EFFECT OF POLYETHYLENEIMINE ON ADSORPTION BEHAVIOR OF LAC DYEING ON BAMBOO FIBERS

SUCHADEE SRIBENJA

A thesis submitted in partial fulfillment of the requirements for
the Master of Science degree in Chemistry
Mahasarakham University
January 2016

EFFECT OF POLYETHYLENEIMINE ON ADSORPTION BEHAVIOR OF LAC DYEING ON BAMBOO FIBERS

SUCHADEE SRIBENJA

A thesis submitted in partial fulfillment of the requirements for
the Master of Science degree in Chemistry
Mahasarakham University
January 2016
Copyright of Mahasarakham University

The examining committee has unanimously approved this thesis, submitted by Miss Suchadee Sribenja, as a partial fulfillment of the requirements for the Master of Science degree in Chemistry at Mahasarakham University.

Examining Committee

Prasong S.
.... Chairman
(Asst. Prof. Prasong Srihanam, Ph.D.) (Faculty graduate committee)

.... Committee
(Assoc. Prof. Sunan Saikrasun, Ph.D.) (Advisor)

.... Committee
(Assoc. Prof. Wanna Kanchanamayoon, Ph.D.) (Faculty graduate committee)

.... Committee
(Assoc. Prof. Sayant Saengsuwan, Ph.D.) (External expert)

Mahasarakham University has granted approval to accept this thesis as a partial fulfillment of the requirements for the Master of Science degree in Chemistry

Wichian
....
(Prof. Wichian Magtoon, Ph.D.)
Dean of the Faculty of Science

Pradit
....
(Prof. Pradit Terdtoon, Ph.D.)
Dean of Graduate School
January 29, 2016

ACKNOWLEDGEMENTS

The author would like to gratefully acknowledge the Center of Excellence for Innovation in Chemistry (PERCH-CIC) and the grant for graduate students, fiscal year 2015, for partial financial support. I am grateful to the Department of Chemistry, Faculty of Science, Mahasarakham University, for providing chemicals, instrumental support and all other facilities.

I wish to express my deepest and sincere gratitude to my advisor, Assoc. Prof. Dr. Sunan Saikrasun and Assist. Prof. Dr. Sisikka Wannajun who gave me valuable instructions, excellent suggestions and kindness which are more than I can describe here, that have enable me to pass through this course successfully.

The thesis would not have been accomplished if without the help from several people. First of all, I would like to thank Asst. Prof. Dr. Prasong Srihanam, Asst. Prof. Dr. Piyanete Chantiratikul, Assoc. Prof. Dr. Wanna Kanchanamayoon, Dr. Onanong Cheerarot and Assoc. Prof. Dr. Sayant Saengsuwan for their valuable suggestions and comments.

I was very fortunate to have many friends both within and outside the Faculty of Accountancy and Management during my doctoral life. I thank them all for their being very supportive.

I wish to express my sincere appreciation to all of my friends for their excellent assistance, encouragement, sincerity and impression friendship. Everything will always be in my mind.

Most of all, I wish to express my heartfelt gratitude here to my family; my beloved parents for their tender love, care, sacrifice, inculcation and encouragement that found me to be a fortitude person.

Suchadee Sribenja

TITLE Effect of Polyethyleneimine on Adsorption Behavior of Lac Dyeing on Bamboo Fibers
CANDIDATE Miss Suchadee Sribenja
DEGREE Master Degree of Science **MAJOR** Chemistry
ADVISORS Assoc. Prof. Sunan Saikrasun, Ph.D.
UNIVERSITY Mahasarakham University **YEAR** 2016

ABSTRACT

In this work, the effect of polyethyleneimine (PEI) as a mordant on adsorption behavior of lac dyeing on controlled (alkali-treated) and PEI treated bamboo fibers (BF_s) was investigated. The optimal conditions were pH 3.0, material to liquor ratio (MLR) 1:200, initial dye concentration 250 mg/L, dyeing temperature 30°C and dyeing time 200 min were used. The use of PEI as a mordant significantly improved the adsorption capacity of lac dye. Isotherms, kinetics and thermodynamics of the adsorption were also investigated. The Langmuir and Freundlich adsorption isotherms were applied to describe the adsorption behavior. The adsorption behavior of the controlled and PEI treated BFs were found to fit well with Langmuir isotherm. The adsorption kinetics of both systems were likely to be pseudo-first-order reaction. The free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) for the dyeing system were also determined. The observed thermodynamic parameter indicated that the lac dyeing process is an exothermic, non-spontaneous and physisorption process.

Key Word : Polyethyleneimine, Adsorption, PEI, Bamboo Fibers, Kinetics, Lac Dye.

ชื่อเรื่อง ผลของพอลิเอทิลีนอิมีนที่มีต่อพฤติกรรมการดูดซับของเส้นใยไผ่ที่ย้อมด้วยสีครั่ง
ผู้วิจัย นางสาวสุชาดี ศรีเบ็ญจา
ปริญญา วิทยาศาสตรมหาบัณฑิต **สาขาวิชา** เคมี
กรรมการควบคุม รองศาสตราจารย์ ดร.สุนันท์ สายกระสุน
มหาวิทยาลัย มหาวิทยาลัยมหาสารคาม **ปีที่พิมพ์** 2559

บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาผลของพอลิเอทิลีนอิมีนซึ่งทำหน้าที่เป็นสารช่วยสีติด ที่มีต่อพฤติกรรมการดูดซับของสีครั่งบนเส้นใยไผ่ที่แปรผิวด้วยวิธีอัลคาไลน์ (ควบคุม) และเส้นใยไผ่ที่แปรผิวด้วยพอลิเอทิลีนอิมีน โดยทำการศึกษาที่สภาวะที่เหมาะสมคือ พีเอช 3 อัตราส่วนปริมาตรของสีครั่งต่อเส้นใยไผ่ (MLR) 1:200 ความเข้มข้นเริ่มต้นของสารละลายสีครั่ง 250 มิลลิกรัมต่อลิตร อุณหภูมิที่ใช้ในการย้อม 30 องศาเซลเซียส และเวลาที่ใช้ในการดูดซับ 200 นาที จากผลการทดลองพบว่า พอลีเอทิลีนอิมีนสามารถเพิ่มความสามารถในการดูดซับสีครั่งได้อย่างชัดเจน นอกจากนี้ยังได้มีการศึกษาไอโซเทอร์ม จลนพลศาสตร์ และอุณหพลศาสตร์ของการดูดซับของสีครั่งบนเส้นใยไผ่ การนำแบบจำลองไอโซเทอร์มของแลงเมียร์และฟรุนด์ลิชเพื่อศึกษาพฤติกรรมของการดูดซับ พบว่า พฤติกรรมของการดูดซับของเส้นใยไผ่ควบคุมและเส้นใยไผ่ที่แปรผิวด้วยพอลีเอทิลีนอิมีนสอดคล้องกับแบบจำลองไอโซเทอร์มของแลงเมียร์ และจลนพลศาสตร์ของการดูดซับสอดคล้องกับปฏิกิริยาอันดับหนึ่งเทียม จากการศึกษาอุณหพลศาสตร์ของการดูดซับโดยการวัดพลังงานอิสระกิบส์ (ΔG°) เอนทาลปี (ΔH°) และเอนโทรปี (ΔS°) ผลที่ได้แสดงให้เห็นว่า กระบวนการดูดซับเป็นแบบคายความร้อน ไม่สามารถเกิดขึ้นได้เอง และเป็นกระบวนการดูดซับทางกายภาพ

คำสำคัญ : พอลีเอทิลีน; การดูดซับ; เส้นใยไผ่; จลนพลศาสตร์; สีครั่ง

CONTENTS

CONTENTS

CONTENTS

PAGE

CONTENTS

PAGE

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

PAGE

List of Abbreviations

AATCC	American Association of Textile Chemists and Colorists
AR	Analytical Reagent
ATR-FTIR	Attenuated Total Reflection-Fourier Transform Infrared
b	Langmuir constant
BFs	Bamboo fibers
C_0	Initial dye concentration
C_e	Concentration of dye at equilibrium
C_t	Concentration of dye at any time
ºC	Degree Celsius
Ea	Activation energy
Eq.	Equation
FTIR	Fourier Transform Infrared Spectroscopy
$\Delta G^{\#}$	Free energy of activation
h	Planck’s constant
$\Delta H^{\#}$	Enthalpy of activation
hi	The initial dye adsorption rate
ISO	International Organization for Standardization
k_1	Rate constant of pseudo-first-order adsorption
k_2	Rate constant of pseudo-second-order adsorption
k_b	Boltzmann’s constant
M	Molarity
MLR	Material to liquor ratio
λ_{max}	Maximum wavelength
NaOH	Sodium hydroxide
$1/n$	The favourability of adsorption
PEI	Polyethyleneimine
Q	Adsorption capacity of the Langmuir isotherm
q_e	Amount of dye adsorbed per unit weight of fiber at equilibrium
Q_f	The adsorption capacity of Freundlich isotherm
q_t	Amount of dye adsorbed per unit weight of fiber at any time

List of Abbreviations

R_L	Separation factor for equilibrium parameter
R^2	Correlation coefficient
rpm	Revolutions per minute
SDC	Society of Dyers and Colorists
SEM	Scanning electron microscope
$\Delta S^{\#}$	Entropy of activation
V	Volume of dye solution
W	Weight of bamboo fibers

CHAPTER 1

INTRODUCTION

1.1 Background

Nowadays, textile materials are colored for value addition, looks and fulfilling the desires of the customers. Anciently, this purpose of coloring textile was initiated using natural sources, until synthetic dyes were invented. Almost all the synthetic dyes being synthesized from petrochemical sources through hazardous chemical processes pose threat to the environment. However, worldwide environment protection and safety renewed the interest of the people on natural products like natural fibers and natural dyes. For successful commercial application of natural dyes for any particular fibers, the appropriate and standardized techniques of dyeing for that particular fiber dye system need to be adopted. Relevant scientific studies and optimization of dyeing process variables, dyeing kinetics studies and test of compatibility of selective natural dyes are very important.

Natural dyes are known for their beautiful, soft and multi-hued shades. There is considerable current interest in dyeing of textile fibers with natural dyes on account of their compatibility with environment and because of their generally lower toxicity and allergic reaction [1]. Lac dye is a natural reddish dyestuffs extracted from stick lac which is a secretion of the insect *Coccus laccae* (*Laccifer lacca* Kerr). The insect C. laccae is often found in South and Southeast Asia, especially in Thailand and India. Lac dye is used extensively as a natural food additive, cosmetics ingredient, oil painting and dyeing textiles such as silk, cotton, wool, kenaf, flax, etc. In the north and the northeast of Thailand, it is used as a natural red dyestuff for cotton and silk dyeing for a long time. However, this natural dye has a limited usefulness in fibers dyeing as it does not readily adsorb to fibers because the fastness properties and reproducibility to give consistency in production are still problems to be solved. As part of the approach to tackle these problems, fundamental physical studies on the dyeing process are important. Therefore, Impact study and processes absorbing dyes are particularly important in dyeing fibers [2, 3]. At present, the process of dyeing bamboo fiber with lac dye is not widely used.

