, analysis, monolayer

Table of Contents

List of Tables

List of figures

List of abbreviations

Abbreviation	Full form
a_w	Water activity
CCT	Central Campus of Technology
CMC	Critical moisture content
ERH	Equilibrium Relative Humidity
M_e/EMC	Equilibrium moisture content
RMSE	Root mean square error
RH	Relative humidity
SSE	Sum of square error

Part I

Introduction

1.1 General introduction

Turmeric is a spice derived from the rhizomes of *Curcuma longa*, which is a member of the ginger family (Zingiberaceae). Rhizomes are horizontal underground stems that send out shoots as well as roots. The bright yellow color of turmeric comes mainly from fat-soluble, polyphenolic pigments known as curcuminoids. Curcumin, the principal curcuminoid found in turmeric, is generally considered its most active constituent. Other curcuminoids found in turmeric include demethoxycurcumin and bisdemethoxycurcumin (Akram *et al.*, 2010).

Several studies have shown that curcumin, the phytonutrient in rhizomes of turmeric (*Curcuma longa* L.), has antioxidant (Kumar *et al.*, 2006), anti-inflammatory, anti-mutagenic and hypolipidaemic (Kim *et al.*, 2008). Negi *et al.* (1999), have found that curcumine, a major component in Turmeric possess an as anti-oxidant, anti-inflammatory, anti-mutagenic, anti-carcinogenic and anti-microbial properties. Curcumin has different functional groups such as parahydroxy, keto and double bonds, which are responsible for its antioxidative, anti-inflammatory, anti-cancer and anti-mutagen activities (Kim *et al,* .2008).

In South East Asian civilization, especially Hindus regard turmeric as a boon spices from the ancient time (Gupta and Sadhana, 2005). Turmeric (*Curcuma longa*) is extensively used as spice, food preservative and coloring material in Nepal, India, China and South East Asia. In the East, turmeric is precious as the therapeutic goldmine inhabits significant position in the psyche of Hindu. It forms an important part of various sanctified Hindu rituals focus its importance for mankind. It is mentioned in Ayurveda, Hindus age old system of medicine, and one encounters its name and use recorded in Sanskrit, the ancient Hindu's language describing the ageless *Vedas* between 1700 and 800BC during the period known as the *Vedic* age (Kim *et al,* .2008)..

The moisture sorption isotherm is a very important tool for food technologists as it can be used to predict the possible changes that can take place in the stability of food, used to find out

the storing method and selection of packaging material which helps to optimize or maximize retention of color, flavor, texture, nutrients and biological stability. Sorption isotherms of food materials are vital for design, modelling and optimization of different processes like aeration, drying and storage (Rahman, 2006).

Water activity (a_w) has long been considered as one of the most important quality factors, especially for long-term storage. All chemical and microbial deterioration reactions are directly affected by changing water activity; therefore, the determination of the relationship between water activity and moisture content is significant. Moisture sorption isotherms describe the relationship between the equilibrium moisture content (EMC) and the water activity at constant temperatures and pressures. For food material, these isotherms give information about the sorption mechanism and the interaction of food biopolymers with water (Rahman and Labuza, 2007).

Numerous mathematical models for the description of the moisture sorption behavior of foods are available in the literature. Some of these models are based on the theories of the mechanism of sorption, others are purely empirical or semi empirical. Vanden Berg and Bruin (1981) have collected and classified 77 such equations. However, due to the complex composition and structure of food, the mathematical prediction of sorption behavior is difficult. Furthermore, since irreversible changes can occur at high temperatures, experimental measurements at these temperatures are required. Since the moisture sorption isotherms of food materials represent the integrated hygroscopic properties of various constituents and since the sorption properties may change as a result of chemical and physical interactions induced by heating or other pre-treatment methods, it is difficult to have a unique mathematical model whether theoretical or empirical that describes accurately the sorption isotherm over the whole range of water activities and for various types of foods (Rahman and Labuza, 2007).

The critical moisture content i.e. the moisture at which the product becomes unacceptable and the equilibrium moisture content is established from the moisture sorption isotherm (Ranganna, 1986). From packaging point of view, hygroscopicity is one of the important characteristics of dry products and is influenced considerably by original moisture content of

the product. The products having less than 50% are usually considered hygroscopic and that having more than 50% is considered hygroemmisive. A product always tries to equilibrate with its environment and during this process it gains or losses moisture from or to the environment. Thermodynamically, the equilibrium is reached when free energy change for a material is zero. To ensure that the quality of food stuff is not lost before the intended shelf life, the material should be packed in such material that it has the desired permeability which does not allow appreciable moisture into the packet (Ranganna, 1986).

1.2 Statement of the problem

Nepal and agriculture are synonymous to each other. Spices are the one of the major product of Nepal which has been exported worldwide. And the increasing demand of spices leading to increasing production of spices especially turmeric in Nepal. Considerable research has been carried out on the moisture sorption behavior of various dry products like flours, breakfast cereals, weaning food, sukuti etc. but information on sorption characteristics of dried spices is scanty. Spices tend to have strong flavors and are used in small quantities. In the context of world, turmeric powder is widely used. So this research importance is felt in terms of developing systematic preservation and stability of turmeric by control of water activity in order to facilitate and promote the effectiveness and application of turmeric.

Dried turmeric powders are very sensitive to moisture gain. There is the high probability of microorganisms attack (Kwon and Magnuson, 2009). This not only creates problems in production, packaging and storage; but also limits consumer acceptability of product.

1.3 Objectives

1.3.1 General objective

The general objective of this dissertation was to study the mathematical modeling of moisture sorption characteristics of dried turmeric (*Curcuma longa* L.) powder.

1.3.2   Specific objectives

The specific objectives of this study were:

1. To calculate EMC over entire a_w ranging from 0.16-0.92 at three different temperatures i.e., 20±1, 30±1 and 40±1°C.

2. To test, determine and evaluate the applicability of different sorption models to the experimental data.

3. To calculate the different sorption models parameters.

4. To obtain best model over different sorption isotherm models.

1.4   Significance of the study

Mainly dried powder form of turmeric is widely produced and used in Nepal and also supplied to the worlds market. Thus sorption isotherm study allows understanding various thermodynamic properties, shelf life studies, chemical and physical stability, packaging requirement, designing of drying equipmentetc. This study thus has scientific, commercial as well as sociological significance in giving impetus towards preserving and commercializing the turmeric powder which is being destroyed due the lack of proper preservation technique.

The significance of this research was to provide new data of the water activity and moisture content relationship in terms of adsorption isotherms of dried turmeric powder by exploring the appropriate mathematical description. This investigation will be useful for the assessment of product stability, selection of the suitable packaging material to preserve the usefulness of turmeric.

1.5   Limitation of the study

1. Only one local variety of turmeric (*Curcuma longa*) was taken for study.
2. Study was carried out only on 20-40°C temperature.

Part II

Literature review

2.1   Turmeric

Curcuma, a very important genus in the family Zingiberaceae, consists of about 110 species, distributed in tropical Asia and the Asia–Pacific region. The greatest diversity of the genus occurs in India, Myanmar, and Thailand, and extends to Korea, China, Australia, and the South Pacific. Many species of *Curcuma* are economically valuable, the most important being *Curcuma longa*, known as turmeric commercially. In spite of its economic importance, the genus is poorly understood, botanically and chemically(Ishimine *et al.*, 2003).

Turmeric (*Curcuma longa* L.) is a popular spice in many countries of Asia. It is now important in medical science because curcumin and volatile oils of turmeric rhizomes have anti-inflammatory, antimutagen, anticancer, antibacterial, anti-oxidant, antifungal, antiparasitic and detox properties. These components also promote liver and kidney functions, and alleviate biliary disorders, diabetic and hepatic disorders. Calcium, Mg, Fe, protein and fat are also considered to be important quality parameters of turmeric. Various supplements and drinks derived from the turmeric are widely being used for keeping good health (M.A. Hossain *et al.*, 2005).

2.1.1   Historical background

Turmeric has a long history of medicinal use in tropical Asia. It is mentioned in Ayurveda, Hindus age old system of medicine, and one encounters its name and use recorded in Sanskrit, the ancient Hindu's language describing the ageless *Vedas* between 1700 and 800 B.C. during the period known as the *Vedic* age. It also known as "Indian saffron" has been in use dating back to 4000 BC. In *Sanskrit*, it is referred to as "*Haridara*," a word which has two parts: "Hari" and "Dara," meaning Vishnu, also known as "Hari," the omnipresent Hindu deity; and "Dara" meaning what one wears, obviously referring to the fact that Vishnu used it on his body. Turmeric is much revered by the Hindus, and interestingly, is given as "*Prasad*" (a benedictory material) in powdered form, in some temples (Khajehdehi, 2012).

Turmeric derives its name from the Latin word "*terra merita*," meaning meritorious earth, which refers to the color of ground turmeric, resembling a mineral pigment. The botanical name is *Curcuma domestica*Val. Syn.*Curcuma longa* L. belongs to the family Zingiberaceae. Turmeric is believed to be cultivated first as a dye and then became valued as a condiment as well as for cosmetic purposes. In Malaysia, a paste of turmeric is spread on the mother's abdomen and on the umbilical cord after childbirth in the belief that it would ward off evil spirits, and also would provide some medicinal value, primarily antiseptic. Both the East and the West have held turmeric in high esteem for its medicinal properties. The Indus Valley Civilization dating back to 3300 BC in western India was involved in the spice trade, of which turmeric was an important constituent (Raghavan, 2006).

Because of its unique color and history, turmeric has a special place in both Hindu and Buddhist religious ceremonies. Initially, it was cultivated as a dye because of its brilliant yellow color. With the passage of time, ancient populations came to know of its varied uses and they began introducing it into cosmetics. The plant's roots are used in one of the most popular Indian *Ayurvedic*preparations called "*Dashamularishta*," a concoction prepared from 10 different types of roots, which relieve fatigue, and have been in use since thousands of years. The plant's flowers are used as an antidote against worms in the stomach of humans and can also cure jaundice and venereal diseases, and have been known to have specific properties to combat mental disorders. Human breast tumors can be treated with turmeric leaf extracts (Nair, 1994).

2.1.2   Botanical profile

*Curcuma longa*L. belongs to the family Zingiberaceae which falls under the order Zingiberales of monocots and is an important genus in the family. The family is composed of 47 genera and 1400 species of perennial tropical herbs, found usually in the ground flora of lowland forests (Ravindran *et al.*, 2007).

Despite systematic investigation by taxonomists, starting from Linnaeus, Hooker, Rendle, Watt, Valeton, and Hutchinson, the classification and nomenclature of *Curcuma* remained quite confusing. Classification of the Zingiberaceae family is presumed to be the most authoritative to date, wherein he divided the family into two subfamilies, namely

Zingiberoideae and Costoideae, and *Curcuma* was included in Zingiberoideae, under the tribe Hedychieae.

A fleshy complex rhizome, the base of each aerial stem consisting of an erect, ovoid, or ellipsoid structure (primary tuber), ringed with the bases of old-scale leaves, bearing several horizontal or curved rhizomes, when mature, which are again branched. Fleshy roots, many of them bear ellipsoid tubers. Leafy shoots bearing a group of leaves surrounded by bladeless sheaths, the leaf sheaths forming a pseudostem; total height of leafy shoots ranging from 1 to 2 m. Leaf blades usually more or less erect, often with a purple-flushed strip on either side of the midrib; size and proportional width varying from the outermost to the innermost (uppermost) leaf. Petioles of outermost leaf short or none, of inner leaves fairly long, channeled. Ligule forms a narrow up growth across the base of the petiole; its ends join to form thin edges of the sheath, the ends in most species simply decurrently, rarely raised as prominent auricles. Inflorescence either terminal on the leafy shoot, the scale covered by rather large bladeless sheaths (Ravindran *et al.*, 2007).

Bracts are large, very broad, each joined to those adjacent to it for about half of its length, the basal parts thus forming enclosed pockets, the free ends more or less spreading, the whole forming a cylindrical spike; uppermost bracts usually larger than therestand differently colored; a few of them sterile (the group is called coma). Filament of stamen short and broad, constricted at the top, anther versatile, the filament joined to its back, the pollen sacs parallel, with usually a curved spur at the base of each; connective sometimes protruded at the apex into a small crest. Stylodes cylindrical, 4–8 mm long, Ovary trilocular; fruit ellipsoid, thin-walled, dehiscing and liberating the seeds in the mucilage of the bracht pouch; seeds ellipsoid with a lacerate aril of few segments which are free to the base. The above description was adapted by many of the later taxonomists and reviewers as a basis for describing or redescribing the genus *Curcuma* (Ravindran *et al.*, 2007).

2.1.3 Processing of turmeric

Processing of raw rhizomes assumes importance from the point of view of the appearance and color of the end product. The processing consists of three stages i.e. curing, drying, and polishing (Anandaraj *et al*., 2001).

2.1.3.1 Curing

Turmeric rhizomes are cured before drying. Curing essentially involves boiling fresh rhizomes in water until soft before drying. Boiling destroys the vitality of fresh rhizomes, obviates the raw odor, reduces drying time, and yields a uniformly colored product. Some traditional methods for curing turmeric are no longer in practice. In the contemporary curing process, the cleaned rhizomes are boiled in copper or galvanized iron or earthen vessels with water just enough to soak them. Boiling is stopped when froth comes out, with the release of white fumes having the typical turmeric aroma (Rao *et al*., 1975; Spices Board, 1995; Anandaraj *et al*., 2001). The cooking lasts for 45 to 60 min when the rhizomes become soft; but the duration could be longer depending on the batch size. The stage at which boiling is stopped largely influences the color and aroma of the final product. Over-cooking spoils the color of the final product while under-cooking renders the dried product brittle (Weiss, 2002).

2.1.3.2 Drying

The cooked rhizomes are allowed to cool gradually and spread out to dry in the open in 5 to 7 cm thick layers on uncoated plain bamboo mats or concrete drying floor. A thinner layer is not desirable as this may result in surface discoloration (Sankaracharya and Natarajan, 1975; Spices Board, 1995; Anandaraj *et al*., 2001). The rhizomes are turned over intermittently to ensure uniformity in drying. During night time, they are heaped or covered with a material that allows adequate aeration. It may take 10 to 15 days for the rhizomes to become completely dry. In most growing areas, the cooked rhizomes are dried in the sun. But, where unfavorable seasonal conditions prevail, improved drying methods using mechanical dryers are also used. Drying using cross-flow hot air at a maximum temperature of 60°C is found to give a satisfactory product (Spices Board, 1995). Artificial drying gives a brighter product than sun drying. Solar driers can also be economically used for drying turmeric. However, the

maximum temperature achieved by the drier depends on the outside climatic conditions (Anandaraj *et al*., 2001).

2.1.3.3   Polishing

Dried turmeric has a rough appearance and dull surface color. The outer surface can be polished to give a better finish. Polishing removes the surface roughness by getting rid of the surface scales, the small rootlets, and any remaining soil particles. Polishing is done either by manual or mechanical means Manual polishing consists of rubbing the dried turmeric on a hard surface or trampling themunder feet wrapped with gunny bags. Shaking the rhizomes with stones in a gunny bag or bamboo basket is also practiced. Mechanical polishing is carried out in polishing drums. Sprinkling turmeric water during polishing is said to improve the color in manualoperated drums. Cured and polished turmeric is brittle; it has a smooth and shining yellow color. Polishing is not necessary for turmeric intended for solvent extraction and recovery of color matter (Anandaraj *et al*., 2001).

2.1.3.4   Coloring

In order to improve the surface color, the dried rhizomes are sometimes coated with turmeric powder in the course of polishing. This is done to half-polished rhizomes in two ways, known as dry and wet coloring. In the dry process, turmeric powder is added to the polishing drum in the last 10 min of polishing, whereas in the wet process, turmeric powder suspended in water is sprinkled over the rhizomes at the final stage (Anandaraj*et al*., 2001). Treatment with emulsions containing alum, turmeric powder, castor seed paste, sodium bisulfite and sulphuric acid, or hydrochloric acid in different combinations has also been recommended to impart attractive surface color. However, chemical treatments are largely discouraged. The use of lead chromate, once practiced to achieve the same result, has now been abandoned due to potential toxicity. The yield of polished turmeric from fresh rhizomes varies from 15 to 25% (Anandaraj *et al*., 2001).

2.1.4   Cultivation and production

The turmeric plant is propagated by division of an underground stem or rhizome which produces erect leafy shoots of height of upto 1m leaves, alternate, obliquely erect or sub

sessile, are oblong lanceolate and dark green, surmounting leaf sheaths tapering near the leaf and broadening near the base, enveloping in the succeeding shoot. Turmeric is grown at hilly areas of Nepal (hot and moist climate). It is usually grown in regions with an annual rainfall of 1000-2000 mm; below 1000 mm, irrigation is required. Cultivation has been extended into wetter areas with over 2000 mm of rain per annum can be grown up to 1220 mm in Himalayan foothills loamy or alluvial, loose, friable, fertile soils and cannot withstand water logging (Purseglove *et al.*, 1981). Turmeric is grown in on the mid- July along with finger millet, rice and sugarcane as an alternative crop. Mulching is necessary during growing stage (Anandaraj *et al.*, 2001).

India is the largest producer, exporter, and consumer of turmeric in the world, with 82% of world production and 45% of export. Turmeric occupies about 6% of total area under spices in India. In India, the main turmeric growing states are Andhra Pradesh, Tamil Nadu, Orissa, Karnataka, West Bengal, Maharashtra, Meghalaya, and Kerala. Andhra Pradesh, the lead state of turmeric cultivation, shares 38% of area and 45% of production (Spices Board, 2004). Other states in the order of ranking in production are Tamil Nadu (21%), Orissa (12%), Karnataka (6.4%), West Bengal (3.9%), Maharashtra (1.5%), Meghalaya (1.5%), and Kerala (1.4%) (Board, 2004).

2.1.5   Chemical and nutritional composition of turmeric

Chemical Composition and nutritional composition of turmeric is shown in Table 2.1 and Table 2.2 respectively.