Bamboo is a naturally occurring composite material as it consists of cellulose fibers embedded in a lignin matrix. It grows abundantly in most of the tropical countries. Cellulose fibers are aligned along the length of the bamboo, providing maximum tensile strength and rigidity in that direction. It is an environmentally friendly product. Through a process of hydrolysis-alkalization and multi-phase bleaching, starchy pulp is refined from bamboo. Alter that, chemical fiber factories process it into bamboo fibers. Repeated technological analysis has proved that this kind of fiber has thinness and whiteness close to finely bleached viscose and has a strong durability, stability and tenacity. Currently, bamboo fiber is gaining a wide popularity in the textile industry because it has natural anti-bacterial, green and biodegradable, breathable and cool, soft hand feel and luxurious shiny appearance properties. The bamboo fibers through a process called bamboo yarn can be applied, such as coats, scarves, towels, pillowcases, etc. [4] Recently, the reported was found that used of natural dyes for bamboo fiber dyeing, but the fastness properties and reproducibility to give consistency in production are still problems to be solved. In general, the routes to solve these problems consist of fundamental physical studies on the dyeing process and chemical modifications to improve the lac dye adsorption on the fibers. For the latter route, various types of mordants such as salts of various metals used Fe, Al, Cu, Pb, Sn are some that are frequently used or tannins and bio-mordants [5-8] were used as surface modifiers to promote the binding of dyes to fabric by forming a chemical bridge from dye to fiber enhancing the staining ability of dye along with increasing its fastness properties, depth of shade or difference colors for dyeing nylon, wool, silk, leather, cotton, and other textile fibers [9,10]. However, most of the mordants used are toxic, expensive and have serious detrimental effects on the environmental.

Polyethyleneimine (PEI) is a mordant used for improvement of adsorption capacity of natural dye on natural fibers. This is because PEI has some characteristics such as wettability, bondability, toxicologically benign, and of opposite charge to the acid dye. These characteristics make PEI a suitable candidate for use as a mordant [11-15].

In this work, the main aim is to improve the adsorption capacity of lac dye on bamboo fibers. The effect of PEI as a mordant on adsorption capacity of lac dye on bamboo fibers will be investigated. The isotherms, kinetics and thermodynamics of adsorption will be studied.

1.2 Research objectives

1. To improve the adsorption capacity of lac dye on bamboo fibers.
2. To study the effect of PEI as a mordant on adsorption capacity of lac dye on bamboo fibers.
3. To study the kinetics and thermodynamics of the adsorption.

1.3 Expected results obtained from the research

1. The optimum dyeing conditions of lac dyeing on bamboo fibers will be known.
2. The use of PEI as a mordant is expected to clearly improve the adsorption capacity.
3. The adsorption behavior (isotherms, kinetics and thermodynamics) of lac dyeing on bamboo fibers will be known.

1.4 Scopes of research

1. The effects of pH, initial lac dye concentration, contact time and temperature on the adsorption behavior of lac dye on bamboo fibers will be firstly investigated.
2. The effects of PEI on the adsorption capacity of lac dye will then be studied. In addition, the isotherms, kinetics and thermodynamics for all dyeing systems will be examined, in relation with the interaction interpretation.

1.5 Research Place

SC1 – (404, 406, 407, 410), Department of Chemistry, Faculty of Science, Mahasarakham University

CHAPTER 2

LITERATURE REVIEW

2.1 Fibers

Fibers from natural sources have been used for thousands of years for producing textiles and related products. With the advent of the spinning jet in the mid-19th century, fibers could be formed by forcing dissolved polymeric materials through a small orifice (spinneret) into a coagulating bath. Regenerated natural and synthetic man-made fibers have been formed by this basic spinning technique or variations thereof since then. By the turn of the 20th century, rayon, a regenerated cellulosic and the first man-made fiber of commercial importance, was in full production. By the 1920s the cellulose derivatives acetate and triacetate were introduced as fibers of commerce, and inorganic glass fibers appeared during the mid-1930s. The first synthetic fiber (nylon) chemically synthesized from basic monomeric units and based on petroleum feed stocks appear in the late 1930s. The advent of nylon marked a new era for fiber production, and several new types of synthetic fibers, including polyester, acrylic, modacrylic, polyolefin, and vinyl fibers, appeared in the 1940s, 1950s, and 1960s.

In less than 40 years we have gone from a period where fibers were available only from natural or regenerated sources to a time where abroad spectrum of fibers are available. The wide range of properties available in fibers today has greatly expanded the applications and areas in which fibers can be used. Even with such a range of properties available in fibers, each class of fiber has inherent deficiencies that require that chemical finishes or physical modifications be applied to the fiber. Also, addition of color to the fiber through dyeing or printing is necessary to meet the demand of the consumer for a wide spectrum of colors and patterns in textile products. Since 1945 a number of new textile processes have been introduced providing unique methods to form yarns and textile substrates of widely varying structure and properties [16].

2.1.1 Classification of fibers

Fiber is the basic unit for textiles. A fiber is a very thin strand of a material having a good length to diameter ratio. Fibers are the raw materials for all fabrics. Some fibers occur in nature as fine strands that can be twisted into yarns. In a broader perspective fibers can be classified as natural fibers and manmade fibers. Natural fibers can further be classified as vegetable fibers and animal fibers .Some prominent examples of vegetable fibers are cotton, jute, hemp, flax / linen, bamboo and some animal fibers are wool, silk etc. Manmade fibers are well known for their strength properties and can further be classified as synthetic fibers for polyester, polyamide (nylon), acrylic, polyolefin, spandex/elastane (lycra) and regenerated fibers for viscose rayon, cuprammonium rayon, acetate rayon, bamboo viscose, modal, lyocell (tencel) (cellulose based) and protein (soya) (protein based). Sometimes different types of fibers are mixed with one another in different proportions in order to achieve the properties of all the fibers getting mixed. This mixing of fibers is known as Blending. Figure 2.1 shows a classification chart for the major fibers.

Fiber Classification Chart

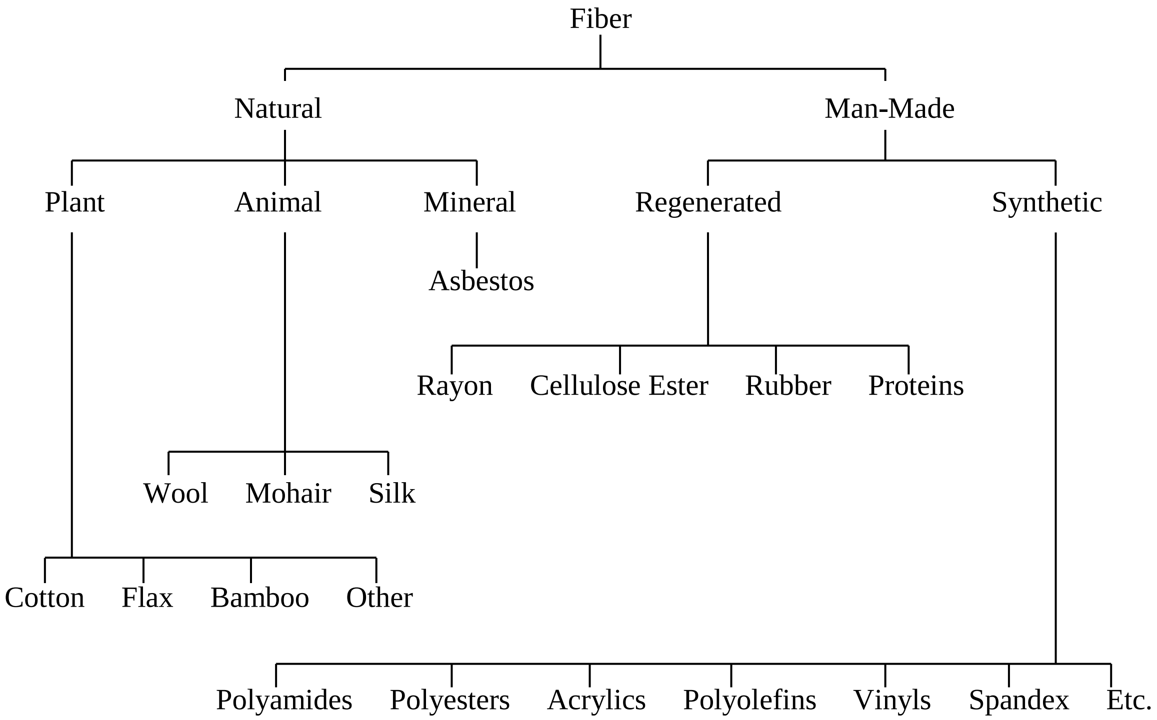


Figure 2.1 Classification of natural and man-made fibers [17].

2.1.2 Cellulose Fibers

Cellulose is a fibrous material of plant origin and the basis of all natural and man-made cellulosic fibers. The natural cellulosic fibers include cotton, flax, hemp, jute, and ramie. The major man-made cellulosic fiber is rayon, a fiber produced by regeneration of dissolved forms of cellulose. The cellulose acetates are organic esters of cellulose. Cellulose is a polymeric sugar (polysaccharide) made up of repeating 1,4-8-anhydroglucose units connected to each other by 8-ether linkages. The number of repeating units in cellulosic fibers can vary from less than 1000 to as many as 18,000, depending on the fiber source. Cellulose is a hemi-acetal and hydrolyzes in dilute acid solutions to form glucose is a simple sugar. The long 1inear chains of cellulose permit the hydroxyl functional groups on each anhydroglucose unit to interact with hydroxyl groups on adjacent chains through hydrogen bonding and van der Waal s forces. These strong intermolecular forces between chains, coupled with the high linearity of the cellulose molecule, account for the crystalline nature of cellulosic fibers. It is believed that a gradual transition from alternating areas of greater molecular alignment or crystallinity to more disordered or amorphous areas occurs in cellulose. The number, size, and arrangement of crystalline regions within celluloses determine the ultimate properties of a particular fiber. Figure 2.2 shows structure of cellulose fibers [17-19].

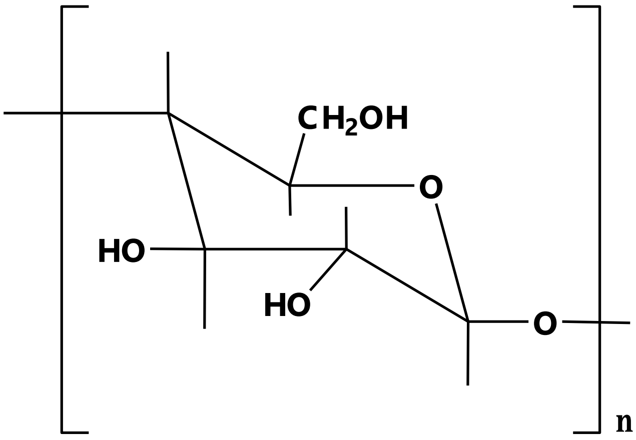


Figure 2.2 Structure of cellulose fibers [17].