Table 2.1 Chemical composition of turmeric

S.N	Parameter	Value (%)
1	Moisture	6-13
2	Carbohydrate	60-70
3	Protein	6-8
4	Fiber	2-7
5	Mineral matter	3-7
6	Fat	5-10
7	Volatile oil	3-7
8	Curcuminoids	2-6

Source: Board (2004)

Table 2.2 Nutritional composition of turmeric per 100 g

S.N	Parameter	Amount
1	Moisture, g	6
2	Food energy, kcal	390
3	Protein, g	8.5
4	Fat, g	8.9
5	Carbohydrate, g	69.9
6	Ash, g	6.8
7	Calcium, g	0.2
8	Phosphorus, mg	260
9	Sodium, mg	10
10	Potassium, mg	2500
11	Iron, mg	47.5
12	Thiamine, mg	0.09
13	Riboflavin, mg	0.19
14	Niacin, mg	4.8
15	Ascorbic acid, mg	50

Source: Board (2004)

2.2   Water activity

Water activity is a fundamental property of aqueous solutions, and by definition is the ratio of the vapor pressure of the water in the substrate (p) to that of pure water at the same temperature (p_o)

$$\text{Water activity, } a_w = \frac{f}{f_o} = \frac{p}{p_o}$$

The water activity is related to the equilibrium relative humidity, %ERH, as follows (Rahman and Labuza, 2007):

$$\text{Water activity, } a_w = \frac{\%ERH}{100} = \frac{p}{p_o}$$

Water activity is a measure of how efficiently the water present can take part in a chemical (physical) reaction. If half the water is so tightly bound to a protein molecule that icould not take part in a hydrolysis reaction the overall water activity would be reduced. Water activity (a_w) is defined as where p and Po are the partial pressures of water above the food and a pure solution under identical conditions respectively. The tightly bound water has no tendency to escape from a food as a vapor and therefore exerts no partial pressure and has an effective water activity of zero.

Water activity is clearly a function of composition but is also a function of temperature. The a_w is related to the boiling and freezing points, equilibrium relative humidity, and osmotic pressure. Water activity ranges from zero (water absent) to 1.0 (pure water). For an ideal solution aw is independent of temperature, and in actual practice, aw of a given solution varies only slightly with temperature within the range of temperature permitting microbial growth(Rahman, 2010).

2.2.1   Minimum a_w for microbial growth and spore germination

Table 2.3 lists the measured minimum $a_w$values for microbial growth or spore germination. If $a_w$is reduced below these values by dehydration or by adding water binding agents like sugars, glycerol or salt, microbial growth is inhibited. Such additives should not affect the flavor,

taste, or other quality criteria, however. Since the amounts of soluble additives needed to depress a_w even by 0.1 is quite large, dehydration becomes particularly attractive for high moisture foods as a way to reduce a_w (Mujumdar and Devahastin, 2000).

Table 2.3 Minimum water activity, a_w, for microbial growth and spore germination

Microorganism	Water activity
Organisms producing slime on meat	0.98
Pseudomonas, Bacillus cereus spores	0.97
B. subtilis, C. botulinum spores	0.95
C. botulinum, Salmonella	0.93
Most bacteria	0.91
Most yeast	0.88
Aspergillus niger	0.85
Most molds	0.80
Halophilic bacteria	0.75
Xerophilic fungi	0.65
Osmophilic yeast	0.62

Source: Abbas *et al.* (2009)

2.2.2 Water activity (a_w) concept

The concept of aw has been very useful in food preservation and on that basis many processes could be successfully adapted and new products designed. Water has been called the universal solvent as it is a requirement for growth, metabolism, and support of many chemical reactions occurring in food products. Free water in fruit or vegetables is the water available for chemical reactions, to support microbial growth and to act as a transporting medium for compounds. In the bound state water is not a available to participate in these reactions as it is bound by water soluble compounds such as sugar, salt gums, etc. (osmotic binding), and by the surface effect of the substrate matrix binding (Gustavo *et al.*, 2007).

These water-blinding effects reduce the vapor pressure of the food substrate according to Raoult's Law. Comparing this vapor pressure with that of pure water (at the same

temperature) results in ratio called water activity (aw). Pure water has an aw of 1, one molar solution of sugar has a water activity of 0.98, and one molar solution of sodium chloride has a water activity of 0.9669. A saturated solution of sodium chloride has a water activity of 0.755. This same NaCl solution in a closed container will develop an equilibrium relative humidity (ERH) in a head space of 75.5%. 42 Water Activity Concept and its role in food preservation A relationship therefore exists between ERH and aw since both are based on vapor pressure (Gustavo *et al.*, 2007):

$$\text{water activity} = \frac{\text{ERH}}{100}$$

The ERH of a food product is defined as the relative humidity of the air surrounding the food at which the product neither gains nor loses its natural moisture and is in equilibrium with the environment. The definition of moisture conditions in which pathogenic or spoilage microorganisms cannot grow is of paramount importance to food preservation. It is well known that each microorganism has a crystal a_w below which growth cannot occur. For instance, pathogenic microorganisms cannot grow at $a_w < 0.62$. The so-called intermediate moisture foods (IMF) have aw values in the range of 0.65 - 0.90 as shown in Fig. 2.1.
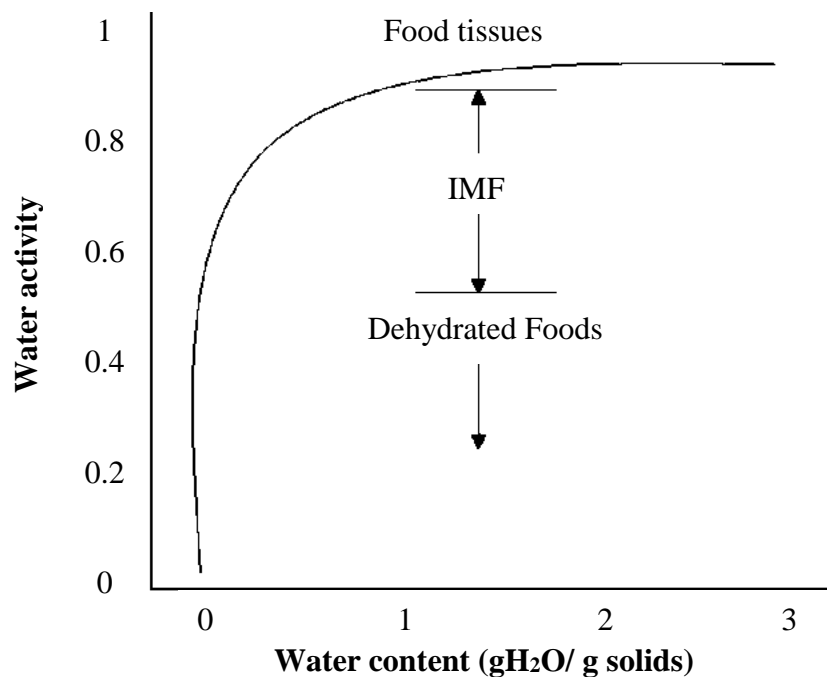
Fig. 2.1 Typical equilibrium of water content vs. water activity in foods (Gustavo *et al.*, 2007).

With a_w at 0.3, the product is most stable with respect to lipid oxidation, non-enzymatic browning, enzyme activity, and of course, the various microbial parameters. As a_w increases toward the right, the probability of the food product deteriorating increases (Gustavo *et al.*, 2007). The stability diagram based on water activity concept is shown in Fig. 2.2.
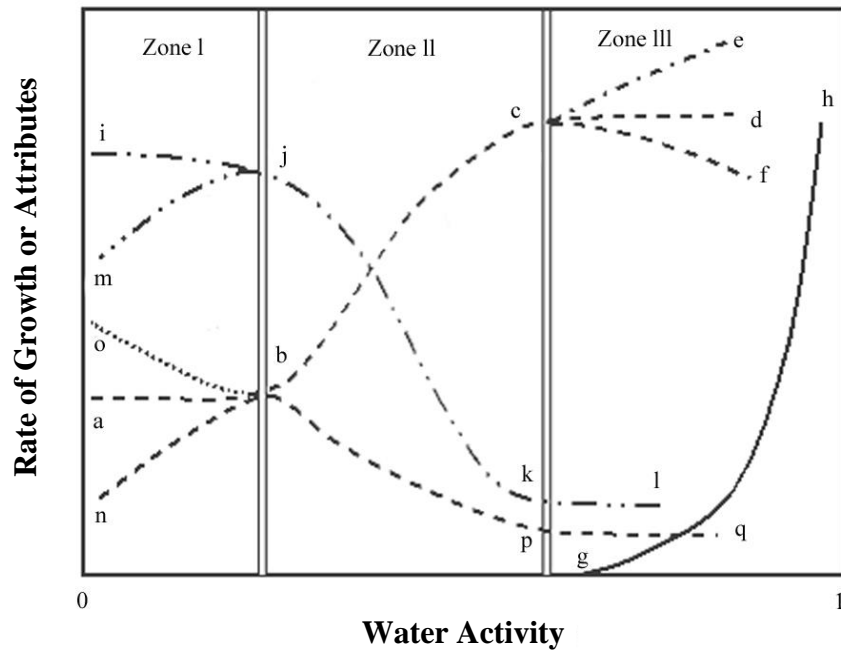
Fig. 2.2. Stability diagram based on the water activity concepts (Novasima, 2005).

where:

gh = Microbial growth trend;

oa, ab, nb = chemical reaction trends below BET-monolayer;

bc, bp= chemical reaction trends in the adsorbed water; ce,

cd, cf, pq = chemical reaction trends in the solvent water region;

ij, mj = mechanical properties trends belowBET-monolayer;

jk = mechanical properties trend in the adsorbed water region;

ki = mechanical properties trend in the solvent water region .

The Enzymatic browning rate at 70°C in gelatinized starch medium is shown in Fig. 2.3.
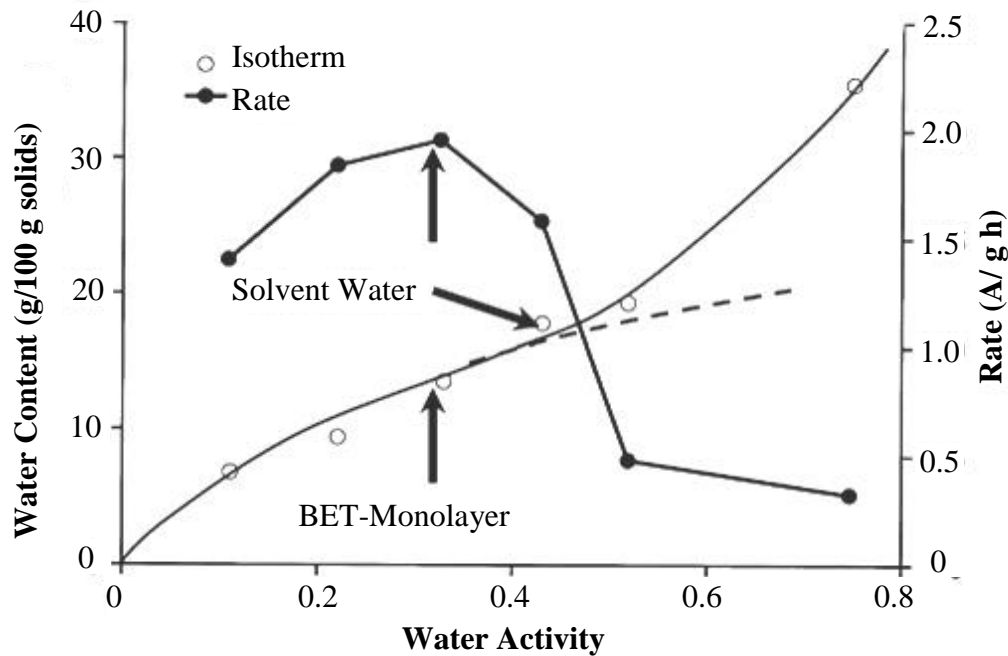
Fig. 2.3 Enzymatic browning rate at 70°C in gelatinized starch medium (Acevedo, 2006).

In general the rule of water activity concept is: Food products are most stable at their ''BET monolayer moisture'' content or ''BET-monolayer water activity'' and unstable above or below BET monolayer. However, experimental evidence showed that optimal moisture for stability was in the multilayer adsorption region. In many other instances it has been shown that optimal water content for stability is not exactly the BET monolayer. The reason for this variation is due to the fact that the BET theory of adsorption was developed based on many simplified assumptions, which are not realistic when food is considered (Rahman, 2010).

2.3   Equilibrium moisture content

The equilibrium moisture content is defined as the moisture content of the material after it has been exposed to a particular environment for a infinitely long period of time. The equilibrium moisture content is dependent upon the relative humidity and temperature condition of the environment (Bala, 1993). A product when exposed to a certain environment at a certain temperature tries to come in equilibrium with that environment thus in this process

adsorption/desorption of moisture too occurs until it reaches the equilibrium. The moisture content of the product in equilibrium with its environment is known as equilibrium moisture content (EMC) and the relative humidity of that environment is known as equilibrium relative humidity (ERH) (Ranganna, 1986).

Equilibrium moisture content may be classified as: (1) Static equilibrium moisture content and (2) Dynamic equilibrium moisture content. Dynamic equilibrium moisture content is obtained best by fitting the thin layer drying equation to experimental data, whereas the static equilibrium moisture content is obtained after the prolonged exposure of the product to a constant atmosphere. McEwen, Simmonds and Ward further suggested that dynamic and static equlibrium moisture contents should be used for drying and storage design respectively (Bala, 1993).

2.4   Moisture sorption isotherm

The moisture sorption isotherm is the dependence of moisture content and the water activity of one sample at a specified temperature. It is usually presented in graphical form or as an equation.The quality of most foods preserved by drying depends to a great extent upon their physical, chemical and microbiological stability. This stability is mainly a consequence of the relationship between the equilibrium moisture content (EMC) of the food material and its correspondence water activity (a_w), at a given temperature. These water sorption isotherms are unique for individual food materials and can be used directly to solve food processing design problems, predict energy requirements and determine proper storage conditions (Mujumdar, 2006).

Water sorption isotherm equations can be used to predict water sorption properties of foods. Many empirical and semi-empirical equations describing the sorption characteristicsof foods have been proposed in the literature. This is attributed to the fact that the water is associated with the food matrix by different mechanisms in different water activity regions (Mujumdar, 2006).

Fig. 2.4 shows the general shape of the typical sorption isotherms. They are characterized by three distinct zones: A, B and C, which are indicative of different water binding

mechanisms at individual sites on the solid matrix. In region A, water is tightly bound to the sites and is unavailable for reaction. In this region, there is essentially monolayer adsorption of water vapor and no distinction exists between the adsorption and desorption isotherms. In region B, the water is more loosely bound. The vapor pressure depression below the equilibrium vapor pressure of water at the same temperature is due to its confinement in smaller capillaries. Water in region C is even more loosely held in larger capillaries. It is available for reactions and as a solvent (Mujumdar, 2006).
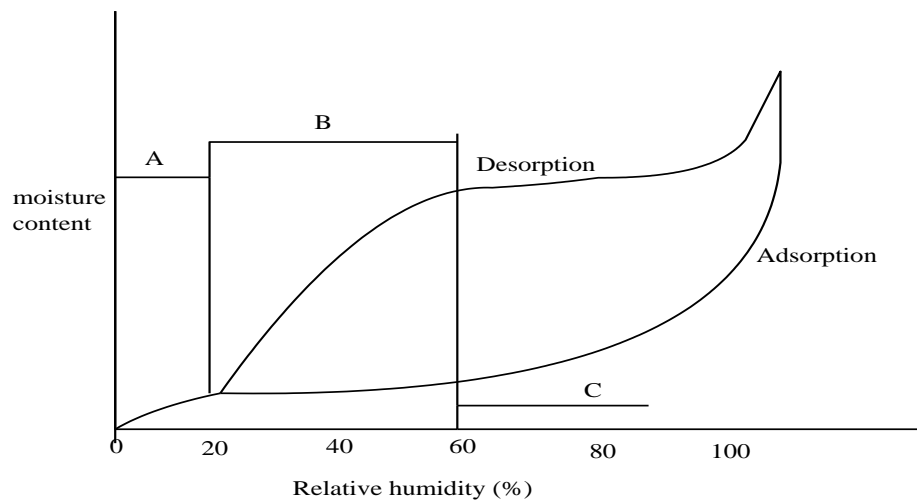
Fig. 2.4 Typical sorption isotherm (Mujumdar, 2006)

Sorption isotherm can be divided into several categories: kinetic models based on a monolayer (Mod-BET model), kinetic models based on a multi-layer and condensed film (GAB model), semi-empirical (Henderson and Halsey models) and empirical models (Smith and Oswin models). The BET model represents a fundamental milestone inthe interpretation of multilayer sorption isotherms, particularly Types II and III (Timmermann *et al.*, 2001). Smith model is useful in describing the sorption isotherm of biological materials such as starch and cellulose (Bhattarai, 2012).

Iglesias and Chirife (1982) found that Halsey and Oswin models are also versatile. Iglesias and Chirife (1982) reviewed the 23 equations existing in the literature for fitting moisture sorption isotherms of foods and food products. Later, they evaluated eight equations for 39 different foods. Vanden Berg and Bruin (1981)collected and classified 77 such equations.

Among the sorption models, the Guggenheim-Anderson and de Boer (GAB) equation has been applied successfully to various foods (Vanden Berg, 1984) and it is recommended by the European project Cost 90 on physical properties of foods (Wolf *et al.*, 1984). A curve obtained on plotting the equilibrium moisture content against the equilibrium relative humidity (or water activity) at constant environmental condition is known as the moisture sorption isotherm. The shape of the curve may be different depending on the types of material. In case of foods containing the water soluble crystalline components like sugar and salts, the isotherm appears concave shape (Rahman and Labuza, 2007).

2.4.1 Effect of temperature on sorption isotherm

It has been found in various literatures that increase in temperature decrease the equilibrium moisture content of the product. Iglesias and Chirife (1982)found that as the temperature increases the hygroscopicity of most food product decreases. The isotherm shifts due to temperature can usually be estimated by Clausius-Clapeyron equation (Labuza *et al.*, 1985):

$$ln\frac{(a_w)1}{(a_w)2} = \frac{q+\lambda w}{R}[\frac{1}{T1} - \frac{1}{T2}]$$

The slope of a plot of $ln a_w$ versus $1/T$ should give:

$$\text{Slope} = \frac{q+\lambda w}{R}$$

where, q is the excess heat of sorption (kJ/kg) and $\lambda_w$is the latent heat of vaporization for water (kJ/kg).

2.4.2 Effect of hygroscopicity of the product on sorption isotherm

Hygroscopicity of the moisture sensitive product is the most important consideration in determining the moisture sorption ability of the product. Hygroscopicity is the ability of a material to interact with moisture from the surrounding atmosphere. In general materials unaffected by water vapor are termed as non-hygroscopic while those in dynamic equilibrium with water in the atmosphere are hygroscopic.