2.1.3 Bamboo

The bamboo is grown in various continents of the world, it has been divided accordingly; Asia–Pacific bamboo region, American bamboo region, African bamboo region and European and North American region (Table 2.1). The Asia–Pacific bamboo region is the largest bamboo growing area in the world. In Asian countries, bamboo is known by different names, In China it is known as "friend of people", "wood of the poor" in India, "the brother" in Vietnam [20, 21] FAO provided the data of bamboo production at global level as shown in Fig 2.3. In Asia, large area of bamboo is occupied by six countries viz. India, China, Indonesia, Philippines, Myanmar, Vietnam and others. Globally among sympodial and monopodial, sympodial type of bamboo dominates major part. The extensive awareness of bamboo plantation in China has lead to an increase in monopodial bamboo by about 30% [22].

Table 2.1 shows bamboo regions along with countries [20].

Bamboo region	Countries
1. Asia - Pacific	China, India, Burma, Thailand, Bangladesh, Cambodia, Vietnam, Japan, Indonesia, Malaysia, Philippines, Korea, and Sri Lanka
2. American (Latin American, South American and North American)	Mexico, Guatemala, Costa Rica, Nicaragua, Honduras, Columbia, Venezuela and brazil
3. African	Mozambique, Eastern Sudan
4. European	England, France, Germany, Italy, Belgium, Holland, United States and Canada have introduced a large number of bamboo species from Asian and Latin American bamboo – producing countries

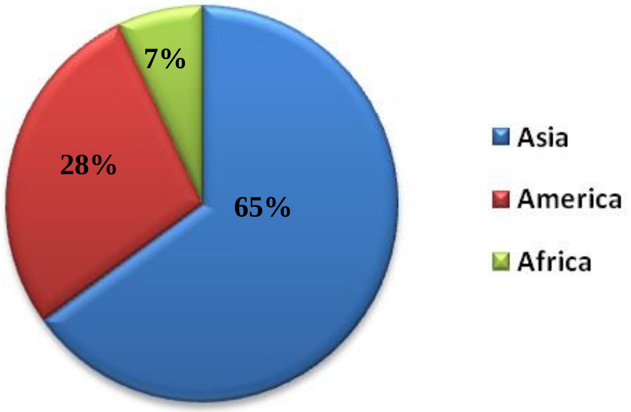
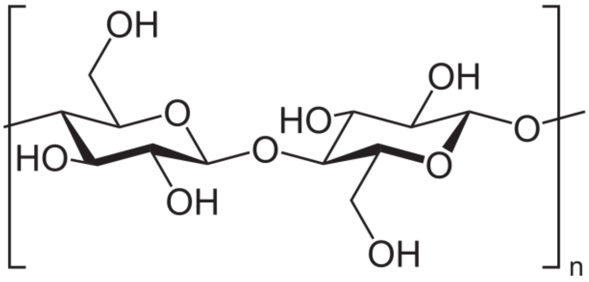


Figure 2.3 World percentage of bamboo from different continents [22].

2.1.4 Bamboo fibers

Bamboo fiber is a regenerated cellulosic fiber produced from bamboo. Starchy pulp is produced from bamboo stems and leaves through a process of alkaline hydrolysis and multiphase bleaching. Further chemical processes produce bamboo fiber. Repeated technological analysis has proved that this kind of fiber has a thinness degree and whiteness degree close to normal finely bleached viscose and has a strong durability, stability and tenacity. Bamboo fiber fabric is made of 100% bamboo pulp fiber. It is characterized by its good hygroscopicity, excellent permeability, soft feel, easiness to straighten and dye and splendid color effect of pigmentation. Figure 2.4 shows the main chemical structure of cellulose fiber [23].



.

Figure 2.4 The main chemical structure of cellulose fibers [23].

2.1.5 Extraction of bamboo fibers

The bamboo fiber is obtained from bamboo tree and it is divided into two kinds of fiber according to different process flow and method: Natural original bamboo fiber and bamboo pulp fiber (namely bamboo viscose fiber or regenerated cellulose bamboo fiber). Original bamboo fiber is directly picked up from natural bamboo without any chemical additive, using physical and mechanical method. In order to differentiate from bamboo pulp fiber (bamboo viscose fiber), we call it as original bamboo fiber or pure natural bamboo fiber. But bamboo pulp (viscose) fiber belongs to regenerated cellulose fiber as chemical fiber. Broadly there are two types of processing to obtain bamboo fibers viz. mechanical processing and chemical processing. Both processes initially include splitting of bamboo strips, which is followed by either mechanical processing or chemical processing depending upon the further use of bamboo fibers. Chemical processing includes initial alkali hydrolysis (NaOH) to yield cellulose fibers. Alkali treated cellulose fibers are then passed through carbon disulshide via multiphase bleaching. Most of the manufactures use this process as it is least time consuming procedure to yield the bamboo fibers.

However, in mechanical process, the initially crushed bamboo is treated by enzymes leading to formation of spongy mass and by the help of mechanical comb fiber technology, individual fibers are obtained. This method is environment friendly as compared to chemical process, although it is less economic process. Researchers reported detailed method of fiber extraction and it was divided into rough and fine bamboo preparation. The rough bamboo fibers were obtained by cutting, separation, boiling and fermentation with enzymes of bamboo. While as to obtain fine bamboo, the steps followed are boiling, fermentation with enzyme, wash and bleach, acid treatment, oil soaking and air-drying. The detailed outline is given in Figure 2.5 [24].

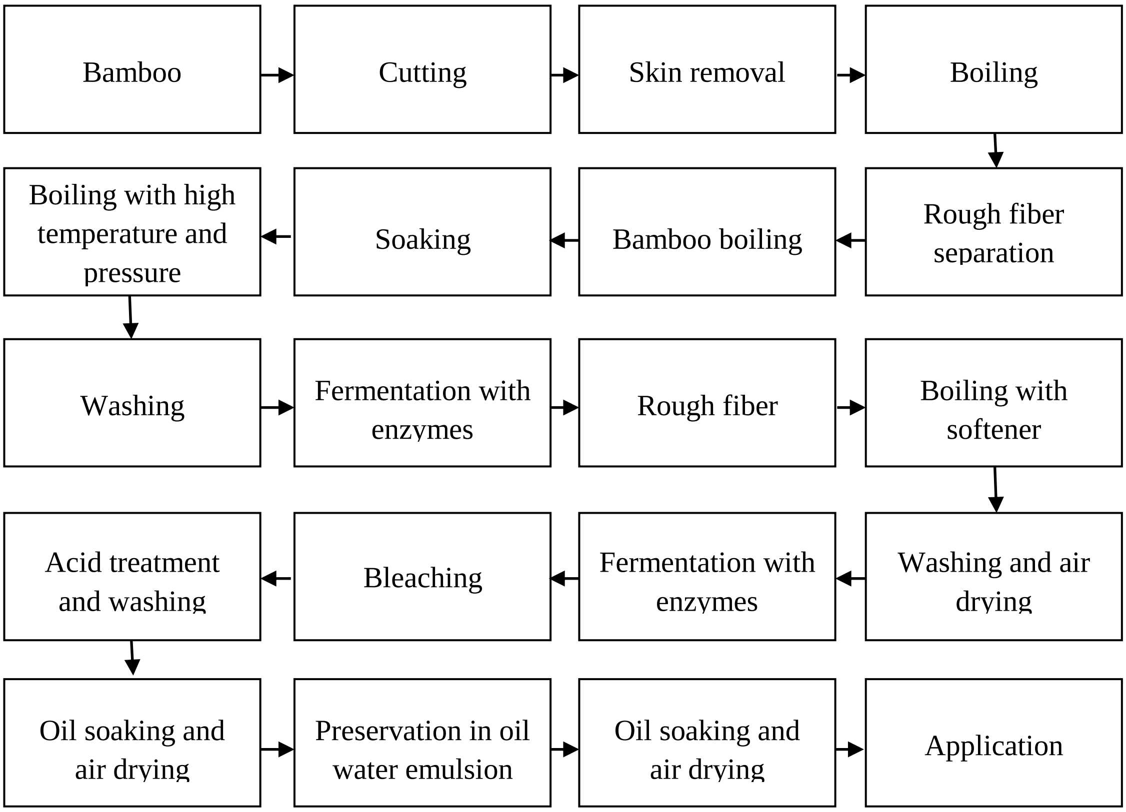


Figure 2.5 Extraction of rough and fine bamboo fibers [24].

2.1.6 Chemical composition and structure of bamboo fibers

The chemical composition of bamboo fiber constitutes mainly cellulose, hemicelluloses and lignin. These components are actually same high glycans and make about 90% of total weight of bamboo fiber. The other constituents are protein, fat, pectin, tannins, pigments and ash. These constituents play important role in physiological activity of bamboo and they are found in cell cavity or special organelles. The chemical composition of the bamboo fibers is given in Figure 2.6 [25]. Usually the chemical content of bamboo changes with age of the bamboo, particularly cellulose content keeps on decreasing while age of bamboo is increased so directly it directly affects the chemical composition of bamboo fibers. The lignin is considered to provide stiffness and yellow color to bamboo fibers. Different treatments cannot remove all the lignin content of the bamboo fibers, as lignin has been found quite resistant too various alkalis. Non cellulosic components have enough contribution to fiber properties such as strength, flexibility, moisture, and even density [26]. The unidirectional arrangement of bamboo fibers in tissues and cell wall structure of bamboo is one off unique property of bamboo [27-29]. Bamboo fibers possess alternate broad and narrow polylamellate structure with alternating broad and narrow lamella as compared to sandwich like structure of wood fiber [30]. One the characteristic of ultra-structure of bamboo fibber is variation in arrangement of cellulose fibrils along their longitudinal axis. The alternate narrow and broad layers have different arrangement of cellulose microfibrils, with large microfibril angle in narrow layers and low microfibril angle perpendicular and parallel to the main cell axis, respectively [31]. The lignin plays important role and is present in different concentration in different layers of cell wall. In addition, hemicellulose and phenolic acids (e.g. ferulic and *p*-coumaric acids) are responsible for covalent bonding in the cell wall structure. This variation of different components across the cell wall provides novel design to bamboo fiber wall, enhancing its various mechano physical properties [32, 33]. Recently, two researchers reported extensive studies on structure of bamboo fiber of different species and investigated the cell wall structure of different bamboo species. A study on bamboo species Guadua angustifolia revealed three presence of irregular form and more precisely beam shaped pattern of bamboo fibers [34]. Their size was found to depending upon the position across the cell wall. However, irrespective of position of bamboo fiber across the cell wall, a fiber with pentagonal or hexagonal, arranged in a honeycomb pattern was observed [35].

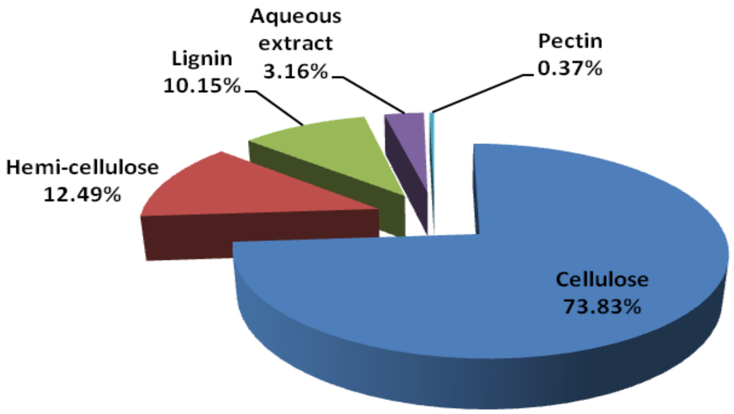


Figure 2.6 Chemical constituents of Bamboo fiber [25, 26].

2.1.7 Properties of bamboo fiber

1. Softer than cotton, with a texture similar to a blend of cashmere and silk because the cross-section of the fiber is filled with various micro-gaps and micro-holes, it has much better moisture absorption and ventilation. Moisture absorbency is twice than that of cotton with extraordinary soil release.

2. Natural antibacterial elements (bio-agent “bamboo kun”) in bamboo fiber keep bacteria away from bamboo fabrics.

3. Garment of bamboo fiber can absorb and evaporate human sweat in a split of second just like breathing. Such a garment makes people feel extremely cool, comfortable and never sticking to skin even in hot summer.

4. Great elasticity: 100% bamboo yarns show a great elasticity i.e. nearly 20%. Even in 100% bamboo woven fabrics a remarkable elasticity can be obtained where in the use of elastomeric fibers like elastanes may be eliminated.

5. Bamboo fabrics need less dyestuff than cotton, modal or viscose. It seems that the absorption of dyestuffs is remarkably better. Bamboo absorbs the dyestuffs faster and shows the colors better.

6. Anti-ultraviolet nature of bamboo fiber has made it suitable for summer clothing, especially for the protection of pregnant ladies and children from the effect of ultraviolet radiation.

7. Product of bamboo fiber is eco-friendly and bio-degradable [36].

2.1.8 End uses of bamboo fiber

1. Intimate apparels include sweaters, bath-suits, underwear, t-shirt, socks.

2. Due to its anti-bacterial nature, non-woven fabric has wide prospects in the field of hygiene materials such as sanitary napkin, masks, mattress, food-packing, bags.

3. Sanitary materials: bandage, mask, surgical clothes, nurses wears and so on. It has incomparably wide foreground on application in sanitary material such as sanitary towel, gauze mask, absorbent pads, and food packing.

4. Decorating items: curtain, television cover, wall-paper and sofa slipcover.

5. Bathroom products: towel and bath robe [37].

2.2 Dye

Dyes may be defined as substances that, when applied to a substrate provide color by a process that alters, at least temporarily, any crystal structure of the colored substances. Such substances with considerable coloring capacity are widely employed in the textile, pharmaceutical, food, cosmetics, plastics, photographic and paper industries [38]. The dyes can adhere to compatible surfaces by solution, by forming covalent bond or complexes with salts or metals, by physical adsorption or by mechanical retention [39]. Dyes are classified according to their application and chemical structure, and are composed of a group of atoms known as chromophores and responsible for the dye color. These chromophore containing centers are based on diverse functional groups, such as azo, anthraquinone, methine, nitro, aril-methane, carbonyl and others. In addition, electrons withdrawing or donating substituents so as to generate or intensify the color of the chromophores are denominated as auxochromes. The most common auxochromes are amine, carboxyl, sulfonate and hydroxyl [40-42]. It is estimated that over 10,000 differen dyes and pigments are used industrially and over 7×10^5 tons of synthetic dyes are annually produced worldwide [43]. Textile materials can be dyed using batch, continuous or semi-continuous processes. The kind of process used depends on many characteristics including type of material as such fiber, yarn, fabric, fabric construction and garment, as also the generic type of fiber, size of dye lots and quality requirements in the dyed fabric. Among these processes, the batch process is the most common method used to dye textile materials [44].

2.2.1 Dye classification

There are several ways for classification of dyes. It should be noted that each class of dye has a very unique chemistry, structure and particular way of bonding. While some dyes can react chemically with the substrates forming strong bonds in the process, others can be held by physical forces, some of the prominent ways of classification. A very common classification of the dyestuff is based on the source from which it is made. Accordingly the classification could be:

2.2.1.1 Synthetic Dyes

Dyes derived from organic or inorganic compound are known as synthetic dyes. Examples of this class of dyes are Direct, Acid, Basic, Reactive, Mordant, Metal complex, Vat, Sulphure, Disperse dye etc. However, the using general dye chemistry as the basis for classification shown in table 2.2 [39].

Table 2.2 shows the using general dye chemistry as the basis for classification [45].

Group	**Application**
Direct	Cotton, Cellulosic and Blends
Vat dyes	Cotton, Cellulosic and Blends
Sulphur	Cotton, Cellulosic fibers
Organic pigments	Cotton, Cellulosic, Blended Fabrics, paper
Reactive	cellulosic fibers and fabric
Dispersed dyes	Synthetic fibers
Acid Dyes	Wool, Silk, Synthetic fibers, leather
Azoic	Printing inks and pigments
Basic	silk, wool, cotton
Oxidation dyes	Hair
Developed Dyes	Cellulosic fibers and Fabric,
Mordant dyes	Cellulosic fibers and Fabric, Silk, Wool
Optical/Fluorescent Brighteners	synthetic fibers, leather, cotton, sports goods
Solvent dyes	Wood Staining, solvent inks, waxes, coloring oils

2.2.1.2 Natural dyes

The natural dyestuffs used to dye clothing were commonly extracted either from vegetable sources, including plants, trees, roots, seeds, nuts, fruit skins, berries and lichens, or from animal sources such as crushed insects and mollusks [40]. The important natural dye classes from plant sources are chlorophyll, carotenoids, flavonenoids and quinones as given below: Chlorophyll is a green compound found in leaves and green stems of plants [45]. Carotenoids are the most widely occurring in the animal and vegetable kingdoms. They are mostly fat soluble, nitrogen-free yellow to reddish violet dyes, which contain a long chain of conjugated double bonds, and so constitute aliphatic polyenes [46].

Natural dyes are often negatively charged. Positively charged natural dyes do exist, but are not common. In other words, the colored part of the molecule is usually the anion. Although the molecular charge is often shown on a specific atom in structural formulae, it is the whole molecule that is charged. Many, but by no means all, natural dyes require the use of a mordant. The use of dyes is very ancient. Kermes (natural red 3) is identified in the bible book of Exodus, where references are made to scarlet colored linen. Similar dyes are carmine (natural red 4) and lac (natural red 25). These three dyes are close chemical relatives, obtained from insects of the genus Coccus. All require a mordant. The most commonly used natural dye is undoubtedly hematein (natural black 1), obtained from the heartwood of a tree. This dye also requires a mordant. Saffron (natural yellow 6), is obtained from the stigmata of Crocus sativus, and is used without a mordant, staining as an acid dye. Although its use is very ancient, it is more common now as a coloring and spice for food than for dyeing, due to its expense [47-50].

2.2.1.3 Lac dye

Lac dye is a natural reddish dyestuff extracted from stick lac, which is a secretion of the insect *Coccus laccae* (*Laccifer lacca Kerr*) [3]. It is categorized into the quinone group. In general, the insect *Coccus laccae*, together with the other lac insect species (*Lakshadidia (Tacharddia, Laccifeer)* spp.), is found in South and Southeast Asia, especially in Thailand and India. In Thailand, lac insect grows most commonly on the Rain tree, *Samanea saman* (Jacq.) Merr. (*Pithecolobium saman, Mimosaceae*) [1]. However, the lac insect also grows on *Combretum quadrangulare* Kurz (Combretaceae) and on *Dallbergia cochinchinensis* Piere (Fabaceae) but only rarely. The lac insect looks like a mite as shown in Figure 2.7. The female insect has a short and rounded body whereas the male insect has a long body. They have six legs. Lac insects settle closely on the twigs of certain host tress, suck the plant sap and grow, all the while secreting lac resin from their bodies. Since the insects are closely spaced on the twigs, the resin forms continuous encrustations over the twigs of the host trees. The resin is called the stick lac. It is only the female insects that produce the red dyestuff. The red color is derived from a water-soluble part of stick lac which consists of laccaic acids A, B, C, D and E (Figure 2.8). All of these acids have an anthraquinone moiety with dicarboxylic acid groups, except for laccaic acid D which is a monocarboxylic acid [51-59]. The quantities of these components depend on the locality and the season. Erythrolaccin is another component of the lac dye, but this can be removed by ethanol extraction. The chemical structures of the laccaic acids and erythrolaccin are shown in Figure 2.8 [52, 60, 61]

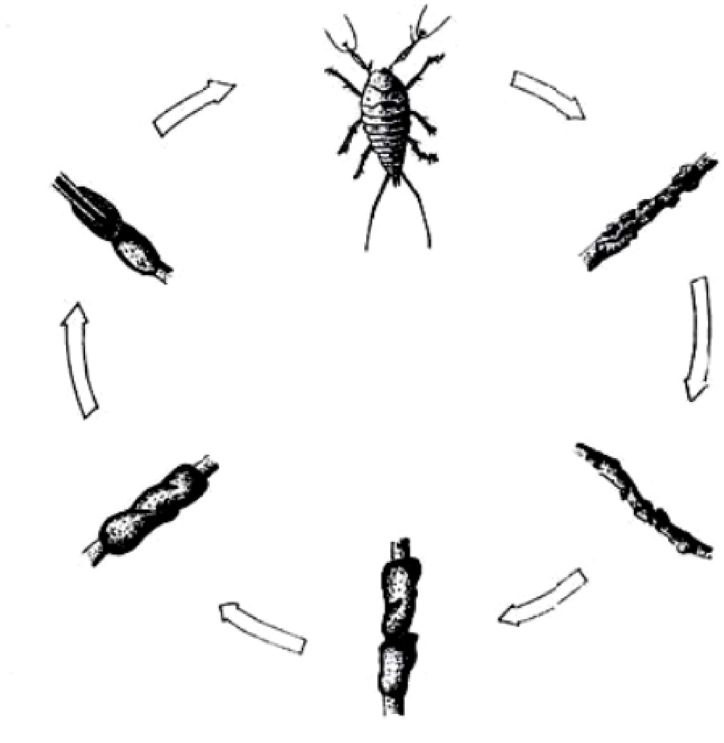
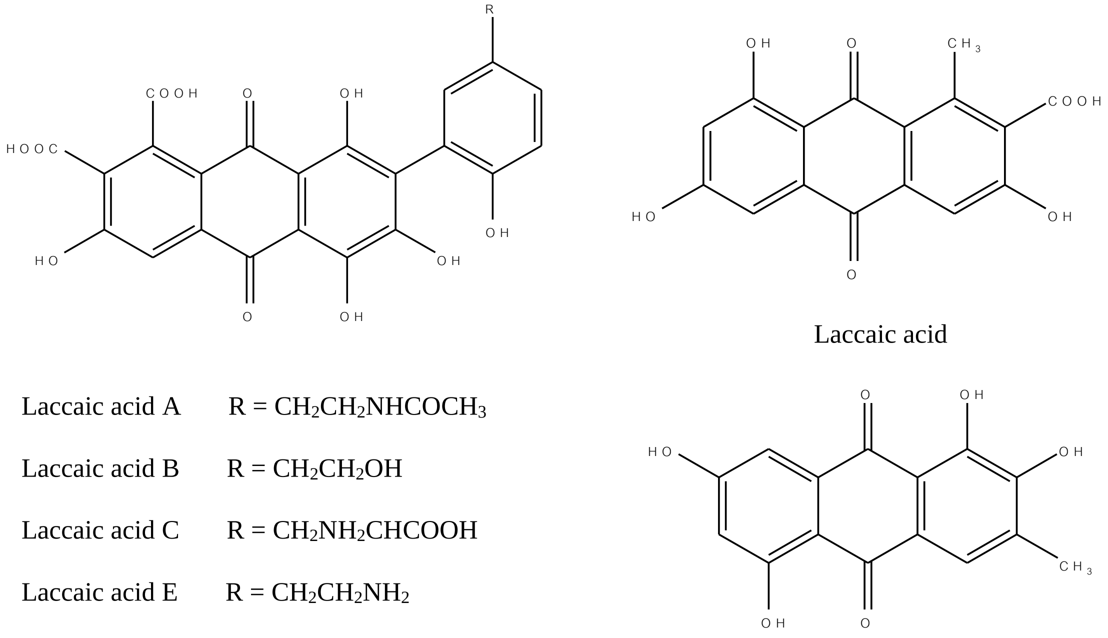