Rahman and Labuza (2007)have classified the degree of hygroscopicity into four classes:

i. Non-hygroscopic solids: No increase in water content at<90%RH and increase after storage for one week above 90% RH is less than 20%.

ii. Slightly hygroscopic solids: No moisture increase at <80%RH and increase after one week storage less than 40% at > 80% RH.

iii. Moderately hygroscopic solids: Moisture increase is less than or equal to 5% after storage at below 60% RH and after storage for one week at > 80% RH is less than 50% moisture.

iv. Very hygroscopic solids:Moisture content increase may occur at 40-50% RH and increase may exceed 30% after storage for one week at >90% RH.

2.4.3 Classification of sorption isotherm

Callahan *et al.* (1982) classified the isotherms into five types (Fig. 2.5). The type I and type II isotherm are known as Langmuir isotherm and Sigmoid or 'S' shaped isotherm respectively. Other three are not given name. Type I isotherms are exhibited by predominantly microporous adsorbents having a relatively small external surface area, the limiting uptake may be governed by the accessible micropore volume rather than by the internal surface area. This type of isotherm is typical of anticaking agents (Bell and Labuza, 2000). Type II isotherm is shown by the biological materials and are normally associated with monolayer-multilayer sorption on non porous and macroporous surface of a powder. This isotherm with hysteresis is obtained with plate like particles with non-rigid slit shaped pores. The resultant curve is caused by the combination of colligative effects (physical properties of solution), capillary effects, and surface-water interactions (Bell and Labuza, 2000). A distinct 'knee' usually indicates a formation of a well defined monolayer. Type III isotherm appearswhen all the sorption occurs according to a multilayer mechanism throughout the pressure range. Some crystalline materials, e.g. sugars and salts, may have a fairly low adsorption of water until deliquescence, at which point the sorption increases and follows the type III isotherm (Rouquerol *et al.*, 1999). The characteristic shape of a type IV isotherm is a consequence of

surface coverage of the mesopore walls followed by capillary condensation or pore filling (Singh, 1998).

Type IV and Type V are related to the Type II and Type III, where in the former the maximum adsorption is attained or almost attained at some pressure lower than the vapour pressure of the gas whereas in the later cases (type II and type III) the adsorption increases as the vapour pressure of the adsorbed approaches p_o. Type II and IV isotherms show a significant uptake at low partial pressures followed by small adsorption at intermediate vapor concentration and again a high uptake at elevated partial pressures (Rouquerol *et al.*, 1999; Sing *et al.*, 1985). Type III and V isotherms indicate weak adsorbent-adsorbate interactions and they show a characteristic low uptake at low concentration and a strong increase in sorption at higher vapor concentration (Rahman and Labuza, 2007).

The inflection point in the sorption isotherm indicates the change of the water-binding capacity or the relative amounts of free or bound water. The steeper the curve, the more hygroscopic the material and less steeper or flatter the curve the less hygroscopic the material (Rahman and Labuza, 2007).
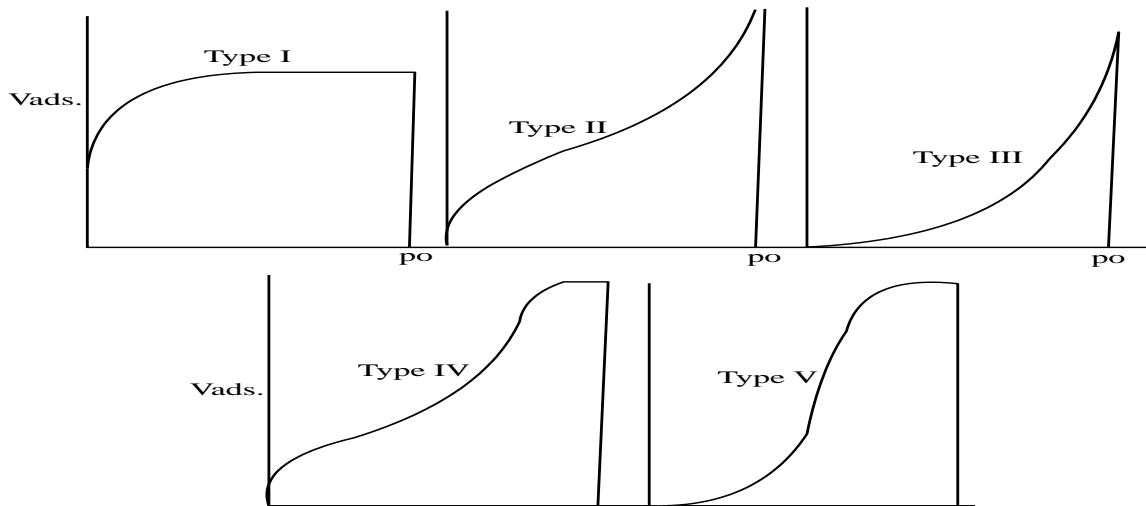
Fig. 2.5 The five types of van der Waals adsorption isotherms (Rahman and Labuza, 2007)

2.4.4 Measurement of sorption isotherm

For food products, the sorption isotherm can be measured by means of three different measuring techniques: gravimetric, manometric or hygrometric, according to Moraes *et al.* (2008). In the gravimetric methods, the weight of the sample is measured with a balance. In the manometric methods, the vapour pressure of water is measured when it is in equilibrium with a sample at given moisture content. In the hygrometric methods, the equilibrium relative humidity with a sample at a given moisture content is measured. Two examples of more modern techniques to measure the concentration in a sample are the impedance spectroscopy technique and the light reflection and/or attenuation technique, such as the infrared spectroscopy (Moraes *et al.*, 2008).

2.5 Monolayer moisture content

The monolayer moisture content is the moisture content that affords a food material the longest period with minimum quality loss at a given storage temperature. Below the monolayer moisture content, the rate of biochemical reactions are minimal with the exception of the oxidation of unsaturated fats. Consequently, the safest water activity is that corresponding to the monolayer moisture content at a given storage temperature (Goula *et al.*, 2008). Ariahu *et al.* (2006) stated that the monolayer moisture content is the moisture content of the food material when the entire surface is covered by a unimolecular moisture layer.

The most common method of determining the monolayer moisture content is by the using the BET or GAB equation where they remain as the constants of the equations. The BET monolayer is still more common in various fields particularly due to the approval of International Union of Pure and Applied Chemistry (IUPAC) while the latter is more common in food technology. The monolayer moisture content of the product determined by these two equations is not equal and experimentally it has been found that GAB monolayer moisture content is always greater than BET monolayer value. The GAB monolayer moisture content is 10-40% higher than the BET monolayer moisture content. It has been concluded that the GAB monolayer moisture content represents the better physical reality (Timmermann *et al.*, 2001).

2.6   Fitting of the sorption isotherm to different model's equation

Modeling the sorption isotherm data is an essential way for predicting and comparing the adsorption performance, which is critical for optimization of the adsorption mechanism pathways, expression of the adsorbents capacities and effective design of the adsorption systems (Thompson *et al.*, 2001). In general, the modeled sorption isotherm is an invaluable non-linear curve describing the adsorption phenomenon at a constant temperature and pH; and the mathematical correlation which is depicted by the modeling analysis is important for operational design and applicable practice of the adsorption systems (Foo and Hameed, 2010). On the other hand, linear analysis of isotherm data into isotherm models is an alternative mathematical approach to predict the overall adsorption behavior. Over the past few decades, researchers found that it is easier to estimate the parameters by the linear analysis. The equations developed are empirical, semi-empirical or theoretical type. A re-arrangement of the equations was performed to facilitate the determination of the appropriate parameters using statistical modelling. The list of isotherm equations used for fitting experimental data are presented below:

2.6.1   BET (Branauer-Emmett-Teller) equation

The BET equation, which is the most widely used model in food systems, was first proposed by Brunauer, Emmett and Teller (Brunauer *et al.*, 1998). It represents a fundamental milestone in the interpretation of multilayer sorption isotherms, particularly the types II and III. It is also an effective method for estimating the amount of bound water in specific polar sites of dehydrated food systems.In the past, the well-known Brunauer-Emmett-Teller (BET) sorption isotherm was the model with the greatest application to water sorption isotherms of foods and foodstuffs, although it was known to hold only for a limited range of water activity. This equation can be derived based on the kinetic statistical andmechanics or thermodynamic consideration (Timmermann *et al.*, 2001). From this model, two constants namely the monolayer moisture content and the energy constant C_B can be obtained. This two parameter equation is proposed based on the monolayer adsorption on the surface.

The theory behind the development of the BET equation has been questioned due to the assumptions that:(a) the rate of condensation on the first layer is equal to the rate of

evaporation from the second layer; (b) the binding energy of all of the adsorbates on the first layer is same; and (c) the binding energy of the other layers is equal to the one of pure adsorbates. These assumptions ofa uniform adsorbent surface and the absence oflateral interactions between adsorbed molecules are incorrect, considering the heterogeneous food surface interactions (Blahovec and Yanniotis, 2009). Despite the theoretical limitations of BET adsorption analysis, the BET monolayer concept was found to be a reasonable guide with respect to various aspects of interest in dried foods (Iglesias and Chirife, 1982; Karel, 1973). The equation can be used upto water activity 0.55 (Labuza, 2002), 0.3-0.4 (Timmermann *et al.*, 2001).The BET equation in a linear form is as follows (Timmermann *et al.*, 2001):

$$\frac{a_w}{(1-a_w)M_e} = \frac{(C_B-1)a_w}{X_{mB}C_B} + \frac{1}{X_{mB}C_B} \qquad \text{Eq(2.1)}$$

where,

a_w= water activity,

M_e= equilibrium moisture content,

X_{mB}= monolayer moisture content (BET monolayer) at which the water attached to each polar and ionic groups starts to behave as a liquid-like phase, and

C_B=energy constants of BET equation, related to logarithmically to the difference between the chemical potential of the sorbate molecules in the pure liquid state and in the first sorption layer

2.6.2   Guggenheim-Anderson and DeBoer (GAB) equation

The term GAB model comes from the names Guggenheim, Anderson and De Boer, who independently derived the equation in 1966, 1946 and 1953, respectively (Vanden Berg, 1984). In more recent years, among the sorption models, the Guggenheim-Anderson-deBoer (GAB) equation has been applied most successfully to various foods. It has a reasonably small numbers of parameters (three) and adequately presents the experimental data in the range of water activity of most practical interest in foods (i.e. 0.05 to 0.90), within which the water activity of most foods remains (Timmermann *et al.*, 2001). It is based on the BET theory and

involves three coefficients which have physical significance, two of them being functions of temperature on isotherms to be described by means of Arrhenius-type equations(Brunauer *et al.*, 1998). These parameters may be estimated using either the non-linear regression method or the polynomial regression method.

It is also recommended as the fundamental equation for the characterization of water sorption of food materials by European Project Group COST 90. The GAB equation, according toBizot (1983), is as follows:

$$\frac{M_e}{X_{mG}} = \frac{C_G K a_w}{(1 - K a_w)(1 - K a_w + C_G K a_w)} \qquad \text{Eq(2.2)}$$

where,

M_e= equilibrium moisture content (db),

X_{mG} = water content corresponding to saturation of all primary adsorption sites by single molecular layer (analogous to BET monolayer moisture),

a_w= water activity,

K = factor related to the heat of sorption of the multilayer (dimensionless), and

C_G = constant related to the monolayer heat of sorption (dimensionless)

Both the BET and GAB isotherms are closely related as they follow the same statistical model(Basu *et al.*, 2006b). The BET constant, C_B is related logarithmically to the difference between the chemical potential of the sorbate molecules in the pure liquid state and in the first sorption layer.On the other hand, the GAB constant,$C_G$is related to the difference of this magnitude in the upper layers and in the monolayer, while the constant $K$is related to this difference in the sorbate's pure liquid state and in the upper layers and the product of both ($C_G K$) represents the equivalent to C_B of BET i.e., $C_G K = C_B$ (Timmermann *et al.*, 2001). It is to be mentioned that the third GAB constant,K,is, practically without exception, near to but less than unity (Chirife *et al.*, 1992), a fact which constitutes a definitive characteristic of this isotherm.

Now, if both isotherms (BET and GAB) are used for regression analysis of sorption data, two sets of values of the monolayer capacity and of the energy constant are obtained, which should be comparable. The monolayer capacity of BET is always less than the GAB value, while the energy constant of BET is always larger than the GAB value (Basu *et al.*, 2006b).

2.6.3 Iglesias and Chirifie equation

The analysis of sorption phenomena in high sugar foods like most fruits, is complicated by the dissolving of sugars and by this reason, the theoretical prediction of this isotherm is difficult. Accordingly, an empirical equation for describing the water sorption behavior of various foods and related high sugar items was proposed (Iglesias and Chirife, 1982). The proposed equation may be written as:

$$M_e = a(\frac{a_w}{1 - a_w}) + b \qquad \text{Eq(2.3)}$$

where,

M_e = equilibrium moisture content, and

a and *b* are constants

The proposed equation described adequately equilibrium moisture content for seventeen isotherms (Iglesias and Chirife, 1982).

2.6.4 Halsey equation

This equation provides an expression for the condensation of multilayers at a relatively large distance from the surface, assuming that the potential energy of a molecule varies as the inverse of bth power of its distance from the surface. This equation is a good representation of adsorption data regarding isotherms type I, II, or III.Halsey equation is also widely used to represent the sorption isotherm of foods (Iglesias and Chirife, 1982). This equation can be written as follows:

$$a_w = \exp(-\frac{a}{RT})M_e^b \qquad \text{Eq(2.4)}$$

where, M_e = equilibrium moisture content (db),

a_w = water activity, and

a and *b* are constants

The model was first proposed by Halsey in the exponential form with parameter a and b. Later, the parameter *a* was analyzed and found to be related to the absolute temperature by empirical exponential function (Basu *et al.*, 2006a).

2.6.5 Chung and Pfost equation

Starting with a thermodynamic procedure, obtained heat and free energy changes of adsorption and desorption of corn hulls and its products. They also developed a general isotherm equation by adopting the framework of potential theory. This equation was developed based on the relationship between the moisture content of a material and the change in free energy for sorption. The equation may be written as:

$$\ln a_w = -\frac{a}{RT}\exp(-bM_e) \qquad \text{Eq(2.5)}$$

where, *a* and *b* are constants

The equation is based on the following assumptions: (i) potential theory with modified assumptions (ii) free energy decreases exponentially with moisture content (iii) free energy also varies with temperature(Lavoyer *et al.*, 2013).

2.6.6 Henderson equation

The most widely used and best known model for the sorption isotherm of biological materials is the semi-emperical equation derived from Gibbs adsorption theory (Chen, 1990). Henderson (1952) presented this equation as:

$$1 - a_w = \exp(-kTM_e^n) \qquad \text{Eq(2.6)}$$

where,

k and *n* are constant

The basic assumptions are (i) quantity of water adsorbed is a function of surface area upon which it is adsorbed, (ii) partially empirical.This equation can be employed over a water activity range from 0 to 1.0. Henderson equation was modified by Thompson by adding another constant into temperature term. The practical effect of the modification is to move the temperature of absolute zero to higher temperature (Chen, 1990). The modified equation becomes:

$$1 - a_w = \exp(-k(T+c)M_e^n) \qquad \text{Eq(2.7)}$$

where,

k, c and *n* constants

2.6.7 Oswin equation

Oswin (1946) proposed a fully emperical isotherm equation with two parameters. The Oswin equation was able to fit the sorption data better for protein and starchy foods. Oswin equation is a mechanical series expansion for sigmoid shaped and can be written as:

$$M_e = a(\frac{a_w}{1-a_w})^n \qquad \text{Eq(2.8)}$$

where, *a* and *n* are constants

Presented by Oswin (1946), this equation primarily was adopted to solve a packaging problem. Labuza (1980) applied the equation to correlate the EMC data in non fat dry milkand freeze dried soluble tea. The Oswin equation has been found as a good fit model for the sorption of various food products (Ariahu *et al.*, 2006).

2.6.8 Smith equation

Smith (1947) developed an an empirical model to describe the final curved portion of water sorption isotherm of high molecular weight biopolymers assuming that there are two fractions

of water that are sorbed onto a dry surface: the first fraction exhibits a higher condensation heat than the normal and it would be expected to follow the Langmuir model and the second fraction which can only be formed after the first fraction has been sorbed. Smith based his model on the second fraction and considered that the second fraction consists of multilayers of condensed water molecules, which effectively prevent any possible evaporation of the initial layer.He theorized that the moisture content in the second fraction was proportional to the logarithm of the difference between the $a_w$of the sample and pure water.

It has been shown by Iglesias and Chirife (1982) that the final curved proportion of the water sorption isotherms of bio-polymers were closely described by the equation:

$$M_e = a - b\ln(1-a_w) \qquad \text{Eq(2.9)}$$

where,

a = quantity of water in the first sorbed fraction and is dimensionless constant, and

b = quantity of water in the multilayer moisture fractionand is dimensionless   constant

2.6.9   Caurie equation

Caurie (1970)proposed the following equation based on purely mathematical manipulation.

$$\ln C = \ln a - ra_w$$

$$\text{C = water concentration} = \frac{100 - \% \ water}{\% \ water} \qquad \text{Eq(2.10)}$$

where,

r and a are constants.

PART III

Materials and methods

3.1 Materials

3.1.1 Raw material

The turmeric powder was brought from the Baraha department store of Dharan.

3.1.2 Chemicals

All the required chemicals during this work were provided by CCT lab. The lists of chemicals are shown in appendix E.

3.1.3 Glasswares and apparatus

All the required glasswares and apparatus during this work were provided by CCT lab. The lists of glasswares and apparatus required are shown in appendix E.

3.2 Methods

3.2.1 Preparation of different water activities

Water vapor pressure of sulphuric acid solution varies depending on their water concentration. The ERH in the headspace increases with an increase in temperature. Different concentrations of sulphuric acid solution was used in the similar sized glass dessicators to maintain different water activities ranging from of 0.16 to 0.92 as shown in the Appendix A. Around 2-3 cm of the bottom was filled with the sulphuric acid solution. Small amount of toluene was added in the dessicators having RH higher than 50% to prevent fungal growth during experiment. The dessicators were placed in incubator for 24 h at particular temperature to maintain the required water activities.