Figure 2.7 The life cycle of the insect *Coccus laccae* [3].



Laccaic acid

Laccaic acid A R = $CH_2CH_2NHCOCH_3$

Laccaic acid B R = CH_2CH_2OH

Laccaic acid C R = $CH_2NH_2CHCOOH$

Laccaic acid E R = $CH_2CH_2NH_2$

Erythrolacc

Figure 2.8 Chemical structures of laccaic acids and erythrolaccin [51].

2.3 Dyeing process

The dyeing process is one of the key factors in the successful trading of textile products. In addition to the design and beautiful color, the consumer usually looks for some basic product characteristics, such as good fixation with respect to light, perspiration and washing, both initially and after prolonged use. To ensure these properties, the substances that give color to the fiber must show high affinity, uniform color, resistance to fading, and be economically feasible [16, 17].

Modern dyeing technology consists of several steps selected according to the nature of the fiber and properties of the dyes and pigments for use in fabrics, such as chemical structure, classification, commercial availability, fixing properties compatible with the target material to be dyed, economic considerations and many others. Dyeing methods have not changed much with time. Basically water is used to clean, dye and apply auxiliary chemicals to the fabrics, and also to rinse the treated fibers or fabrics. The dyeing process involves three steps: preparation, dyeing and finishing, as follows:

1. Preparation is the step in which unwanted impurities are removed from the fabrics before dyeing. This can be carried out by cleaning with aqueous alkaline substances and detergents or by applying enzymes. Many fabrics are bleached with hydrogen peroxide or chlorine containing compounds in order to remove their natural color, and if the fabric is to be sold white and not dyed, optical brightening agents are added [62].

2. Dyeing is the aqueous application of color to the textile substrates, mainly using synthetic organic dyes and frequently at elevated temperatures and pressures in some of the steps. It is important to point out that there is no dye which dyes all existing fibers and no fiber which can be dyed by all known dyes. During this step, the dyes and chemical aids such as surfactants, acids, alkali/bases, electrolytes, carriers, leveling agents, promoting agents, chelating agents, emulsifying oils, softening agents etc. [44] are applied to the textile to get a uniform depth of color with the color fastness properties suitable for the end use of the fabric. This process includes diffusion of the dye into the liquid phase followed by adsorption onto the outer surface of the fibers, and finally diffusion and adsorption on the inner surface of the fibers. Depending on the expected end use of the fabrics, different fastness properties may be required. For instance, swimsuits must not bleed in water and automotive fabrics should not fade after prolonged exposure to sunlight. Different types of dye and chemical additives are used to obtain these properties, which is carried out during the finishing step. Dyeing can also be accomplished by applying pigments (pigments differ from dyes by not showing chemical or physical affinity for the fibers) together with binders (polymers which fix the pigment to the fibers) [38].

3. Finishing involves treatments with chemical compounds aimed at improving the quality of the fabric. Permanent press treatments, water proofing, softening, antistatic protection, soil resistance, stain release and microbial/fungal protection are all examples of fabric treatments applied in the finishing process.

Dyeing can be carried out as a continuous or batch process. The most appropriate process to use depends on several factors, such as type of material (fiber, yarn, fabric, fabric construction, garment), generic type of fiber, size of dye batch and quality requirements for the dyed fabric, but batch processes are more commonly used to dye textile materials. In continuous processing, heat and steam are applied to long rolls of fabric as they pass through a series of concentrated chemical solutions. The fabric retains the greater part of the chemicals while rinsing removes most of the preparation chemicals. Each time a fabric is passed through a solution, an amount of water equivalent to the weight of the fabric must be used. In batch processing, sometimes called exhaust dyeing, since the dye is gradually transferred from the dye bath to the material being dyed over a relatively long period of time, the dyeing occurs in the presence of dilute chemicals in a closed equipment such as a kier, kettle, beam, jet or beck. Unlike the continuous process, instead of being passed through various baths in a long series of equipment sections, in the batch process the fabric remains in a single piece of equipment, which is alternately filled with water and then drained, at each step of the process. Each time the fabric is exposed to a separate bath, it uses five to ten times its own weight in water. Some batch dyeing machines only operate at temperatures up to 100ºC. However, the system can be pressurized, allowing for the use of temperatures above 100ºC. Cotton, rayon,nylon, wool and some other fibers dye well at temperatures of 100ºC or below. Polyester and some other synthetic fibers dye more easily at temperatures above 100ºC [42].

Since the degree of dye fixation depends on the nature of the fiber, it is important to consider this topic. The fibers used in the textile industry can be divided into two main groups denominated natural fibers and synthetic fibers. Natural fibers are derived from the environment (plants or animals), such as wool, cotton, flax, silk, jute, hemp and sisal, most of which are based on cellulose and proteins. On the other hand, synthetic fibers are organic polymers, mostly derived from petroleum sources, for example, polyester, polyamide, rayon, acetate and acrylic. The two most important textile fibers are cotton, the largest, and polyester.

The dye can be fixed to the fiber by several mechanisms, generally in aqueous solution, and may involve primarily four types of interaction: ionic, Van der Waals and hydrogen interactions, and covalent bonds.

1. Ionic interactions result from interactions between oppositely charged ions present in the dyes and fibers, such as those between the positive center of the amino groups and carboxyl groups in the fiber and ionic charges on the dye molecule, and the ionic attraction between dye cations and anionic groups (-SO_3- and -CO_2-)

present in the acrylic fiber polymer molecules. Typical examples of this type of interaction can be found in the dyeing of wool, silk and polyamide.

2. Van der Waals interactions come from a close approach between the π orbitals of the dye molecule and the fiber, so that the dye molecules are firmly "anchored" to the fiber by an affinity process without forming an actual bond. Typical examples of this type of interaction are found in the dyeing of wool and polyester with dyes with a high affinity for cellulose [39].

3. Hydrogen interactions are formed between hydrogen atoms covalently bonded in the dye and free electron pairs of donor atoms in the center of the fiber. This interaction can be found in the dyeing of wool, silk and synthetic fibers such as ethyl cellulose.

4. Covalent bonds are formed between dye molecules containing reactive groups (electrophilic groups) and nucleophilic groups on the fiber, for example, the bond between a carbon atom of the reactive dye molecule and oxygen, nitrogen or sulfur atom of a hydroxy, amino or thiol group present in the textile fiber. This type of bond can be found in the dyeing of cotton fiber [16, 17, 39, 40, 61].

2.4 Mordants

Few natural dyes are colour-fast with fibres. Mordants are substances which are used to fix a dye to the fibres. They also improve the take-up quality of the fabric and help improve colour and light-fastness. The term is derived from the Latin mordere, to bite. Some natural dyes, indigo for example, will fix without the aid of a mordant; these dyes are known as “substantive dyes”. Others dyes, such as madder and weld, have a limited fastness and the colour will fade with washing and exposure to light. Traditionally, mordants were found in nature. Wood ash or stale urine may have been used as an alkali mordant, and acids could be found in acidic fruits or rhubarb leaves (which contain oxalic acid), for example. Nowadays most natural dyers use chemical mordants such as alum, copper sulphate, iron or chrome (there are concerns, however about the toxic nature of chrome and some practitioners recommend that it is not used). Other mordants are: Iron (ferrous sulphate), Tin (stannous chloride), Chrome (bichromate of potash), Copper sulphate, Tannic acid, Oxalic acid et al…, were used as surface modifiers to promote the binding of dyes to fabric by forming a chemical bridge from dye to fiber enhancing the staining ability of dye along with increasing its fastness properties, depth of shade or difference colours [63, 64-66] for dyeing nylon, wool, silk, leather, cotton, and other textile fibers [67]. However, most of the mordants used are toxic, expensive and have serious detrimental effects on the environmental. Using a different mordant with the same dyestuff can produce different shades, for example;

1. Iron is used as a 'saddener' and is used to darken colours.
2. Copper sulphate also darkens but can give shades which are otherwise very difficult to obtain.
3. Tin brightens colours.
4. Tannic acid, used traditionally with other mordants, will add brilliancy.
5. Chrome is good for obtaining yellows.
6. Oxalic acid is good for extracting blues from berries.
7. Cream of Tartar is not really a mordant but is used to give a luster to wool.

The mordant can be added before, during or after the dyeing stage, although most recipes call for mordanting to take place prior to dyeing. It is best to follow the instructions given in the recipe being used or experiment on a sample before carrying out the final dyeing. Later in this brief we will explain how the mordant is mixed and used as part of the dyeing process [68, 69-72).

2.4.1 Polyethyleneimine

Polyethyleneimine (PEI) a highly branched aliphatic polyamine is characterized by the repeating chemical unit denoted as $–(CH_2–CH_2–NH)–$. PEI is manufactured by the acid-catalyzed ring opening homopolymerization of ethyleneimine (or aziridine) monomer. The amine groups in PEI exist in primary, secondary and tertiary forms in the approximate ratio of 1:2:1 with a branching site every 3–3.5 nitrogen atoms along any given chain segment. PEIs function as weak Lewis bases in aqueous environments [73]. As the molecular weight of PEI increases, the polymer coils in solution assume a Gaussian conformation. This implies that there are charged nitrogen groups both on the surface and in the sterically protected interior of the molecule. It has been demonstrated in empirical studies that the attachment of the highly charged PEI molecule to anionic surfaces results in a near monolayer of polymer at the interface. In aqueous solution PEI exhibits a strong affinity to anionic materials such as polyanions and negatively charged organic and inorganic solids. PEIs are highly soluble in most polar materials including water, alcohols, glycols and certain organic solvents. The most prominent feature of PEI is its extremely high cationic charge density [74]. Therefore, PEI is widely used, for example, as an excellent brightener and retention aid for low-toxicity for paper [12], dispersant for toner compositions [13], densifying agents which improves H-bonding ability of fiber [14], cationic coagulant for heavy metal sequesting from effluent stream, adhesion promoters for pretreatment of nonwoven cellulosic fibers for improved wet strength [15], corrosion inhibitor for acid cleaning of metal and a retention aid for inorganic pigments (clay, calcium carbonate, titanium dioxide) on cellulosic paper fibers. Accordingly, the fact that PEI promotes adhesion between similar and dissimilar materials, a schematic diagram of the interaction is shown in Fig. 2.9. The situation is rather more complex than the simple representation as laccaic acid A, one of two the principal components of the lac dye, has one –NH–, one –COOH rather than two acid groups. This –NH– group could bind a second molecule of acid. Enhances surface characteristics such as wettability, bondability, toxicologically benign, and of opposite charge to the lac dye, makes PEI a suitable candidate for a mordant [11].

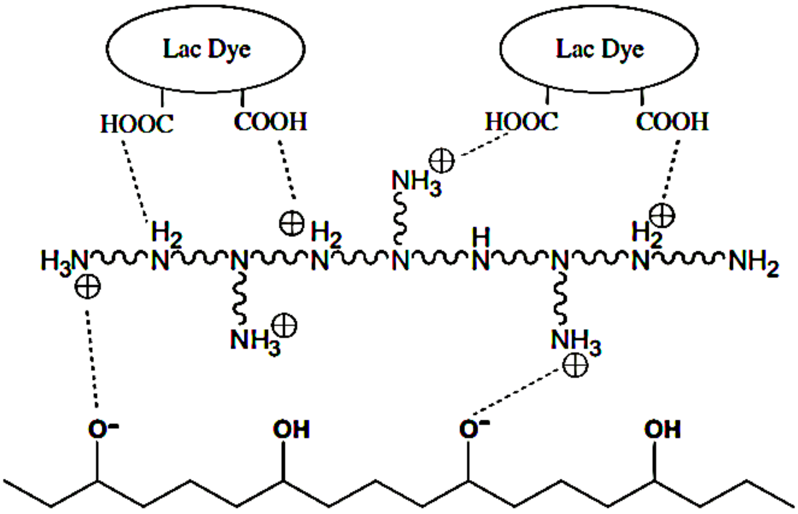


Figure 2.9 Schematic diagram of cotton-PEI-lac dye interaction [11]

2.5 Adsorption isotherms

2.5.1 The Langmuir isotherm

The Langmuir isotherm is based on the hypothesis that uptake occurs on a homogeneous surface by monolayer adsorption without interaction between the absorbed materials. The equilibrium adsorption isotherm is fundamental in describing the interaction behavior between solutes and adsorbents, and is important in the design of an adsorption system. The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes [75]. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The saturated monolayer curve can be represented by the expression:

$$q_e = \frac{QbC_e}{1+bC_e} \qquad (2.1)$$

A linear form of this expression is:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right)C_e \qquad (2.2)$$

For lower concentrations, the following form of Langmuir equation is found to be more satisfactory [76]:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e} \qquad (2.3)$$

In the above equation, Q is the maximum amount of the dye per unit weight of fiber to form complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e, q_e is the amount of dye adsorbed per unit weight of fibre at equilibrium, and b the Langmuir constant related to the affinity of binding sites. The value of Q represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance [75]. The values of Q and b are calculated from the intercepts and slopes of the straight lines of plot of $1/q_e$ versus $1/C_e$. The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimension less constant separation factor for equilibrium parameter, R_L, defined as follows:

$$R_L = \frac{1}{1+bC_0} \qquad (2.4)$$

where C_0 is the initial concentration of dye (in ppm or mg/L) and b is the Langmuir constant (L/mg). The values of RL indicates the type of isotherm to be irreversible (R_L=
0), favourable ($0 < R_L < 1$), linear ($RL = 1$) or unfavourable ($R_L > 1$) [77].

2.5.2 The Freundlich isotherm

The Freundlich isotherm is commonly used for investigating the non-linear adsorption of a variety of dyes on various materials. The Freundlich isotherm is a special case for heterogeneous surface energy in which the energy in the Langmuir equation varies as a function of surface coverage strictly due to variation of the sorption. The Freundlich equation is given as:

$$q_e = Q_f C_e^{1/n} \qquad (2.5)$$

where Q_f is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity. A linear form of the Freundlich expression in the equation (2.5) will yield the constants Q_f and $1/n$.

$$\ln q_e = \ln Q_f + \frac{1}{n} \ln C_e \qquad (2.6)$$

Therefore, Q_f and $1/n$ can be determined from the linear plot of ln q_e versus ln C_e. The magnitude of the exponential $1/n$ gives an indication of the favourability of adsorption. Values of $n > 1$ obtained represent favourable adsorption conditions [75].

2.6 Kinetics of adsorption

In order to examine the controlling mechanism of the adsorption process, pseudo first-order and pseudo second-order equations were used to test the experimental data.

2.6.1 Pseudo-first-order kinetic model

A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form:

$$\frac{dq_t}{dt} = k_1 \left(q_e - q_t \right) \qquad (2.7)$$

where k_1 is the rate constant of pseudo-first-order adsorption and q_e represents adsorption capacity (i.e. the amount of adsorption corresponding to monolayer coverage). After definite integration by applying the initial conditions $t = 0$ to t and $q_t = 0$ to q_t, Eq. (2.7) becomes:

$$\ln \left(q_e - q_t \right) = \ln q_e - k_1 t \qquad (2.8)$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at any time t, k_1 is the rate constant of pseudo-first-order adsorption. The plot of log (q_e $-q_t$) versus t gives a straight line for the pseudo-first-order adsorption kinetics. The values of the pseudo-first-order rate constant k_1 were obtained from the slopes of the straight lines.

2.6.2 Pseudo-second-order kinetic model

The pseudo-second-order model can be represented in the following form:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \qquad (2.9)$$

where k_2 is the rate constant of pseudo-second-order adsorption. Integration of Eq. (2.9) and applying the initial conditions gives [78]:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (2.10)$$

and

$$h_i = k_2 q_e^2 \qquad (2.11)$$

where hi is the initial dye adsorption rate (mg/g min). If the pseudo second order kinetics are applicable, the plot of t/q_t versus t show a linear relationship. The slope and intercept of (t/q_t) versus t were used to calculate the pseudo second-order rate constant k_2 and q_e. It is likely that the behavior over the whole range of adsorption is in agreement with the chemisorption mechanism being the rate-controlling step [79, 80].

2.7 Thermodynamic studies

In general, the rates of chemical reactions increase with an increase in the temperature. In the rate law, temperature dependence appears in the rate constant. The dependence of rate constants on temperature over a limited range can usually be represented by an empirical equation proposed by Arrhenius in 1889 [81]:

$$k = Ae^{-Ea/RT} \qquad (2.12)$$

where A is the pre-exponential factor and E_a is the activation energy. The pre-exponential factor A has the same units as the rate constant. An alternative form is obtained by taking the logarithm of each side.

$$\ln k = \ln A - \frac{Ea}{RT} \tag{2.13}$$

A straight line is obtained by plotting of the logarithm of the rate constant against with the reciprocal of the absolute temperature. Such a graph is often referred to as an Arrhenius plot.

The enthalpy ($\Delta H°$), entropy ($\Delta S°$) and free energy ($\Delta G°$) of activation can be also calculated using the Eyring equation as follows:

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{2.14}$$

where k_b and h refer to Boltzmann's constant and Planck's constant respectively. The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of activation were calculated from the slope and intercept of a plot of ln (k/T) versus $1/T$. Gibbs energy of activation ($\Delta G°$) can be written in terms of enthalpy and entropy of activation [82]:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{2.15}$$

2.8 Color fastness

Color fastness refers to the resistance of color to fade or bleed of a dyed or printed textile materials to various types of influences e.g. water, light, rubbing, washing, perspiration etc. to which they are normally exposed in textile manufacturing and in daily use.

2.8.1 Standards of Color Fastness

1. AATCC (American Association of Textile Chemists and Colorists) technical manual: describes 66 numbers of different color fastness tests.

2. SDC (Society of Dyers and Colorists): In 1927, SDC (Europe) made fastness test committee.

3. ISO (International Organization for Standardization): In 1947, ISO made color subcommittee. ISO also grades the fastness: For light fastness: 1~8 and other fastness: 1~5.

2.8.2 Factors Affecting the Color Fastness Properties

1. The chemical nature of the fiber. For example, cellulosic fibers dyed with reactive or vat dyes will show good fastness properties. Protein fibers dyed with acid mordant and reactive dyes will achieve good fastness properties and so on. That is to say compatibility of dye with the fiber is very important.

2. The molecular structure (e.g.) of a dye molecule: If the dye molecule is larger in size, it will be tightly entrapped inside the inter-polymer chain space of a fiber. Thus the fastness will be better.

3. The manner in which the dye is bonded to the fiber or the physical form present.

4. The amount of dye present in the fiber i.e. depth of shade. A deep shade will be less fast than a pale or light shade.

5. The presence of other chemicals in the material.

6. The actual conditions prevailing during exposure.

2.8.3 Type of color fastness test

1. Color fastness to washing
2. Color fastness to water
3. Color fastness to rubbing/crocking
4. Color fastness to perspiration
5. Color fastness to light
6. Color fastness to sea water
7. Color fastness to chlorinated water
8. Color fastness to hot pressing

2.8.4 Rating for color fastness

Rating for color fastness is used to check the resistance of color to fade or bleed of a dyed or printed textile materials. There are 5 levels of rating as the followed:

5 = No color change / staining
4 = Slightly color change / staining
3 = Noticeable color change / staining
2 = Considerable color change / staining
1 = Excessive color change / staining

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Chemicals and materials

3.1.1 Chemicals

The chemicals used in this research were listed in Table 3.1

Table 3.1 Chemicals used in this research.

Chemicals	**Grade**	**Brand**
Sodium Hydroxide	AR	Carlo Erba Reagent
Hydrochloric Acid	AR	Quality Reagent Chemical
Acetic Acid	AR	Quality Reagent Chemical
Poly(ethyleneimine)	AR	Acros Organics

3.1.2 Materials

The materials used in this research were bamboo fibers (BFs) and lac dye. The bamboo fibers were donated by Assist. Prof. Dr. Sisikka Wannajun, a teacher from Faculty of Cultural Science, Mahasarakham University. The Bfs were prepared from alkaline hydrolysis. Lac dye was purchased from the villages located in Khon Kean Province.

3.1.3 Instruments

The main items of instruments used in this research were listed in Table 3.2.

Table 3.2 Instruments used in this research.