3.2.2 Determination of sorption isotherm

A static gravimetric technique was used to get the EMC data of the dried turmeric powder samples at three different temperatures i.e., 20±1, 30±1 and 40±1°C. This method requires a lot of time for reaching the hygroscopic equilibrium but has the advantage of presenting a more restricted domain of moisture content variation. Triplicate samples each of 5 ± 0.001g were taken in tared petri dishes and then kept in the dessicators containing different concentration of sulphuric acid solutions (60%, 50%, 45%, 40%, 35%, 30%, 25% and 15%) v/v to maintain the water activity. The water activity of sulphuric acid solutions at different concentratiuons and temperature is shown in Appendix A. Finally these 8 dessicators were kept inside the temperature controlled incubator to maintain 30°C and 40°C whereas 20°C was maintained at ambient temperature during winter. Each sample was weighed after 1 h, 2 h, 4 h, 6 h, 24 h and 48 h. Then the final equilibrated mass of the sample was taken. Equilibrium was defined to have been reached when the consecutive weighing was less than ±1 mg. The mass transfer between the sample and the environment in the desiccators is by natural diffusion process. The ERH inside the dessicator was checked by the Barigo hygrometer.

The Equilibrium Moisture Content (EMC) was calculated at each Equilibrium Relative Humidities (ERH) using the expression given by Konopacka and Plocharski (2002).

$$m = \frac{(W_2 - W_1) + \dfrac{\% H_2O}{100} \times W_1}{W_1(\dfrac{100 - \% H_2O}{100})} \times 100$$

where,

      m = Equilibrium Moisture Content (db %),

      W_2 = final weight,

      W_1 = initial weight, and

      % H_2O = initial moisture content of sample (wb)

3.2.3 Moisture sorption isotherm plot

Moisture sorption isotherm curve was drawn using different EMC values against different a_w. Each EMC (db %) was plotted against their respective a_w to obtain the sorption isotherm curve at three different temperatures i.e., 20±1, 30±1 and 40±1°C using Microsoft Excel 2010.

3.2.4 Fitting of the sorption data

Out of 270 proposed isotherm models, the sorption data at temperatures 20±1, 30±1 and 40±1°C were fitted to the nine different sorption models (BET model, GAB model, Iglesias and Chirife model, Halsey model, Chung and Pfost model, Henderson model, Oswin model, Smith model and Caurie model). The GAB equation was solved as polynomial equation and other equations (Appendix C) were linearly solved to obtain the model parameters by regression analysis using MS-Excel software.

3.2.5 Statistical analysis for determination of appropriate models

In order to find best suitable model to explain drying behaviour of any product with different drying methods or different conditions, statistical methods were generally used. The main methods used for drying studies in the literatures were given below:

3.2.5.1 Coefficient of determination

It is used in the context of statistical models whose main purpose is the prediction of future outcomes on the basis of other related information. It is the proportion of variability in a data set that is accounted for by the statistical model. It provides a measure of how well future outcomes are likely to be predicted by the model. The coefficient of determination is not likely to be 0 or 1, but rather somewhere in between these limits. The closer it is to 1, the greater relationship exists between experimental and predicted values (Neter *et al.*, 2004). This value is used for the quantitative comparison criteria and shows the level of agreement between measured and predicted values (Hossain, M. A. and Bala, 2002). It is sometimes called as correlation coefficient (Gunhan *et al.*, 2005) or determination coefficient (Vega-Galvez *et al.*, 2011). Although there are several different definitions of R^2, it can be calculated by:

$$R^2 = \frac{\left(\sum M_{exp} M_{pre}\right)^2}{\sum M_{exp}^2 \times M_{pre}^2}$$

3.2.5.2 Coefficient of correlation (r)

It is the square root of R^2 (Neter *et al.*, 2004). This is a measure of the correlation (linear dependence) between two variables, giving a value between +1 and −1 inclusive. It is widely used in the sciences as a measure of the strength of linear dependence between two variables. It is called as correlation coefficient (Magalhaes and Pinho, 2008; Erbay and Icier, 2009) or correlation index (Sander and Kardum, 2009) and given as:

$$r = \frac{N\sum_{i=1}^{N} MR_{pre,i} MR_{exp,i} - \sum_{i=1}^{N} MR_{pre,i} \sum_{i=1}^{N} MR_{exp,i}}{\sqrt{\left(N\sum_{i=1}^{N} MR_{pre,i}^2 - \left(\sum_{i=1}^{N} MR_{pre,i}\right)^2\right)\left(N\sum_{i=1}^{N} MR_{exp,i}^2 - \left(\sum_{i=1}^{N} MR_{exp,i}\right)^2\right)}}$$

3.2.5.3 Chi-square test (χ2)

It is the mean square of the deviations between experimental and predicted values for the models and used to evaluate the fitting agreement of each model. Lower the values of χ2, better the goodness of the fit (Yang *et al.*, 2007). It is called as mean squared deviation (Cihan *et al.*, 2007; Celen *et al.*, 2010), reduced mean square of deviation (Demir *et al.*, 2007), mean square of deviation (Jain and Pathare, 2004; Doymaz, 2004) and standard deviation (Midilli *et al.*, 2002) and could be calculated as follows:

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2}{N-n}$$

3.2.5.4 Root-mean-square error (RMSE)

It is a frequently used measure of the differences between values predicted by a model or an estimator and the values actually observed from the thing being modeled or estimated. RMSE is a good measure of accuracy and serves to aggregate the residuals into a single measure of predictive power. It is required to reach zero and can be calculated as (Wang *et al.*, 2007)

$$RMSE = \left(\frac{1}{N} \Sigma_{i=1}^{N} \left(MR_{\exp,i} - MR_{pre,i} \right)^2 \right)^{\frac{1}{2}}$$

It is called as root mean square analysis, standard deviation, root mean sum error, standard error, root mean square difference and root mean squire deviation. There is also another form of root mean square deviation (Contreras *et al.*, 2008)

$$RMSD = \frac{1}{N} \sqrt{\Sigma_{i=1}^{N} \left(MR_{\exp,i} - MR_{pre,i} \right)^2}$$

3.2.5.5 Sum of squared errors of prediction (SSE)

In statistics,the sum of squared residuals (SSR) or the sum of squared errors of prediction (SSE), is the sum of the squares of residuals (deviations predicted from actual empirical values of data). It is a measure of the discrepancy between the data and an estimation model. A small SSE indicates a tight fit of the model to the data. It is used as an optimality criterion in parameter selection and model selection (Anon., 2011).

$$\sum_{i=1}^{N} \left(MR_{\exp,i} - MR_{pre,i} \right)^2$$

3.2.6 Proximate analysis of turmeric powder

3.2.6.1 Crude protein content

Nitrogen content was determined by micro Kjeldahl distillation method as per Ranganna (1986).

3.2.6.2 Total ash content

Total ash was determined by ashing in electric muffle furnace as per Ranganna (1986).

3.2.6.3 Fat content

Fat content was determined by semi continuous solvent extraction method (Soxhlet method) using light petroleum ether (b.pt. 60-80°C) as per AOAC (2005).

3.2.6.4 Carbohydrate content

Total carbohydrate was determined by difference method.

$$\text{Total Carbohydrate (\%)} = 100\% - (\text{Protein} + \text{Fat} + \text{Ash})\%$$

3.2.7 Data analysis

The experimental data of equilibrium moisture content was used to obtain the linear and polynomial regression lines by using the Microsoft Excel 2010 software. For mathematical modeling, the different equations were tested to select the best model for describing the sorption isotherm of the dried turmeric powder. The goodness of fit of the tested mathematical models on the experimental data was evaluated using coefficient of determination (R^2) and chi-square test (χ^2), Root Mean Square Error (RMSE) and Sum of Squared Error (SSE) with higher (R^2) values with lower χ^2, SSE and RMSE values indicating a better fit.

Part IV

Results and discussion

Static gravimetric method was used to determine the EMC of dried samples kept at 16-92% RH at temperatures: 20±1, 30±1 and 40±1°C. The sorption isotherm curve was obtained by plotting EMC (db,%) against different water activities. The initial moisture content of the dried turmeric sample before keeping into dessicator was 4.7 % (wb). The experimental data were also fitted to different sorption models to obtain model parameters. Dried turmeric samples stored at different RH was carried out to determine the CMC and critical a_w.

4.1 Chemical composition of Turmeric (*Curcuma longa* L.)

The result in Table 4.1 shows that the turmeric powder contains 4.47% moisture, 6.70% ash, 5.30 % crude fibre and 6.95 % fat. It also contains 7.08 % crude protein and 69.50 % carbohydrate. This implies it could be good source of protein and carbohydrate.The proximate composition are expressed on dry basis. The 6.70 % ash content of turmeric shows that turmeric will contain reasonable amount of mineral. The fibre (5.30 %) presents in turmeric will help to cleanse the digestive tract of its consumer by removing potential carcinogens from the body and prevents the absorption of excess cholesterol. Fibre also adds bulk to the food and prevents the intake of excess starchy food and may therefore guard against metabolic conditions such as hypercholesterdemic and diabeties mellitus (Bamishaiye *et al.*, 2011). Similar results (Protein-9.40%, Fat-6.85%, Ash-4.85, Carbohydrate-67.85,Fiber-4.60%) was reported by Ikpeama *et al.* (2014) during his research on nutritional properties of turmeric.Tainter and Grenis (2001) reported Protein-7.83%, Fat-9.88%, Carbohydrates-64.93% and Ash-6.02% as the chemical composition for turmeric. The results were similar to the findings of this study. The slight variation may be due to the variety of turmeric used, processing conditions, geographic condition of grown area.

Table 4.1 Proximate composition of turmeric powder on dry basis*.

S.N	Components	% dry basis
1	Moisture content	4.47(0.11)
2	Protein	7.08(0.28)
3	Crude fat	6.95(0.13)
4	Total ash	6.70(0.15)
5	Carbohydrate	69.50(0.58)
6	Crude fiber	5.30(0.18)

* Values are the means of three determinations. Figures in the parenthesis are the standard deviation.

4.2   Sorption behaviour of dried Turmeric

Moisture sorption isotherm curves which were obtained by plotting equilibrium moisture content (EMC, db %)of dried turmeric powder samples against different a_w at three different temperature i.e., 20±1, 30±1 and 40±1°C are graphically illustrated in the Fig. 4.1. The temperature was selected considering the normal temperature range of Nepal. Here 20°C, 30°C and 40°C represent the temperatures at which the study of sorption isotherm was carried out.
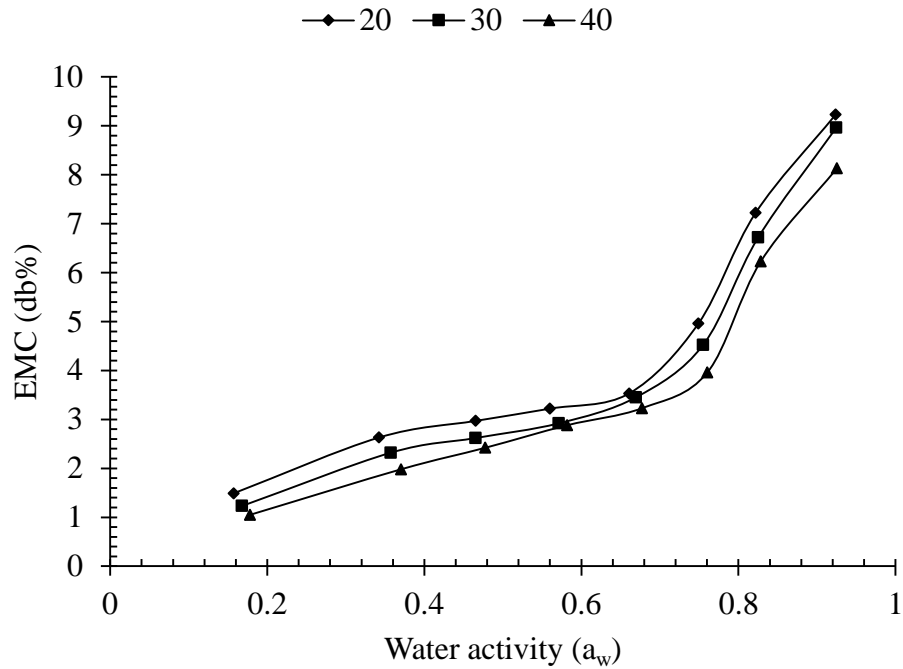
Fig. 4.1 Moisture sorption isotherms of dried Turmeric at 20°C, 30°C and 40°C

It is clear that the isotherms appeared as sigmoid shape type II pattern as classified by Brunauer *et al.* (1940), indicating that the samples held small amount of water at low a_w and large amount of water at high a_w (Garcia-Perez *et al.*, 2008). In the range of water activity of 0.1 to 0.9, the samples reached EMC ranging from 1.05 to 9.23 % (db). The characteristic shape of moisture isotherms depends upon the variety and total amount of hygroscopic materials present in the particular heterogeneous mixture of hydrophilic substances. The EMC was increased with an increase in a_w, the increase was more profound within water activities of 0.7-0.9. This implies that at $a_w > 0.7$, microbial growth, enzymatic reactions and lipid oxidation may occur much faster leading to rapid spoilage of turmeric powder. There was an increase in moisture content at given RH with decreasing temperature. As temperature varies, the excitation of molecules as well as the distance varies and thus the attraction between molecules varies (Al-Muhtaseb *et al.*, 2004). This means that there was an activation of the water molecules due to the increase in temperature which causes them to break away from the water binding sites, thus lowering the EMC.This causes the amount of sorbed water to change with temperature at a given a_w. This negative relationship exist between EMC and temperature.

39

According to BET, Type II isotherm is shown by the biological materials and are normally associated with monolayer-multilayer sorption on non porous and macroporous surface of a powder. The adsorption isotherms of dried turmeric, at different temperatures, are shown in Fig. 4.1. As it can be observed, at a constant water activity, the equilibrium moisture contents increase with decreasing temperature; similar trends were reported by (Vega *et al.*, 2008). This trend can be explained by considering excitation states of molecules. At increased temperatures the molecules are in an increased excitation state, thus increasing their distance apart and decreasing the attractive forces between them (Miranda *et al.*, 2010). This leads to a decrease in the degree of water sorption at a given relative humidity with increasing temperature. According to Catelam *et al.* (2011) the decrease in water activity was due a reduction in the number of active sites due to chemical and physical changes induced by temperature and then depend on the composition of foods. Further, examination of the figure shows that the isotherms are S-shaped (Type II). This is a typical characteristic of many biomaterials and of fruits rich in sugars (Simal *et al.*, 2007).

The average parameters related to various mathematical models, as well as the corresponding statistical data applied are recapitulated in Table 4.11. Graphical representation of the fit goodness of theoretical isothermsat 20, 30 and 40°C are shown in below figures. For all tested models, the parameters a and n are found to be temperature dependent. BET model followed by Caurie and Hasley model gave good fits to experimental data over the range of water activities employed, with highest correlation cofficient (R^2)>0.90, and lowest value of SSE, RMSE and χ^2. The BET and the Caurie models (at T=20°, 30° and 40°C) gave the best fits with highest value of R^2 the lowest average values of SSE, χ^2 and RMSE. The RMSE is the square root of the variance of the residuals, it indicates the absolute fit of model to that how close the observed data points are to the model predicted values. R^2 is a relative measure of fit, RMSE is an absolute measure of fit. So in this case BET model gives the best fit model in comparision between Caurie and Hasley.

These results are comparable to those recorded by others, Lamharrar *et al.* (2007) have also reported that the BET model was the most suitable to estimate adsorption isotherms of dried ginger powder, while Lavoyer *et al.* (2013) found very good adjustment of the GAB model to

adsorption isotherms of green coconut pulp. According to Kohayakawa *et al.* (2005), the GAB modelhas been extensively used for foodstuffs, mainly for fruits.

4.3   Fitting of the experimental data in different sorption models

Nine sorption models were selected to fit the experimental data at three different temperatures i.e., 20±1, 30±1 and 40±1°C. Statistical analysis showed that BET model gave the best fitting followed by Caurie and Hasley model over the entire range of experimental temperatures. Yan *et al.* (2008) reported that Halsey model along with BET model were the most versatile to fit for starchy product. Satimehin and Ezeike (2002) tested the validity of Halsey and BET models on yam at different temperature. It should be noted that the goodness of fit of any sorption model to the experimental data shows only a mathematical quality and not the nature of the sorption process.

4.3.1   Fitting of BET model

The graph was obtained by plotting the $\dfrac{a_w}{(1-a_w)M_e}$ vs. a_w and the plot yield was linear in nature as shown in the Fig. 4.2. In this model, data above a_w 0.5 was excluded as stated by Iglesias and Chirife (1976). The data for plotting was used in the water activity range 0.15-0.58. The working equation and experimental data for fitting the BET model are shown in the Appendix C and Table D.1 respectively.

Fig. 4.2 BET plots of the experimental data at 20°C, 30°C and 40°C
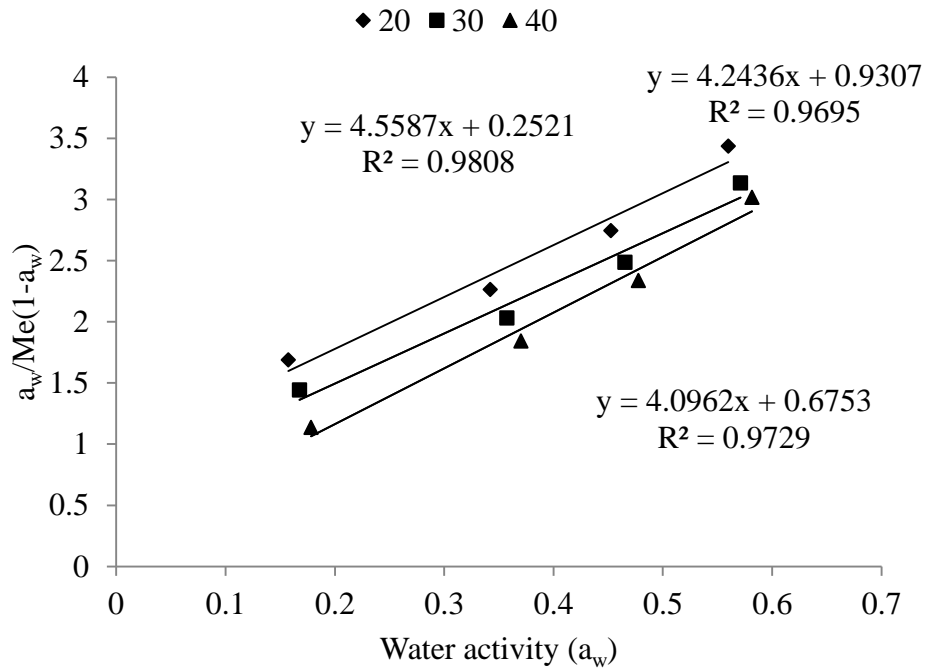
Fig. 4.3 Predicted graph of BET model at 20°C, 30°C and 40°C

The fit of the data was seen satisfactory by statistical analysis at temperatures 20°C, 30°C and 40°C respectively. The monolayer moisture content value (X_{mB}) was found to be 1.527, 1.378 and 1.348 at temperatures 20°C, 30°C and 40°C respectively. The decrease in monolayer value at higher temperature indicates that sorptive property of dried turmeric decreases as temperature increases. The decrease in X_{mB} value also reflects the reduction in the number of active sites due to chemical and physical changes induced by temperature (McMinn and Magee, 1999). This decrease in monolayer moisture content with increasing temperature was in agreement with Ariahu *et al.* (2006), Alikali *et al.* (2009) and Farahnaky *et al.* (2009). These authors reported decreasing X_{mB} values with increasing temperatures for fresh water crayfish, ginger slices and figs respectively. The prediction of X_{mB} values is important because deterioration of foods is very small below X_{mB}, since water is strongly bound to the food below X_{mB} and is not involved in any deteriorative reaction either as solvent or as the substrates (Kaymak-Ertekin and Gedik, 2004). According to Arslan and Togrul (2005), the monolayer moisture content, X_{mB}, could be viewed as the moisture content affording the longest time period with minimum quality loss at a given temperature. Therefore, deteriorative reactions, except oxidative rancidity, were minimal at the moisture content below X_{mB}. Consequently, the safest water activity was that corresponding to X_{mB} or lower. The value of energy constant (C_B) at temperatures 20°C, 30°C and 40°C was found to be 63.129, 30.104 and 10.395 respectively which is shown in the Table 4.2.

Table 4.2 Values of constants and statistical parameters for BET model

Parameters	Temperature (°C)		
	20	30	40
X_{mB} (g/100g dry matter)	1.527	1.378	1.395
C_B	63.129	30.104	10.395
R^2	0.960	0.936	0.966
SSE	0.001519	0.00304	0.00141
RMSE	0.027	0.038	0.026
χ^2	0.00005	0.00101	0.00047

The final BET models at 20, 30 and 40°C after obtaining values of the constants are:

At 20°C: $\dfrac{a_w}{(1-a_w)M_e} = \dfrac{(63.129-1)a_w}{1.527 \times 63.129} + \dfrac{1}{1.527 \times 63.129}$

At 30°C: $\dfrac{a_w}{(1-a_w)M_e} = \dfrac{(30.104-1)a_w}{1.378 \times 30.104} + \dfrac{1}{1.378 \times 30.104}$

At 40°C: $\dfrac{a_w}{(1-a_w)M_e} = \dfrac{(10.395-1)a_w}{1.395 \times 10.395} + \dfrac{1}{1.395 \times 10.395}$

4.3.2 Fitting of GAB model

The graph was obtained by plotting $\dfrac{a_w}{M_e}$ vs. a_w and the plot yield was polynomial in nature as shown in the Fig. 4.4. The working equation and the experimental data for fitting the GAB model are shown in the Appendix D and Table D.2 respectively. The EMC data were analysed using the polynomial regression method on transformed binomial equations for the GAB parameters.
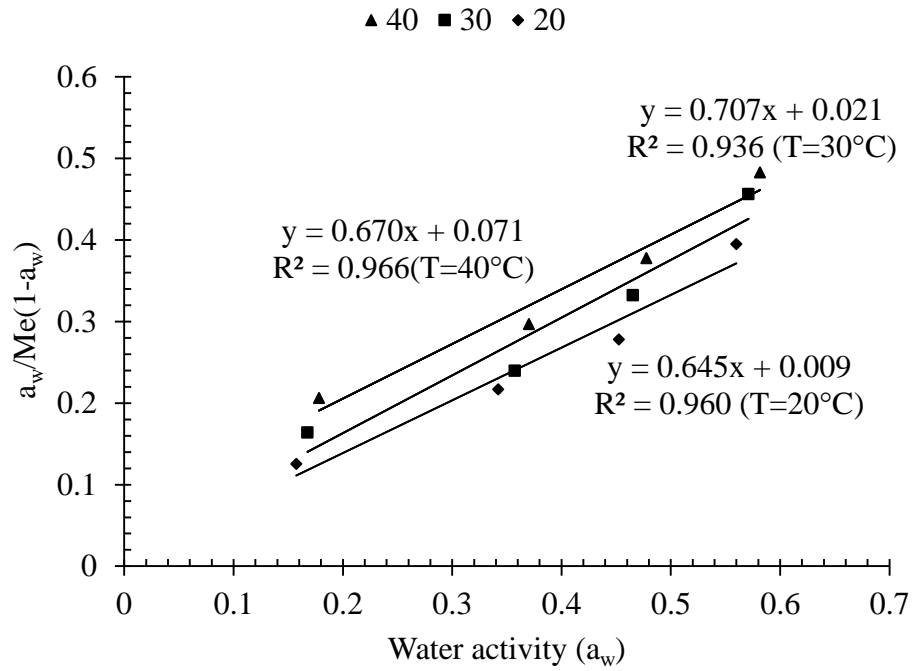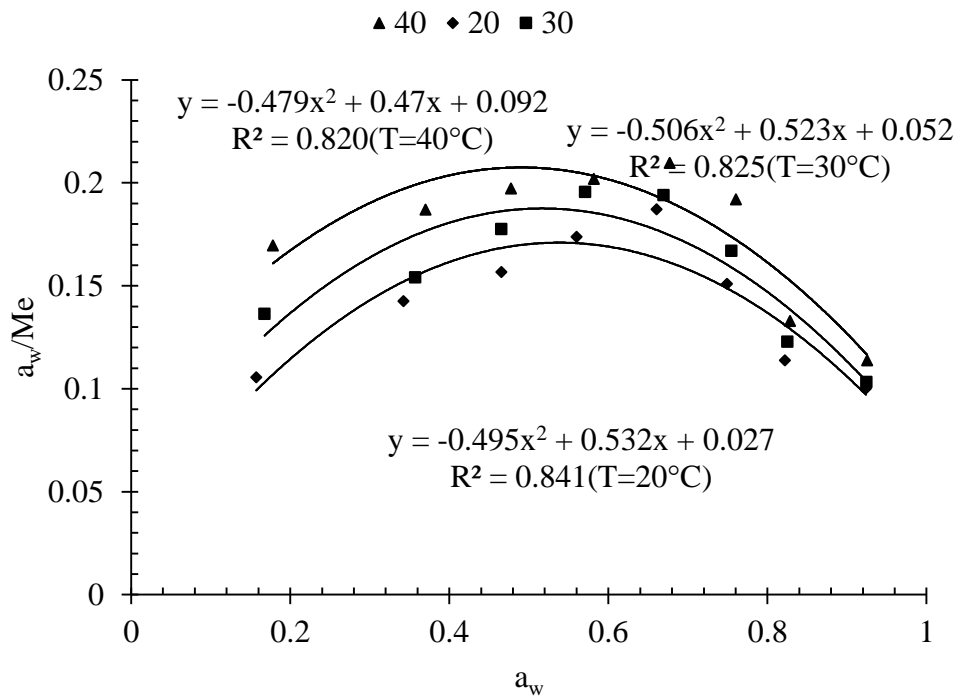

Fig. 4.4 GAB plots of the experimental data at 20°C, 30°C and 40°C

The fit of the data was not seen satisfactory at temperatures 20°C, 30°C and 40°C as seen from statistical analysis. This was due to the GAB model's rigidity which causes problems with the approximation of sorption data (Blahovec and Yanniotis, 2009). Although the GAB model did not give the best fit, parameters obtained from GAB model cannot be neglected. Its parameters, especially the monolayer moisture content (X_{mG}), are widely used in food preservation.

The X_{mG} values were found to be 1.718, 1.623 and 1.585 at temperatures 20°C, 30°C and 40°C respectively. The decrease in monolayer value as temperature increases was due to inability to hold bound water at higher temperatures. This X_{mG} values were found to be comparable with the results obtained by Alakali and Satimehin (2009) at temperatures 20°C, 30°C and 40°C which was 1.91, 1.79 and 1.67 respectively. The decrease in monolayer moisture content (X_{mG}) is indication that there was decrease in the hygroscopicity as temperature increases. By using GAB equation to predict the safest water activity in this experiment, the average value was found to be 1.718, 1.623 and 1.585 at temperatures 20°C, 30°C and 40°C respectively. It was clear from the Table 4.2 and 4.3 that value of monolayer moisture content obtained from GAB model was higher than that from BET model while the reverse was true for energy constant i.e., C_B was greater than C_G. This reverse phenomenon for energy constant signifies that the difference between the chemical potential of the sorbate molecules in the pure liquid state and in the first sorption layer was higher than the difference between the chemical potential of the sorbate molecules in the upper layers and in the monolayer (Timmermann *et al.*, 2001). The value of Guggenheim constant (C_G) and energy constant (K) at different temperatures is shown in the Table 4.3.

Table 4.3 Values of constants and statistical parameters for GAB model

Parameters	Temperature(°C)		
	20	30	40
C_G	23.590	13.254	7.837
X_{mG} (g/100 g dry matter)	1.718	1.623	1.585
K	0.889	0.888	0.871
R^2	0.841	0.825	0.820
SSE	0.0011	0.0013	0.0015
RMSE	0.0138	0.0015	0.010
χ^2	0.00016	0.00019	0.00021

The final GAB models after values of the constants are:

At 20°C:
$$\frac{M_e}{1.72} = \frac{23.590 \times 0.889 \times a_w}{(1-0.889a_w)(1-0.889a_w+23.590 \times 0.889 \times a_w)}$$

AT 30°C:
$$\frac{M_e}{1.63} = \frac{13.254 \times 0.888 \times a_w}{(1-0.888a_w)(1-0.888a_w+13.254 \times 0.888 \times a_w)}$$

AT 40°C:
$$\frac{M_e}{1.58} = \frac{7.837 \times 0.871 \times a_w}{(1-0.871a_w)(1-0.871a_w+7.837 \times 0.871 \times a_w)}$$

4.3.3 Fitting of Iglesias and Chirifie model

The graph was obtained by plotting M_e vs. $\frac{a_w}{1-a_w}$ and the plot yield was linear in nature as shown in the Fig. 4.5. The working equation and experimetal data for fitting the Iglesias and Chirifiemodel are shown in the Appendix D and Table D.3 respectively.

Fig. 4.5 Iglesias and Chirife plots of the experimental data at 20°C, 30°C and 40°C

The fit of the data to Iglesias and Chirife model was not satisfactory at temperatures 20°C, 30°C and 40°C as seen from statistical analysis. The values of the constants a and b is shown in the Table 4.4.

Table 4.4 Values of constants and statistical parameters for Iglesias and Chirife model

Parameters	Temperature (°C)		
	20	30	40
A	0.625	0.612	0.552
B	2.461	2.176	1.967
R^2	0.877	0.899	0.889
SSE	5.914	4.649	4.268
RMSE	0.992	0.880	0.843
χ^2	0.844	0.660	0.609

The final Iglesias and Chirife models after obtaining values of the constants are:

At 20°C: $M_e = 0.625(\frac{a_w}{1-a_w}) + 2.461$

At 30°C: $M_e = 0.621\left(\frac{a_w}{1-a_w}\right) + 2.176$

At 40°C: $M_e = 0.552\left(\frac{a_w}{1-a_w}\right) + 1.967$

4.3.4 Fitting of Halsey model

The graph was obtained by plotting $\ln M_e$ vs. $\ln\{-\ln(a_w)\}$ andthe plot yield was linear in nature as shown in the Fig. 4.6. The working equation and experimental data for fitting Halseymodel are shown in the Appendix D and Table D.4 respectively.

Fig. 4.6 Halsey plots of the experimental data at 20°C, 30°C and 40°C

Fig. 4.7 Predicted graph for Halsey model at 20°C, 30°C and 40°C

The fit of the data to Halsey model was satisfactory at temperatures 20°C, 30°C and 40°C as seen from statistical analysis. The values of the constants a and b is shown in the Table 4.5.

Table 4.5 Values of constants and statistical parameters for Halsey model

Patameters	Temperature (°C)		
	20	30	40
a	4.36RT	3.203RT	2.522RT
b	-1.7182	-1.6129	-1.5578
R^2	0.970	0.968	0.962
SSE	0.113	0.094	0.107
RMSE	0.3355	0..3068	0.3267
χ^2	0.0161	0.0134	0.0152

The final Halsey models after obtaining values of the constants are:

At 20°C: $\qquad a_w = \exp\left(\dfrac{-4.36RT}{RT}\right) m_e^{-1.7182}$

At 30°C: $\quad a_w = \exp\left(\dfrac{-3.203RT}{RT}\right) m_e^{-1.6129}$

At 40°C: $\quad a_w = \exp\left(\dfrac{-2.522RT}{RT}\right) m_e^{-1.5578}$

4.3.5 Fitting of Chung and Pfost model

The graph was obtained by plotting M_e vs. $\ln\{-\ln(a_w)\}$ and the plot yield was linear in nature as shown in the Fig. 4.8. The working equation and experimental data for fitting the Chung and Pfost model are shown in the Appendix D and Table D.5 respectively.

Fig. 4.8 Chung and Pfost plots of the experimental data at 20°C, 30°C and 40°C

The fit of the data to Chung and Pfost model was satisfactory at temperatures 20°C,30°C and 40°C as seen from statistical analysis. The values of the constants a and b is also shown in the Table 4.6.

Table 4.6 Values of constants and statistical parameters for Chung and Pfost model

Parameters	Temperature (°C)		
	20	30	40
a	2.507 RT	2.248 RT	2.13 RT
b	0.393	0.40	0.432
R^2	0.938	0.940	0.944
SE	2.961	2.721	2.150
RMSE	0.3512	0.3367	0.2993
χ^2	0.4230	0.3886	0.3071

The final Chung and Pfost models after obtaining values of the constants are:

AT 20°C: $\ln m_e = -\left(\dfrac{2.507RT}{RT}\right)\exp(-0.393 m_e)$

At 30°C: $\ln m_e = -\left(\dfrac{2.248RT}{RT}\right)\exp(-0.401 m_e)$

At 40°C: $\ln m_e = -\left(\dfrac{2.13RT}{RT}\right)\exp(-0.432 m_e)$

4.3.6 Fitting of Henderson model

The graph was obtained by plotting $\ln M_e$ vs. $\ln\{-\ln(1-a_w)\}$ and the plot yield was linear in nature as shown in the Fig. 4.9. The working equation and experimental data for fitting the Henderson model are shown in the Appendix d and Table D.6 respectively.
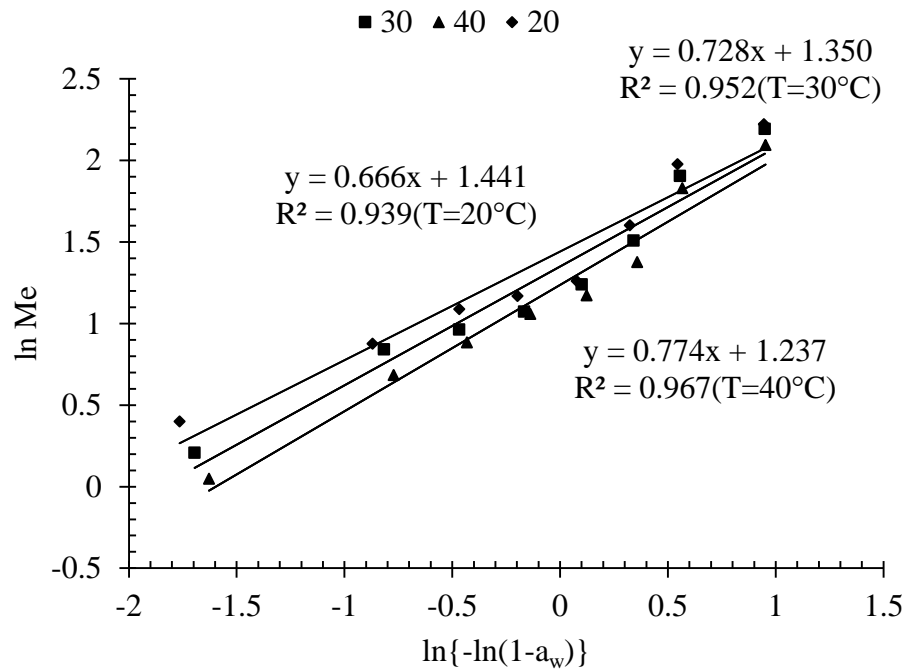
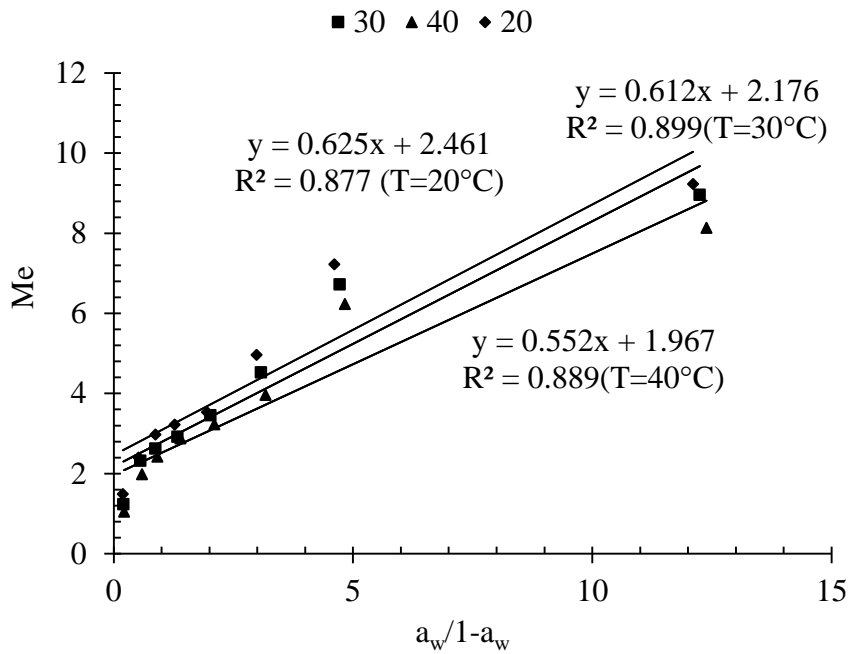**Fig. 4.9** Henderson plots of the experimental data at 20°C, 30°C and 40°C

The fit of the data to Henderson was satisfactory at 20°C, 30°C and 40°Cas seen from statistical analysis which is shown in the Table 4.7. The values of the constants k and n is also shown in the Table 4.7.