Instruments	Model	Company
Spectrophotometer	Thermo Scientific 4001/4	Thermo Electron Co., Ltd.
Fourier transform infrared spectroscope	Spectrum GX-1	Perkin Elmer Co., Ltd.
Scanning electron microscope	OL JSM-6460 LV	JEOL Co., Ltd.
pH meter	CONSORT C-830	Metrohm Siam Co., Ltd.
Thermostatted shaker bath	Heto SBD 50	Scientfic Promotion Co.,Ltd.
UV-Vis spectrophotometer	Jasco V-500	Jasco Co., Ltd.

3.2 Experimental

3.2.1 Preparation of bamboo fibers

To remove the gum, the bamboo fibers (100 g) were dipped into the boiling water (1.5 L) containing soap flakes 6g and sodium hydroxide 15g. The mixture was then boiled for 2 h at 90°C. The bamboo fibers were then removed, washed with water, squeezed to remove excess liquor and then air dried. The fibers were treated with 1 M Hydrochloric acid at room temperature for 30 minutes and then removed and washed the acid away with distilled water until the rinsed water was neutral. The bamboo fibers were then dried at room temperature.

3.2.2 Preparation of lac dye

The lac dye 250 g in the form of powder was extracted with distilled water (1.5 L) at 60°C for 1 h. The aqueous dye solution was filtered with filter paper and the filtrate was concentrated under reduced pressure (rotary evaporator), yielding a crude lac dye. The crude lac dye was then used without further purification.

3.2.3 Treatment of bamboo fibers using PEI

The alkali treated bamboo fibers were immersed in 1,000 ppm of PEI solutions at room temperatures using the material to liquor ratio (MLR) of 0.5: 100 mL for 12 hour and then dried at room temperature.

3.2.4 Conditions optimization

To obtain the optimal conditions, the experiments were conducted in batch mode to evaluate the effects of various parameters, such as initial dye concentration, pH, temperature, contact time and MLR on the adsorption of lac dye were studied:

3.2.4.1 Effect of pH

Lac dye was dissolved in distilled water. The pH of lac dye solution in each erlenmeyer flask was adjusted as 2, 3 and 4 with glacial acetic acid. All solutions were then shaken in a shaker bath at 200 rpm for 15 min. The bamboo fiber (0.5 g) was then immersed in the dye solution and shaken in a thermostatted shaker bath at 150 rpm for 3 h. After 3 h, the bamboo fiber was rapidly withdrawn. The dye concentrations were determined using a calibration curve based on absorbance at λ_{max} 491 nm versus dye concentration in standard lac dye solution.

3.2.4.2 Effect of initial lac dye concentration

Lac dye was dissolved in distilled water. The initial dye concentration of lac dye solution in each erlenmeyer flask was varied as 50, 150, 250 and 350, 450, 500 mg/L. All solutions were then shaken in a shaker bath at 200 rpm for 15 min. The bamboo fiber (0.5 g) was then immersed in the dye solution and shaken in a thermostatted shaker bath at 150 rpm for 3 h. After 3 h, the bamboo fiber was rapidly withdrawn. The dye concentration were determined using a calibration curve based on absorbance at λ_{max} 491 nm versus dye concentration in standard lac dye solution.

3.2.4.3 Effect of material to liquor ratio (MLR)

Lac dye was dissolved in distilled water. The material to liquor ratio of different volume (mL) of lac dye solution in each erlenmeyer flask was adjusted as 60, 80, and 100 mL. All solutions were then shaken in a shaker bath at 200 rpm for 15 min. The bamboo fiber (0.5 g) was then immersed in the dye solution and shaken in a thermostatted shaker bath at 150 rpm for 3 h. After 3 h, the bamboo fiber was rapidly withdrawn. The dye concentrations were determined using a calibration curve based on absorbance at λ_{max} 491 nm versus dye concentration in standard lac dye solution.

3.2.4.4 Effect of temperatures

Lac dye was dissolved in distilled water. The temperature of lac dye solution in each erlenmeyer flask was varied as 30, 45 and 60 °C. All solutions were then shaken in a shaker bath at 200 rpm for 15 min. The bamboo fiber (0.5 g) was then immersed in the dye solution and shaken in a thermostatted shaker bath at 150 rpm for 3 h. After 3 h, the bamboo fiber was rapidly withdrawn. The dye concentrations were determined using a calibration curve based on absorbance at λ_{max} 491 nm versus dye concentration in standard lac dye solution.

The absorbance of the residual solution was measured to enable calculation of the dye concentration.

3.2.5 Batch kinetic experiments

Lac dye was dissolved in distilled water to the required concentrations. The pH of the dye solutions was adjusted to optimum pH (3.0) with glacial acetic acid. The dye solution (100 mL) in each erlenmeyer flask was shaken in a thermostatted shaker bath operated at 200 rpm. After 15 min, the bamboo fiber (0.5 g), which had been pre-warmed in the thermostatted bath for 3 h, was immersed in the dye solution. The bamboo fiber samples were then rapidly withdrawn after different immersion times. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at λ_{max} 491 nm (UV-Visible spectrophotometer) versus dye concentration in standard lac dye solutions. The amount of dye adsorbed per gram of bamboo fiber (q_t) (mg/g bamboo fiber) at any time was calculated by a mass balance relationship (equation (16)) as follows:

$$q_t = \left(C_0 - C_t\right)\frac{V}{W} \tag{16}$$

where C_o and C_t are the initial lac dye concentration and dye concentrations (mg/L) after dyeing time t, respectively. V is the volume of dye solution (mL) and W is the weight of bamboo fibers (g). Kinetic experiments of lac dyeing onto bamboo were repeated three times.

3.2.6 Batch equilibrium experiments

Different lac dye concentrations were firstly prepared in distilled water. The pH of the dye solution was adjusted to optimum pH (3.0) with glacial acetic acid. The experiments were carried out by shaking bamboo fiber (0.5 g) with different concentrations of dye solution (100 mL) in an erlenmeyer flask at 30, 45 and 60 °C in a thermostatted shaker bath operated at 150 rpm. The amount of dye in the solution related with the absorbance was monitored by spectrophotometer at λ_{max} 491 nm. The initial and equilibrium dye concentrations were determined using a calibration curve. Equation (17) was used to calculate the amount of dye adsorbed at equilibrium (q_e) (mg/g bamboo).

$$q_e = \left(C_0 - C_e\right)\frac{V}{W} \tag{17}$$

In equation (17), C_0 and C_e are the initial and equilibrium dye solution concentrations (mg/L), respectively, and V is the volume of the dye solution (mL) and W is the weight of bamboo fibers (g). Equilibrium experiments for the adsorption of lac dyeing onto bamboo fibers were repeated three times.

3.2.7 Calibration curve

Lac dye was dissolved in distilled water at different concentration. The 100 mL of lac dye solution in each erlenmeyer flask was adjusted as 0, 10, 50, 150, 250, 350, 450 and 550 mg/L. All standard lac dye solutions were then shaken in a shaker bath at 200 rpm for 15 min. The standard lac dye concentrations were measured using spectrophotometer at λ_{max} 491 nm. The calibration curve were done by plotting of lac dye concentration (mg/L) versus absorbance.

3.3 Determination of PEI adsorbed on bamboo fibers

The determination amount of PEI adsorbed on bamboo fibers can operated by immerse PEI treated bamboo fibers on complexed with 0.50% w/v of copper sulphate solution, MLR 1:200, temperature 30, 45, and 60 °C, at equilibrium time (12 hr). Temperature has a negligible effect on the adsorption unlike the dye behaviour and the PEI adsorbed amount is independent of substrate concentration. The absorbance of the

PEI/Cu complex was quantified using UV–VIS spectrophotometer and hence the amount of residual PEI was determined.

3.4 Characterization of BFs

3.4.1 Fourier transform infrared spectroscopy (FTIR)

To study the surface properties of BFs prepared under various conditions, the functional groups of the fibers was characterized by Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy (Spectrum GX-1, Perkin Elmer). The scan was conducted in the range of 4000-650 cm^{-1} at resolution of 4 cm^{-1}. The number of scans was set to 32.

3.4.2 Scanning electron microscopy (SEM)

The surface morphological characterization of BFs were performed by scanning electron microscope (SEM) (JEOL; JSM- 6460LV, Tokyo, Japan) operated with an accelerating voltage of 15 kV. The BFs were sputter-coated with gold for enhanced surface conductivity.

3.5 Color fastness

Fastness testing for test the fastness properties of lac dye on untreated and PEI-treated bamboo fibers were followed from ISO (International Organization for Standardization).

3.5.1 Color fastness to washing

The color fastness to washing were carried out following ISO 105-C10: 2006 (E). The solution for washing should be prepared at 40 °C with washing time of 30 min. The standard 50 g/L soap solution was prepared. The liquor material ratio 50:1. After washing the fibers were removed rinsed twice in cold water squeezed and air dried.

3.5.2 Color fastness to water

The color fastness to water were carried out following ISO 105-E01: 2010 (E). The wet sample was added to distilled water at room temperature and then to place in acrylic resin plates and put the weight on to the plates. After that, the sample keep in oven to the temperature at 37± 2 °C for 4 hr. To open the specimen and sample dry in the air hot exceeding 60°C.

CHAPTER 4

RESULTS AND DISCUSSION

In the present work, effect of bamboo fibers (BFs) surface treatment using polyethyleneimine (PEI) on adsorption behavior of lac d ye on BFs is investigated. The adsorption capacity, kinetics and thermodynamics of lac dyeing on BFs was examined. The results are compared between the untreated and the PEI-pretreated BFs dyeing systems.

4.1 ATR-FTIR characterization of BFs before and after treatments

ATR-FTIR spectroscopy is a non-destructive testing method often used for surface analysis of textile materials. Figure 4.1 shows the ATR-FTIR of the untreated and alkali-treated (controlled) BFs. The FTIR spectrum of the untreated (Figure 4.1a) BFs is associated with the typical spectrum of cellulose. Characteristic peak of lignin found at 1639 cm^{-1} indicates an absorption peak of carbonyl group in lignin [83]. For controlled BFs, the $-CH_2$ bending vibration absorption peak of controlled BFs at 1418 cm^{-1} in curve - 4.1b had a slightly right shifts from 1415 cm^{-1} of untreated BFs (Figure 4.1a). For PEI-treated BFs, there is a new peak about of N-H bending of amine at 1573 cm^{-1} is observed (Figure 4.1c).