Table 4.7 Values of constants and statistical parameters for Henderson model

Parameter	Temperature (°C)		
	20	30	40
k	0.188	0.240	0.275
n	1.180	1.089	1.074
R^2	0.959	0.967	0.967
SSE	2.097	1.622	1.330
RMSE	0.576	0.504	0.462
χ^2	0.299	0.230	0.190

The final Henderson models after obtaining values of the constants are:

At 20°C: $1 - a_w = \exp\left(-0.188 m_e^{1.180}\right)$

At 30°C: $1 - a_w = \exp\left(-0.240 m_e^{1.089}\right)$

At 40°C: $1 - a_w = \exp\left(-0.275 m_e^{1.074}\right)$

4.3.7   Fitting of Oswin model

The graph was obtained by plotting $\ln M_e$ vs. $\ln \dfrac{a_w}{1 - a_w}$ and the plot yield was linear in nature as shown in the Fig. 4.10. The working equation andexperimental data for fitting the Oswin model are given in Appendix D and Table D.7 respectively.
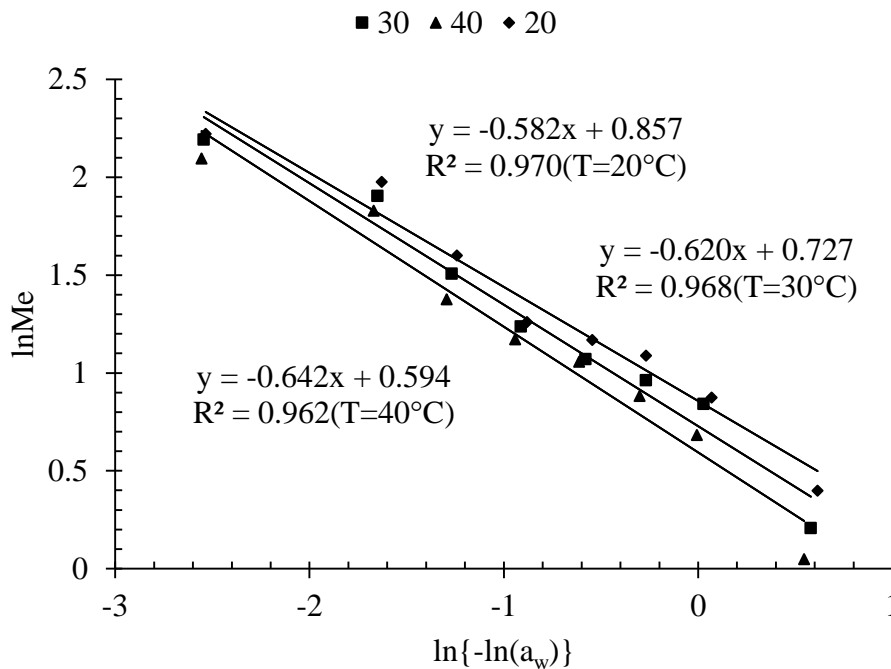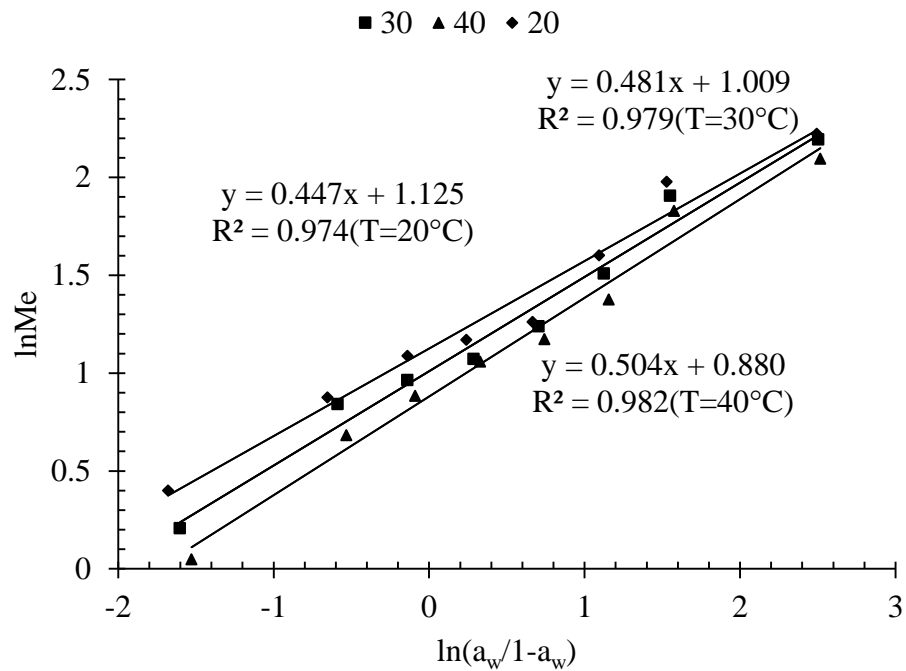

Fig. 4.10 Oswin plots of the experimental data at 20°C, 30°C and 40°C
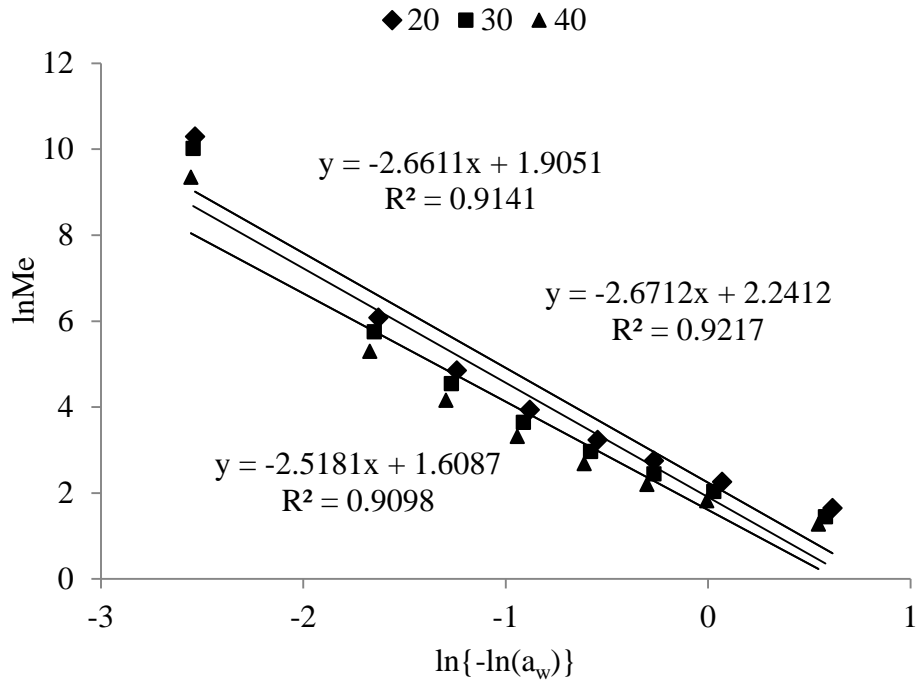
The fit of the data to Oswin model was satisfactory as seen from statistical analysis at temperatures 20°C, 30°C and 40°C. The values of the constants a and n is shown in the Table 4.8.

Table 4.8 Values of constants and statistical parameters for Oswin model

Parameters	Temperature (°C)		
	20	30	40
a	3.098	2.771	2.485
n	0.450	0.479	0.178
R^2	0.964	0.973	0.969
SSE	1.701	1.217	1.170
RMSE	0.532	0.450	0.441
χ^2	0.243	0.174	0.167

The final Oswin models after obtaining values of the constants are:

At 20°C: $m_e = 3.098\left(\dfrac{a_w}{1-a_w}\right)^{0.450}$

At 30°C: $m_e = 2.771\left(\dfrac{a_w}{1-a_w}\right)^{0.479}$

At 40°C: $m_e = 2.485\left(\dfrac{a_w}{1-a_w}\right)^{0.178}$

4.3.8 Fitting of Smith model

The graph was obtained by plotting M_e vs. $\ln(1-a_w)$ and the plot yield was linear in nature as shown in the Fig. 4.11. The working equation and the experimental data for fitting the Smith model are given in Appendix D and Table D.8 respectively.
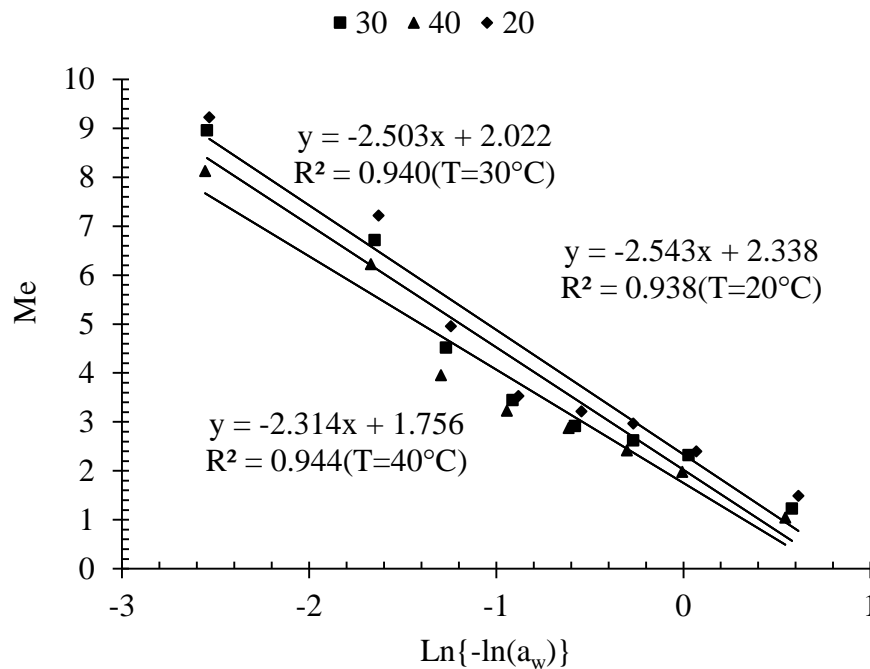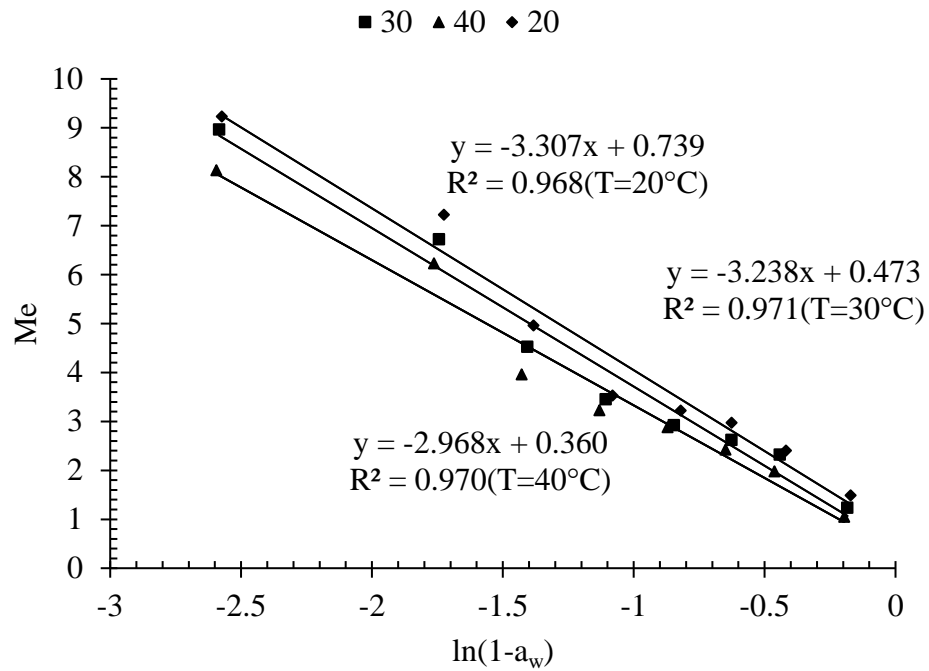
Fig. 4.11 Smith plots of the experimental data at 20°C, 30°C and 40°C

The fit of the data to Smith model was satisfactory as seen from statistical analysis at temperatures 20°C, 30°C and 40°C. The values of the constants a and b is shown in the Table 4.9.

Table 4.9 Values of constants and statistical parameters for Smith model

Parameters	Temperature (°C)		
	20	30	40
a	0.739	0.473	0.360
b	3.307	3.238	2.968
R^2	0.968	0.971	0.970
SSE	1.531	1.297	1.153
RMSE	0.505	0.464	0.430
χ^2	0.219	0.185	0.164

The final Smith models after obtaining values of the constants are:

At 20°C: $\quad m_e = 0.739 - 3.37(1 - a_w)$

At 30°C: $\quad m_e = 0.473 - 3.238(1 - a_w)$

At 40°C: $\quad m_e = 0.360 - 2.968(1 - a_w)$

4.3.9 Fitting of Caurie model

The graph was obtained by plotting $\ln\dfrac{100 - M_e}{M_e}$ vs. a_w and the plot yield was linear in nature as shown in the Fig. 4.12. The working equation and the experimental data for fitting the Caurie model at three different temperatures are given in Appendix D and Table D.9 respectively.
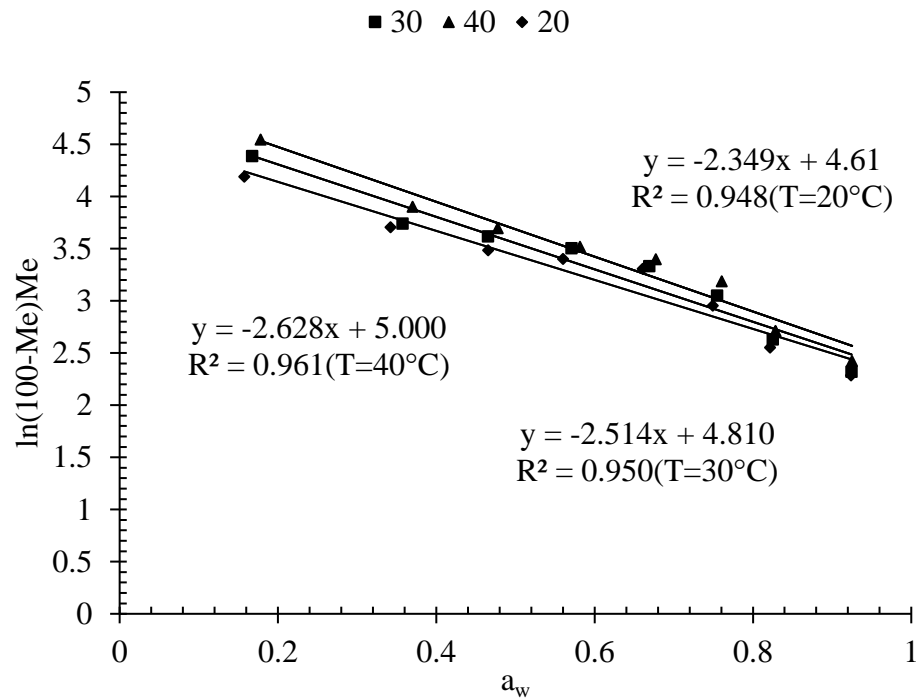
Fig. 4.12 Caurie plots of the experimental data at20°C, 30°C and 40°C
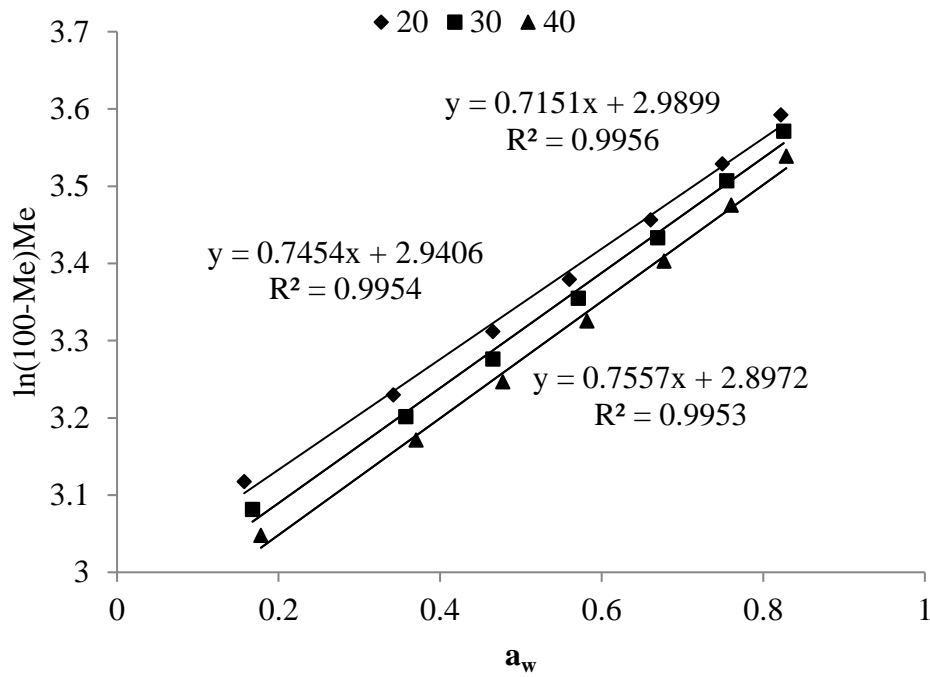
Fig. 4.13 Predicted graph for Caurie model at 20°C, 30°C and 40°C

The fit of the data to Caurie model was satisfactory at 20°C, 30°C and 40°C as seen from statistical analysis. The values of the constants r and a is shown in the Table 4.10.

Table 4.10 Values of constants and statistical parameters for Caurie model

Parameter	Temperature (°C)		
	20	30	40
R	2.349	2.514	2.628
A	100.48	122.76	148.46
R^2	0.948	0.950	0.961
SSE	0.1379	0.1466	0.120
RMSE	0.152	0.156	0.142
χ^2	0.0197	0.0209	0.0172

The final Caurie models after obtaining values of the constants are:

At 20°C: $\ln C = \ln 100.48 - 2.349 a_w$

At 30°C: $\ln C = \ln 122.76 - 2.51 a_w$

At 40°C: $\ln C = \ln 148.46 - 2.628 a_w$

Table 4.11 shows the constant value of different sorption models.

Table 4.11 Overall comparisons between constant values of different sorption models

S.N.	Tempr (^{0}C)	Model	Constant
1		**BET**	**X_{mB}=1.5274; C_B= 63.129**
		GAB	K= 0.889; X_{mG}= 1.718; C_B=23.590
		Iglesias and Chirifie	a= 0.6256; b= 2.461
		Halsey	a= 4.36RT; b= -1.718
	20	Chung and Pfost	a=2.507RT; b= 0.393
		Henderson	k= 0.180; n= 1.18
		Oswin	a= 3.098; n=0.450
		Smith	a= 0.739; b=3.308
		Caurie	a=100.481; r=2.349
2		**BET**	**X_{mB}=1.3784; C_B= 30.103**
		GAB	K= 0.8828; X_{mG}= 1.6229; C_B=13.254
		Iglesias and Chirifie	a= 0.61258; b= 2.1759
		Halsey	a= 3.203RT; b= -1.6129
	30	Chung and Pfost	a=2.248RT; b= 0.40
		Henderson	k= 0.2404; n= 1.0885
		Oswin	a= 2.7708; n=0.4786
		Smith	a= 0.4738; b=3.2386
		Caurie	a=122.7554; r=2.5140
3		**BET**	**X_{mB}=1.3476; C_B= 10.395**
		GAB	K= 0.8714; X_{mG}= 1.6229; C_B=7.8365
		Iglesias and Chirifie	a= 0.5524; b= 1.9674
		Halsey	a= 2.522RT; b= -1.5578
	40	Chung and Pfost	a=2.13RT; b= 0.432
		Henderson	k= 0.27559.; n= 1.07354
		Oswin	a= 2.485; n=0.1781
		Smith	a= 0.36005; b=2.9682
		Caurie	a=148.457; r=2.62867

Table 4.12 shows which model is best fitted for dried turmeric powder by comparing highest value of R^2 with lowest value of $x2$, RMSE and SSE.

Table 4.12 Comparison between different model parameters determined by linear and non-linear regression analysis

S.N.	Tempr(^{0}C)	Model	R^2	x^2	RMSE	SSE
1		**BET**	**0.961**	**0.00051**	**0.027**	**0.00152**
		GAB	0.842	0.00016	0.014	0.00114
		Iglesias and Chirifie	0.877	0.844	0.992	5.914
		Halsey	0.970	0.016	0.335	0.1126
	20	Chung and Pfost	0.938	0.423	0.3512	2.9614
		Henderson	0.958	0.299	0.576	2.097
		Oswin	0.964	0.243	0.532	1.701
		Smith	0.968	0.218	0.505	1.531
		Caurie	0.948	0.0197	0.152	0.138
2		**BET**	**0.936**	**0.00101**	**0.038**	**0.00304**
		GAB	0.825	0.000196	0.015	0.0013
		Iglesias and Chirifie	0.899	0.66	0.88	4.649
		Halsey	0.968	0.0134	0.3068	0.094
	30	Chung and Pfost	0.940	0.3886	0.3367	2.721
		Henderson	0.967	0.23	0.504	1.6218
		Oswin	0.973	0.1739	0.45	1.2174
		Smith	0.971	0.1852	0.464	1.297
		Caurie	0.951	0.0209	0.156	0.1466
3		**BET**	**0.966**	**0.00046**	**0.026**	**0.00140**
		GAB	0.821	0.00021	0.01	0.0015
		Iglesias and Chirifie	0.889	0.6096	0.8433	4.2678
		Halsey	0.962	0.0152	0.3267	0.1068
	40	Chung and Pfost	0.944	0.3071	0.2993	2.1502
		Henderson	0.967	0.1900	0.4619	1.3302
		Oswin	0.969	0.167	0.441	1.1704
		Smith	0.970	0.164	0.43	1.1532
		Caurie	0.961	0.0172	0.1417	0.12

Part V

Conclusions and recommendations

5.1 Conclusions

On the basis of the results obtained, the following conclusions have been drawn:

1) For dried turmeric powder there was a significant effect of temperature on the equilibrium relationship between the equilibrium moisture content, water activity and temperature.

2) According to Brunauer classification, the moisture sorption isotherm of dried turmeric podwer was found to be type II isostherm.

3) The water activity increases with an increase in the temperature and the equilibrium moisture content decreases with an increase in temperature.

4) Of the various models tested via statistical analysis, BET model gave the best fitting followed by Caurie and Hasley model over the entire range of experimental temperatures with the values of R^2, RMSE, SSE, x^2 as 0.936-0.970,0.026-0.327,0.00140-0.138,0.00046-0.0209 respectively.

5.2 Recommendations

Following recommendations have been kept forward for further study in the future:

1) Moisture sorption isotherm of other varieties of starchy product at different tempeartures can be studied.

2) Study on the shelf life of dried turmeric powder at different conditions (temperatures and relative humidities) using recommended packaging material can be carried out.

3) Study on the effects of drying process on physical, chemical and microbiological quality of the turmeric powder can be carried out.

Part VI

Summary

Turmeric (Curcuma longa L.) is a popular spice which very important in food as well as in medical science because of curcumin and volatile oils present in turmeric rhizomes which have anti-inflammatory, antimutagen, anticancer, antibacterial, anti-oxidant, antifungal, properties.

Moisture sorption isotherm is a very important tool for predicting the possible changes that can take place in the stability of food, used to find out the storing method and selection of packaging material which helps to optimize or maximize retention of color, flavor, texture, nutrients and biological stability. Sorption isotherms of food materials are vital for design, modelling and optimization of different processes like aeration, drying and storage. Water activity (a_w) has long been considered as one of the most important quality factors, especially for long-term storage. All chemical and microbial deterioration reactions are directly affected by changing water activity; therefore, the determination of the relationship between water activity and moisture content is significant. Moisture sorption isotherms describe the relationship between the equilibrium moisture content (EMC) and the water activity.

Water vapor pressure of sulphuric acid solution varies depending on their water concentration. The ERH in the headspace increases with an increase in temperature. Different concentration of sulphuric acid solution was used in the similar size. A static gravimetric technique was used to get the EMC data of the dried turmeric powder samples at three different temperatures i.e., 20±1°C, 30±1°C and 40±1°C which provided advantage of presenting a more restricted domain of moisture content variations glass dessicators for maintaining different water activities ranging from of 0.16 to 0.92.

Nine different models (BET model, GAB model, Iglesias and Chirife model, Halsey model, Chung and Pfost model, Henderson model, Oswin model, Smith model and Caurie model) were statistically analyzed. For all tested models, the parameters a and n are found to be temperature dependent. BET model followed by Caurie and Halsey model gave good fits to experimental data over the range of water activities employed, with higher R^2 and lower

values of χ^2, RMSE and SSE compared with other model of sorption models. The Halsey and the BET models (at T=20°, 30° and 40°C) gave the best fits with higher R^2 and lower values of χ^2, RMSE and SSE.Comparison between different model parameters determined by linear and non- linear regression analysisis given below

S.N.	Tempr(^{0}C)	Model	R^2	χ^2	RMSE	SSE
1		BET	0.961	0.00051	0.027	0.00152
		GAB	0.842	0.00016	0.014	0.00114
		Iglesias and Chirifie	0.877	0.844	0.992	5.914
		Halsey	**0.970**	**0.016**	**0.335**	**0.1126**
	20	Chung and Pfost	0.938	0.423	0.3512	2.9614
		Henderson	0.958	0.299	0.576	2.097
		Oswin	0.964	0.243	0.532	1.701
		Smith	0.968	0.218	0.505	1.531
		Caurie	0.948	0.0197	0.152	0.138
2		BET	0.936	0.00101	0.038	0.00304
		GAB	0.825	0.000196	0.015	0.0013
		Iglesias and Chirifie	0.899	0.66	0.88	4.649
		Halsey	**0.968**	**0.0134**	**0.3068**	**0.094**
	30	Chung and Pfost	0.940	0.3886	0.3367	2.721
		Henderson	0.967	0.23	0.504	1.6218
		Oswin	0.973	0.1739	0.45	1.2174
		Smith	0.971	0.1852	0.464	1.297
		Caurie	0.951	0.0209	0.156	0.1466
3		BET	0.966	0.00046	0.026	0.00140
		GAB	0.821	0.00021	0.01	0.0015
		Iglesias and Chirifie	0.889	0.6096	0.8433	4.2678
		Halsey	**0.962**	**0.0152**	**0.3267**	**0.1068**
	40	Chung and Pfost	0.944	0.3071	0.2993	2.1502
		Henderson	0.967	0.1900	0.4619	1.3302
		Oswin	0.969	0.167	0.441	1.1704
		Smith	0.970	0.164	0.43	1.1532
		Caurie	0.961	0.0172	0.1417	0.12

Reference

Abbas, K. A., Saleh, A. M., Mohamed, A. and Lasekan, O. (2009). The relationship between water activity and fish spoilage during cold storage: A review. *J. Food Agric. Environ.* **7**, 86-90.

Acevedo, N. (2006). Water–solids interactions, matrix structural properties and the rate of nonenzymatic browning. *J. Food Engg.* **77**, 1108-1115.

Akram, M., Uddin, S., Ahmed, A., Khan, U., Hannan, A., Mohiuddin, E. and Asif, M. (2010). *Curcuma longa* and curcumin: A review article. *Rom. J. Biol. – Plant Biol.* **55**, 65-70.

Al-Muhtaseb, A. H., Mcminn, W. A. M. and Magee, T. R. A. (2004). Water sorption isotherms of starch powders. *J. Food Engg.* **61**, 297.

Alakali, J. S. and Satimehin, A. A. (2009). Moisture adsorption characteristics of ginger powders. *J. Agric. Engg.* **11**, 1286-1307.

Alikali, J., Irtwange, S. V. and Satimehin, A. (2009). Moisture adsorption characteristics of ginger slices. *Cienc Technol. Alimentos.* **29**, 155-164.

Anon. Reduced sum of square. wikipedia. Retrieved from https://en.wikipedia.org/wiki/Residual_sum_of_squares. (Last update June 9, 2017). [Accessed 30 January, 2018].

Anonymous. (2011). Value chain analysis of turmeric [Report]. Nepal Government. Birendranagar, Surkhet, Nepal. Retrieved from http://thespicejournal.com/about-spice-nepal/turmeric-is-among-the-top-five-spice-crops-in-nepal/.

AOAC. (2005). "Official Methods of Analysis" (13th ed.). Washington DC. Association of Official Analytical Chemists.

Ariahu, C. C., Kaze, S. A. and Achem, C. D. (2006). Moisture sorption characteristics of tropical fresh water crayfish (*Procambarus clarkii*). *J. Food Engg.* Retrieved from www.elsevier.com/locate/jfoodeng.

Arslan, N. and Togrul, H. (2005). Modelling of water sorption isotherms of macaroni stored in a chamber under controlled humidity and thermodynamic approach. *J. Food Engg.* **69**, 133-145.

Bala, B. K. (1993). "Drying and Storage of Cereal Grains". Oxford and IBH Publishig Co. Pvt. Ltd. New Delhi.

Bamishaiye, E. I., Olayemi, F. F., Awagu, E. F. and Bamshaiye, O. M. (2011). Proximate and phytochemical composition of *Moringa oleifera* leaves at three stages of maturation. *J. Food Sci. Technol.* **3** (4), 233-237.

Basu, S., Shivhare, U. S. and Mujumdar, A. S. (2006a). Models for sorption isotherms for foods: A Review. *In:* "Drying Technology" (8th ed., Vol. 24).). pp. 917-930.

Basu, S., Shivhare, U. S. and Mujumdar, A. S. (2006b). Models for sorption isotherms for foods: A review. *J. Dry Technol.* **24** (8), 917-930.

Bhattarai, K. (2012). Study on the moisture sorption characteristics of beaten rice (chiura). M. Tech. Dissertation. Tribhuvan Univ., Nepal.

Bizot, H. (1983). Determination of GAB parameters for various foods. *In:* "Physical properties of foods". (R. Jowitt, F. Escher, F. Hallstrom, H. F. T. Meffert, W. F. L. Spices and G. Vos, Eds.). London. Applied Science Publishers.

Blahovec, J. and Yanniotis, S. (2009). Modified classification of sorption isotherms. *J. Food Engg.* **91**, 72-77.

Board, S. (2004). "Spices Statistics" (25th ed.). Vol. 682. Ministry of Commerce & Industry. pp. 1-281.

Brunauer, S., Deming, L. S., Deming, W. E. and Teller, E. (1940). On a theory of the Van der Waals adsorption of gases. *J. Am. Chem. Soc.* **62**, 1723.

Brunauer, S., Emmet, P. H. and Teller, E. (1998). Adsorption of gases in multimolecular layers. *Am. J. Chem. Soc.* **60** (2309-319).

Callahan, J. C., Cleary, G. W., Elefant, M., Kaplan, G., Kensler, T. and Nash, R. A. (1982). Equilibrium moisture content of pharmaceutical excipients. *Drug Dev. Ind. Pharm.* **8**, 355-369.

Catelam, K. T., Favaro, C. S. and Telis, J. (2011). Water adsorption isotherms and isosteric sorption heat of spray-dried and freeze-dried dehydrated passion fruit pulp with additives and skimmed milk. *J. Food Engg. Sci.* **35**, 1196-1203.

Caurie, M. (1970). Moisture isotherm for uncooked meat emulsions of different composition. *J. Food Technol.* **5**, 301.

Chen, C. C. (1990). Modification of Oswin EMC/ERH equation. *J. Agric. Res. China* **39**, 367-376.

Chirife, J., Timmermann, E. O., Iglesias, H. A. and Boquet, R. (1992). Some features of the parameter k of the GAB equation as applied to sorption isotherms of selected food materials. *J. Food Engg.* **15**, 75-82.

Contreras, C., Martin-Esparza, E., M., Chiralt, A. and Martinez-Navarrete, N. (2008). Influence of microwave application on convective drying: effects on drying kinetics, and optical and mechanical properties of apple and strawberry. *J. Food Engg.* **88**, 55-64.

Farahnaky, A., Ansari, S. and Majzoobi, M. (2009). Effect of glycerol on the moisture sorption isotherms of figs. *J. Food Engg.* **93**, 468-473.

Foo, K. Y. and Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chem. Engg. J.* **156**, 2-10.

Garcia-Perez, J. V., Carcel, J. A., Clemente, G. and Mulet, A. (2008). Water sorption isotherms for lemon peel at different temperatures and isosteric heats. *Lebensmittel-Wissenschaft und-Technologie*. **41**, 18-25.

Goula, A. M., Karapantsios, T. D., Achilias, D. S. and Adamopoulos, K. G. (2008). Water sorption isotherms and glass transition temperature of spray dried tomato pulp. *J Food Engg.* **85**, 73-83.

Gupta, S. and Sadhana, R. (2005). A comparison of the antimicrobial activity of garlic, ginger, carrot, and turmeric pastes against *Escherichia coli*

O157:H7 in laboratory buffer and ground beef. . *Foodborne Pathog. Dis.* **2**, 330-340.

Gustavo, V., Barbosa, C. and Smith, T. M. (2007). "Water Activity in Foods: Fundamentals and Applications.". Blackwell Publishing and Institute of Food Technologists. USA.

Henderson, S. M. (1952). *Agri. Engg.* **33**, 20. [Cited in H. A. Iglesias and J. Chirife. (1978). Equation for fitting water sorption of foods. *J. Food Technol.* **13**, 167].

Hossain, M. A. and Bala, B. K. (2002). Thin-layer drying characteristics for green chilli. *Drying Technol.* **20** (2), 489-505.

Hossain, M. A., Ishimine, Y., Akamine, H. and Motomura, K. (2005). Effects of Seed Rhizome Size on Growth and Yield of Turmeric (*Curcuma longa* L.). *J. Plant Prod. Sci.* **8**, 86-94.

Iglesias, H. A. and Chirife, J. (1982). "Handbook of Food Isotherms". Academic Press. New York.

Ikpeama, A., Onwuka, G. I. and Nwankwo, C. (2014). Nutritional composition of tumeric (*Curcuma longa*) and its antimicrobial properties. *Int. J. Sci. Engg. Res.* **5** (10), 1085-1089.

Ishimine, Y., Hossain, M. A. and Murayama, S. (2003). Optimal planting depth for (*Curcuma longa L.*) cultivation in dark-red soil in Okinawa Island, Southern Japan. *J. Plant Prod. Sci.* **6**, 83-89.

Karel, M. (1973). Recent research and development in the field of low moisture and intermediate moisture foods. *Crit. Rev. Food Technol.* **3**, 329-338.

Kaymak-Ertekin, F. and Gedik, A. (2004). Sorption isotherms and isosteric heat of sorption of grapes, apricots, apples and potatoes. *Lebensmittel-Wissenschaft und-Technologie*. **37**, 429-438.

Khajehdehi, P. (2012). Turmeric: Reemerging of a neglected Asian traditional remedy. *J. Nephropathol*. **1** (1), 17-22.

Kim, T. H., Son, Y. K., Hwang, K. H. and Kim, M. H. (2008). Effects of Angelica keiskei Koidzumi and turmeric extract sulpplementation on serum lipid parameters in hypercholesterolemic diet on P-407-induced hyperlipidemic rats. *Korean Soc. Food Sci. Nutr.* **37**, 708-713.

Kohayakawa, M. N., Bernardi, M., Pedro, A. M., Silveira, V. J. and Telis, J. (2005). Enthalpy-entropy compensation based onisotherms of mango. *J. Food Sci. Technol.* **25**, 293-303.

Konopacka, D. and Plocharski, W. (2002). Water vapour uptake by fat free apple chips decreased by emulsifiers. *J. Food Sci.* **67**, 4.

Kumar, G. S., Harish, N., Shyaja, M. D. and Salimath, P. V. (2006). Phenolic anti-oxidant in amla (*emblica officinalis*) and turmeric (*curcuma longa*). *J. Food.Compos. Anal.* **19**, 446-452.

Kwon, Y. and Magnuson, B. A. (2009). Age-related differential responses to curcumin-induced apoptosis during the initiation of colon cancer in rats. *J. Chem. Toxicol.* **47**, 377-385.

Labuza, T. P. (1980). The effect of water activity on reaction kinetics of food deterioration *Int. J. Food Sci. Technol.* **34**, 36.

Labuza, T. P. (2002). IFT Short Course: Water activity and Sorption isotherms. Retrieved from http://fscn.che.umn.edu/Ted_Labuza/tpl.html.

Labuza, T. P., Kaanane, A. and Chen, J. Y. (1985). Effect of temperature on the moisture sorption isotherm and waer activity shift of two dehydrated foods. *J. Food Sci.* **50**, 391-395.

Lamharrar, A., Idlimam, A. and Kouhila, M. (2007). Thermodynamic properties and moisture sorption isotherms of Artemisia herba-alba. *J. Food engg.* **10**, 311-320.

Lavoyer, C. G., Gabas, A. L., Oliveira, W. P. and Telis, J. (2013). Study of adsorption isotherms of green coconut pulp. *J. Food Sci. Technol.* **33**, 68-74.

McMinn, W. A. M. and Magee, T. R. A. (1999). Studies on the Effect of Temperature on the Moisture Sorption Characteristics of Potatoes. *J. Food Process Engg.* **22**, 113-128. [Cited in K. Bhattarai. (2012). Study on moisture sorption behaviour of beaten rice (chiura). Unpublished M. Tech (Food) Dissertation. Tribhuvan Univ., Nepal].

Miranda, M., Diaz, L. P., Lopez, L. and Rodriguez, K. (2010). Effective moisture diffusivity determination and mathematical modeling of the drying curves of the olive-waste cake. *J. Bioresour Technol.* **101**, 7265-7270.

Moraes, M. A., Rosa, G. S. and Pinto, L. A. (2008). Moisture sorption isotherms and thermodynamic properties of apple Fuji and garlic. *Int. J. Food Sci. Tech.* **43** (10), 1824-1831.

Mujumdar, A. S. (2006). Principles, classification, and selection of dryers. *In:* "Handbook of Industrial Drying". (A. S. Mujumdar, Ed.). pp. 4-31. Boca Raton. CRC Press.

Mujumdar, A. S. and Devahastin, S. (2000). Fundamental principles of drying. *In:* "Handbook of Industrial Drying". (A. S. Devahastin, Ed.). pp. 1-22. Montreal, Canada. Exergex.

Negi, P. S., Jayaprakasha, G. K., Rao, L. J. M. and Sakariah, K. K. (1999). Antibacterial activity of turmeric oil: a byproduct from curcumin manufacture. . *Agric. Food Chem.* **47**, 4297-4300.

Neter, J., Wasserman, W. and Kutner, M. H. (2004). Regression Analysis of Variance and Experimental Designs. *In:* "Applied Linear Statistical Models" (4th ed.). (D. Richard, Ed.). USA. Irwin Inc.

Novasima, A. G. (2005). The meaning of water activity. Novasima. Retrieved from www. novassima.com/The meaning of water activity/html. [Accessed 12 January, 2018].

Oswin, C. R. (1946). The kinetics of package life. *J. Chem. Ind.* **65**, 419.

Purseglove, J. W., Brown, E. G., Green, C. L. and Robin, S. R. J. (1981). "Turmeric In: Spices" (pp. 532-580). Vol. 2. Longman, Essex. UK.

Raghavan, S. (2006). "Handbook of Spices, Seasonings and Flavourings" (2nd ed.). CRC Press. London.

Rahman, M. S. (2006). Drying of fish and seafood. *In:* "Handbook of Industrial Drying". (A. S. Mujumdar, Ed.). pp. 547–559. Boca Raton. CRC Press.

Rahman, M. S. (2010). Food stability determination by macro-micro region concept in the state diagram and by defining a critical temperature. *J. Food Engg.* **99**, 402-416.

Rahman, M. S. and Labuza, T. P. (2007). Water activity and food preservation. *In:* "Handbook of Food Preservation" (2nd ed.). (M. S. Rahman, Ed.). pp. 339-382. New York. Marcel Dekker Inc.

Ranganna, S. (1986). "Handbook of Analysis and Quality Control for Fruit and Vegetable Products" (2nd ed.). Tata McGraw-Hill Publishing Company Ltd. New Delhi.

Ravindran, P. N., Babu, K. N. and Shiva, K. N. (2007). "Turmeric-The genus *Curcuma*" (pp. 15- 17). CRC Press. Boca Raton, Florida.

Rouquerol, F., Rouquerol, J. and Sing, K. (1999). "Adsorption by Powders and Porous Solids". Academic Press. London, Great Britain.

Ruegg, M. (1980). Calculation of the activity of water in sulfuric acid solutions at various temperatures. *Lebensm.-Wiss. Tech.* **13**, 22-24. [Cited in M. A. Rao, S. S. H. Rizvi and A. K. Datta. (2005). "Engineering properties of food" (3rd ed.). Taylor and Francis Group. Boca Raton].

Satimehin, A., A. and Ezeike, G. O. I. (2002). Moisture desorption characteristics of gelatinized white yam (*Dioscorea rotundata*, Poir). *Nig. J. Food Sci.* **20**, 58-64.

Simal, S., Femenia, A. and Rossello, C. (2007). Water desorption thermodynamic properties of pineapple. *J. Food Engg.* **80**, 1293-1301.

Sing, K. S. W. (1998). Adsorption methods for the characterization of porous materials. *Adv. Colloid Interface Sci.* **76**, 3-11.

Sing, K. S. W., Everett, D. H., Haul, R. A. W., Moscou, L., Pierotti., R. A., Rouquerol, J. and Siemieniewska, T. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (recommendations). *Pure Appl. Chem.* **57**, 603-619.

Smith, S. E. (1947). *J. Am. Chem. Soc.*, 646. [Cited in H. A. Iglesias and J. Chirife. (1978). Equation for fitting water sorption isotherms of foods. *J. Food Technol.* **13**, 159-174].

Tainter, D. R. and Grenis, A. T. (2001). "Spices and Seasonings: A Food Technology Handbook". A John Wiley & Sons Inc. Publications. New York.

Thompson, G., Swain, J., Kay, M. and Forster, C. F. (2001). The treatment of pulp and paper mill effluent: A review. *Bioresour. Technol.* **77**, 275-286.

Timmermann, E. O., Chirife, J. and Iglesias, H. A. (2001). Water sorption isotherms of foods and foodstuffs: BET or GAB parameters. *J. Food Engg.* **48**, 19-31.

Vanden Berg, C. (1984). Description of water activity of foods for engineering purposes by means of the GAB modle of sorption. *In:* "Engineering and food" (Vol. 1). (B. M. McKenna, Ed.). pp. 311-321. New York. Elsevier Applied Science Publishers.

Vanden Berg, C. and Bruin, S. (1981). Water activity and its estimation in foods systems: theoretical aspects. *In:* "Water Activity Influence on Food Quality". (S. Bruin, Ed.). pp. 1-61. New York. Academic Press.

Vega, A., Palacios, M., Lemus, R. and Passaro, C. (2008). Moisture sorption isotherms and isosteric heat determination in Chilean papaya (*Vasconcellea pubescens*). *J. Food. Engg. Sci.* **31**, 1417-1421.

Wang, Z., Sun, J., Chen, F., Liao, X. and Hu, X. (2007). Mathematical modelling on thin layer microwave drying of apple pomace with and without hot air pre-drying *J. Food Engg.* **80**, 536–544.

Wolf, W., Spiess, W. E. L., Jung, G., Weisser, H., Bizot, H. and Duckworth, R. B. (1984). The water vapour sorption isotherms of microcrystalline cellulose (MCC) and of purifed potato starch: results of a collaborative study. *J. Food Engg.* **3**, 51-72.

Yan, Z., Sousa, M. and Oliveira, F. (2008). Sorption isotherms and moisture sorption hysteresis of intermediate moisture content banana. *J. Food Engg.* **86** (3), 342-348.

Yang, C. Y., Fon, D. S. and Lin, T. T. (2007). Simulation and validation of thin layer models for peanut drying. *Drying Technol.* **25**, 1515–1526.

Appendices

Appendix A

Table A.1 Water activity of sulfuric acid solutions at different concentrations and temperatures

% H_2SO_4	Density at 25°C (g/cm^3)	Water activity		
		20°C	30°C	40°C
60.00	1.4940	0.1573	0.1677	0.1781
50.00	1.3911	0.3422	0.3574	0.3702
45.00	0.3437	0.4524	0.4653	0.4775
40.00	1.2991	0.5599	0.5711	0.5816
35.00	1.2563	0.6607	0.6693	0.6773
30.00	1.2150	0.7491	0.7549	0.7604
25.00	1.1750	0.8218	0.8252	0.8285
15.00	1.0994	0.9237	0.9245	0.9253

Source: Ruegg (1980)

Appendix B

Table B.1 Equilibrium moisture content (% db) and corresponding water activities of dried Turmeric at various temperatures

aw	EMC at 20°C	aw	EMC at 30°C	aw	EMC at 40°C
0.1573	1.49	0.1677	1.23	0.1781	1.05
0.3422	2.4	0.3574	2.32	0.3702	1.98
0.4524	2.97	0.4653	2.62	0.4775	2.42
0.5599	3.22	0.5711	2.92	0.5816	2.88
0.6607	3.53	0.6693	3.45	0.6773	3.23
0.7491	4.96	0.7549	4.52	0.7604	3.96
0.8218	7.22	0.8252	6.72	0.8285	6.23
0.9237	9.23	0.9245	8.96	0.9253	8.13

Appendix C

Working equation of various models:

S.N	Models	Equation
1	BET model	$$\frac{a_w}{M_e(1-a_w)} = \frac{1}{X_{mB}C_B} + (\frac{C_B-1}{X_{mB}C_B})a_w$$
2	GAB model	$$\frac{a_w}{M_e} = (\frac{K(1-c_G)}{X_{mG}C_G})a_w^2 + (\frac{C_G-2}{X_{mG}C_G})a_w + \frac{1}{X_{mG}C_G K}$$
3	Iglesias and Chirife model	$$M_e = a(\frac{a_w}{1-a_w}) + b$$
4	Halsey model	$$lnM_e = (-\frac{1}{b}ln\frac{a}{RT}) + \frac{1}{b}ln\{-ln(a_W)\}$$
5	Chung and Pfostmodel	$$M_e = \frac{1}{b}ln\frac{a}{RT} + \{-\frac{1}{b}ln(-lna_w)\}$$
6	Handerson model	$$lnM_e = \frac{-lnK}{n} + \frac{1}{n}ln\{-ln(1-a_w)\}$$
7	Oswin model	$$lnM_e = lna_w + nln\frac{a_w}{1-a_w}$$
8	Smith model	$$M_e = a - bln(1-a_w)$$
9	Caurie model	$$lnC = lna + (-r)a_w$$

Table D.1 Experimental data for fitting BET model

20°C		30°C		40°C	
a_w	$\dfrac{a_w}{(1-a_w)M_e}$	a_w	$\dfrac{a_w}{(1-a_w)M_e}$	a_w	$\dfrac{a_w}{(1-a_w)M_e}$
0.1573	0.12527	0.1677	0.16381	0.1781	0.20637
0.3422	0.21676	0.3574	0.23973	0.3702	0.29687
0.4524	0.27817	0.4653	0.33214	0.4775	0.37763
0.5599	0.39509	0.5711	0.45601	0.5816	0.48265

Table D.2 Experimental data for fitting GAB model

20°C		30°C		40°C	
a_w	$\dfrac{a_w}{M_e}$	a_w	$\dfrac{a_w}{M_e}$	a_w	$\dfrac{a_w}{M_e}$
0.1573	0.10557	0.1677	0.13634	0.1781	0.16962
0.3422	0.14258	0.3574	0.15405	0.3702	0.18697
0.4524	0.15667	0.4653	0.17759	0.4775	0.19731
0.5599	0.17388	0.5711	0.19558	0.5816	0.20194
0.6607	0.18717	0.6693	0.19423	0.6773	0.20969
0.7491	0.15103	0.7549	0.16701	0.7604	0.19202
0.8218	0.11382	0.8252	0.12279	0.8285	0.13299
0.9237	0.10007	0.9245	0.10318	0.9253	0.11381

Table D.3 Experimental data for fitting Iglesias and Chirife model

20°C		30°C		40°C	
$\dfrac{a_w}{1-a_w}$	M_e	$\dfrac{a_w}{1-a_w}$	M_e	$\dfrac{a_w}{1-a_w}$	M_e
0.18662	1.49	0.20149	1.23	0.21669	1.05
0.52021	2.4	0.55618	2.32	0.58780	1.98
0.87021	2.97	0.87021	2.62	0.91387	2.42
1.27221	3.22	1.33154	2.92	1.39005	2.88
1.94724	3.53	2.02389	3.45	2.09885	3.23
2.98565	4.96	3.07997	4.52	3.17362	3.96
4.61167	7.22	4.72082	6.72	4.83091	6.19
12.1061	9.23	12.2450	8.92	12.3869	8.13

Table D.4 Experimental data for fitting Halsey model

20°C		30°C		40°C	
$\ln\{-\ln(a_w)\}$	$\ln M_e$	$\ln\{-\ln(a_w)\}$	$\ln M_e$	$\ln\{-\ln(a_w)\}$	$\ln M_e$
0.61497	0.39878	0.5797	0.20701	0.54546	0.04879
0.06986	0.87546	0.02849	0.84156	-0.00631	0.68309
-0.26778	1.08856	-0.26778	0.96317	-0.30219	0.88376
-0.54473	1.16938	-0.57948	1.07158	-0.61254	1.05779
-0.88079	1.26129	-0.91249	1.23837	-0.94253	1.17248
-1.24173	1.60142	-1.26879	1.50851	-1.29495	1.37624
-1.62832	1.97685	-1.64959	1.90508	-1.67058	1.82938
-2.53366	2.22246	-2.54463	2.19277	-2.55571	2.09556

Table D.5 Experimental data for fitting Chung and Pfost model

20°C		30°C		40°C	
$\ln\{-\ln(a_w)\}$	M_e	$\ln\{-\ln(a_w)\}$	M_e	$\ln\{-\ln(a_w)\}$	M_e
0.61497	1.49	0.57974	1.23	0.54546	1.05
0.06986	2.4	0.02849	2.32	-0.00631	1.98
-0.26778	2.97	-0.26778	2.62	-0.3022	2.42
-0.54473	3.22	-0.57948	2.92	-0.61254	2.88
-0.88079	3.53	-0.91249	3.45	-0.94253	3.23
-1.24173	4.96	-1.26879	4.52	-1.29495	3.96
-1.62832	7.22	-1.64959	6.72	-1.67058	6.23
-2.53366	9.23	-2.54463	8.96	-2.55571	8.13

Table D.6 Experimental data for fitting Henderson model

20°C		30°C		40°C	
$\ln\{-\ln(1-a_w)\}$	$\ln M_e$	$\ln\{-\ln(1-a_w)\}$	$\ln M_e$	$\ln\{-\ln(1-a_w)\}$	$\ln M_e$
-1.76525	0.39878	-1.6952	0.20701	-1.62894	0.04879
-0.87023	0.87547	-0.81592	0.84156	-0.77143	0.68309
-0.50715	1.08856	-0.46833	0.96317	-0.43212	0.88377
-0.19753	1.16938	-0.16661	1.07158	-0.13775	1.05779
0.07777	1.26129	0.10124	1.23857	0.12313	1.72482
0.32404	1.60141	0.34081	1.50851	0.35682	1.37624
0.54514	1.97685	0.55625	1.90508	0.56711	1.82938
0.9451	2.22246	0.94919	2.19277	0.95331	2.09556

Table D.7 Experimental data for fitting Oswin model

20°C		30°C		40°C	
$\ln \dfrac{a_w}{1-a_w}$	$\ln M_e$	$\ln \dfrac{a_w}{1-a_w}$	$\ln M_e$	$\ln \dfrac{a_w}{1-a_w}$	$\ln M_e$
-1.67846	0.39878	-1.60202	0.20701	-1.52928	0.04879
-0.65351	0.87547	-0.58667	0.84156	-0.53136	0.68309
-0.19098	1.08856	-0.13902	0.96317	-0.09006	0.88377
0.24076	1.16938	0.28634	1.07158	0.32935	1.05779
0.66642	1.26129	0.70502	1.23857	0.74139	1.72482
1.09382	1.60141	1.12492	1.50851	1.15487	1.37624
1.52859	1.97685	1.55198	1.90508	1.57503	1.82938
2.49371	2.22246	2.50512	2.19277	2.51664	2.09556

Table D.8 Experimental data for fitting Smith model

20°C		30°C		40°C	
$\ln(1-a_w)$	M_e	$\ln(1-a_w)$	M_e	$\ln(1-a_w)$	M_e
-0.17114	1.49	-0.18356	1.23	-0.19614	1.05
-0.41885	2.4	-0.44223	2.32	-0.46235	1.98
-0.60221	2.97	-0.62605	2.62	-0.64913	2.42
-0.82075	3.22	-0.84653	2.92	-0.87132	2.88
-1.08087	3.53	-1.10654	3.45	-1.13103	3.23
-1.3827	4.96	-1.40609	4.52	-1.42878	3.96
-1.72485	7.22	-1.74411	6.72	-1.76317	6.23
-2.57308	9.23	-2.58362	8.96	-2.59428	8.13

Table D.9 Experimental data for fitting Caurie model

20°C		30°C		40°C	
a_w	$\ln \dfrac{100 - M_e}{M_e}$	a_w	$\ln \dfrac{100 - M_e}{M_e}$	a_w	$\ln \dfrac{100 - Me}{M_e}$
0.1573	4.19138	0.1677	4.38578	0.1781	4.54583
0.3422	3.70541	0.3574	3.74013	0.3702	3.90208
0.4524	3.48646	0.4653	3.61545	0.4775	3.69691
0.5599	3.40306	0.5711	3.50395	0.5816	3.51816
0.6607	3.30793	0.6693	3.33169	0.6773	3.39986
0.7491	2.95289	0.7549	3.05041	0.7604	3.18812
0.8218	2.55338	0.8252	2.63052	0.8285	2.71147
0.9237	2.28587	0.9245	2.31853	0.9253	2.42481

Appendix E

Table E.1 List of chemicals and glasswares.

S.N.	List of chemicals, glasswares and apparatus
	Chemicals
1	Concentrated sulfuric acid (conc. H_2SO_4)
2	Toluene
3	Catalyst mixture (Mixture of 2.5 g of powdered SeO_2, 100 g K_2SO_4 and 20 g $CuSO_4.5H_2O$)
4	Boric acid
5	0.01 N HCl
6	30 % NaOH
7	Mixed indicator (Mixture of 10 ml of 0.1% bromocresol green and 2 ml of 0.1% methyl red solution which is prepared seperately in 95% ethanol)
8	Petroleum ether (b.pt. 60-80°C)
	Glasswares and apparatus
9	Measuring cylinder
10	Petri dishes
11	Barigo hygrometer
12	Thermometer (sensitivity: minimum 1°C)
13	Weighing balance (sensitivity: minimum of 1 mg) (MRRS Digi Model MTT-T)
14	Dessicators
15	Digestion flask
16	Kjeldahl distillation set
17	Hot air oven (Vitco, India)
18	Silica crucible
19	Muffle furnace (Vitco, India)
20	Soxhlet appartus

Color plates

Plate 1. Sample analysis

Plate 2. Moisture determination