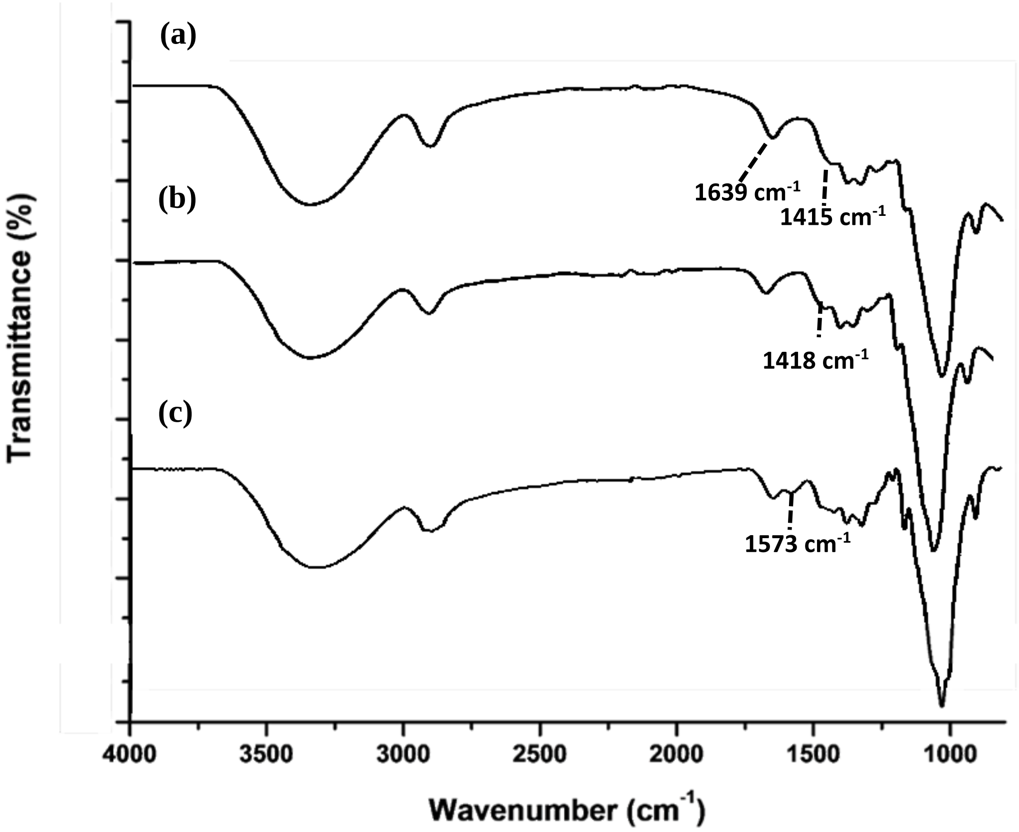


Figure 4.1 ATR-FTIR spectra of (a) untreated, (b) controlled and (c) PEI-treated BFs.

4.2 Surface morphology of BFs

To observe the surface morphology of untreated, controlled and PEI-treated BFs, scanning electron microscope (SEM) is used to examine surface properties of the BFs. The SEM micrographs of BFs are illustrated in Figure 4.2. For the untreated sample (Figure 4.2a), the rough surface is clearly observed whereas the controlled BFs surfaces became smoother when compared with that of the controlled sample. This is due to that the surface of the untreated BFs is normally covered by wax, oil, pectin, impurities and amorphous cellulose [84, 85]. The controlled BFs displayed a cleaner surface (Fig. 4.2b) when compared with the untreated one [86]. Particularly, the NaOH treatment of cellulose resulted in the formation of nano-sized cellulose fibrillations. As reported, the natural cellulose fibers were compose of crystalline cellulose in nano-size and para-crystalline, surrounded by amorphous cellulose [87]. Gaps between the nanofibers were formed after the removal of amorphous cellulose, resulting in splitting the fibers into smaller sizes. In case of PEI-treated BFs, it is seen that the surface of PEI-treated BFs is smoother than that of controlled BFs.

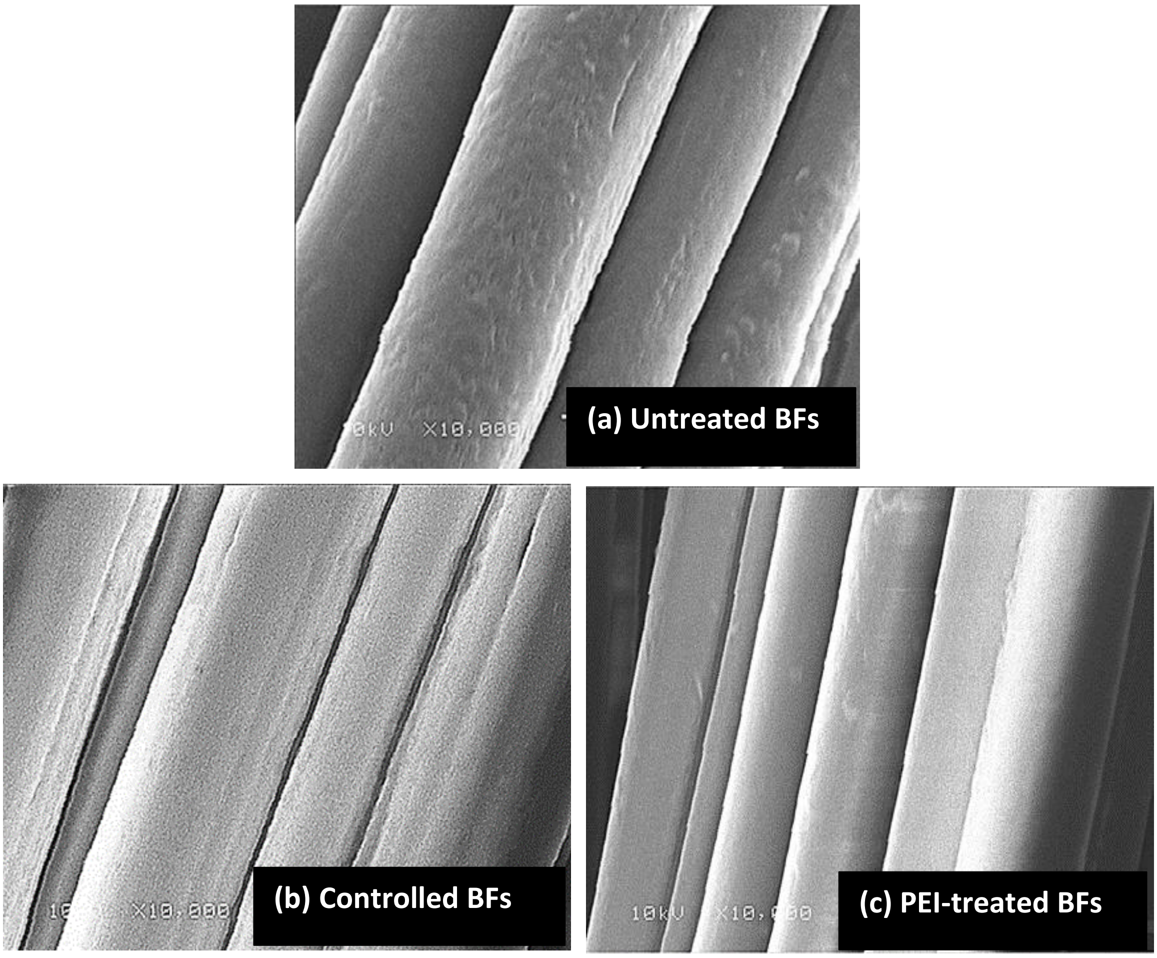


Figure 4.2 SEM micrographs of (a) untreated, (b) controlled and (c) PEI-treated BFs.

4.3 Conditions optimization

Prior to investigating the adsorption of lac dye onto BFs, the optimum experiment conditions, e.g. pH, material to liquor ratio (MLR), contact (dyeing) time, initial dye concentration and dyeing temperature were firstly examined.

4.3.1 Effect of pH

The pH of the dye solution is one of the most important parameters governing the adsorption capacity of lac dye onto BFs. The effect of pH on the adsorption capacity of lac dye is shown in Figure 4.3. It is seen that the adsorption capacity varies with pH 1.0 - 4.0 because the BFs generally carry a weak negative charge in a dye bath with a pH higher than 4.0. The negative charges on the BF surface repel the laccaic acid anion at pH values higher than 4.0. Therefore, the negative charge on the adsorbing surface of BFs clearly creates a very unfavorable situation for the adsorption of lac dye on BFs at a pH higher than 4.0. The highest adsorption capacity is observed at pH 3.0 because acid dye solution has negative charge. The low pH, carboxyl and hydroxyl groups along the polymer chain of BFs are hardly ionized. The dye molecules can reach the surface of the BFs where they can interact with the BFs via hydrogen bonding together with some ion-dipole interactions because these structures contain hydroxyl group of BFs [88]. However, the adsorption capacity dropped gradually at pH values lower than 3.0. This is due to the carboxyl groups in the side chains are essentially unionized at a pH lower than 3.0. Therefore, the preparation of lac dye solution for using throughout this work is adjusted as pH = 3.0.

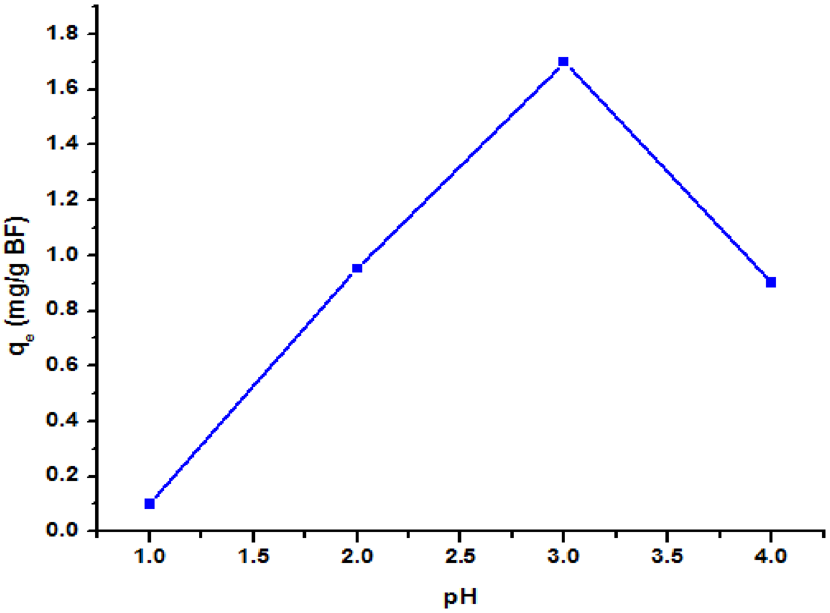


Figure 4.3 Effect of pH on adsorption capacity at equilibrium of lac dye onto BFs. The dyeing conditions are C_0 = 250 mg/L, MLR = 1:200, dyeing time = 200 min and dyeing temperature = 30°C.

4.3.2 Effect of initial lac dye concentration

The adsorption ability of lac dye onto BFs at different initial dye concentrations is investigated as a function of contact time in order to determine the equilibrium adsorption time. The amount of dye adsorbed at any time is shown in Figure 4.4. It is found that the adsorption capacity increases with increasing initial concentration of the lac dye. In the same meaning, an increase in the initial dye concentration leads to increase the adsorption rate and capacity. This may arise from an increase in the driving force of the concentration gradient with increasing initial dye concentration [89]. Since the adsorption capacity at equilibrium lies in a narrow range values (2.25-2.75) with using C_0 = 250 – 500 mg/L, an initial dye concentration of 250 mg/L was used throughout this work. The equilibrium adsorption time was used at 200 min.

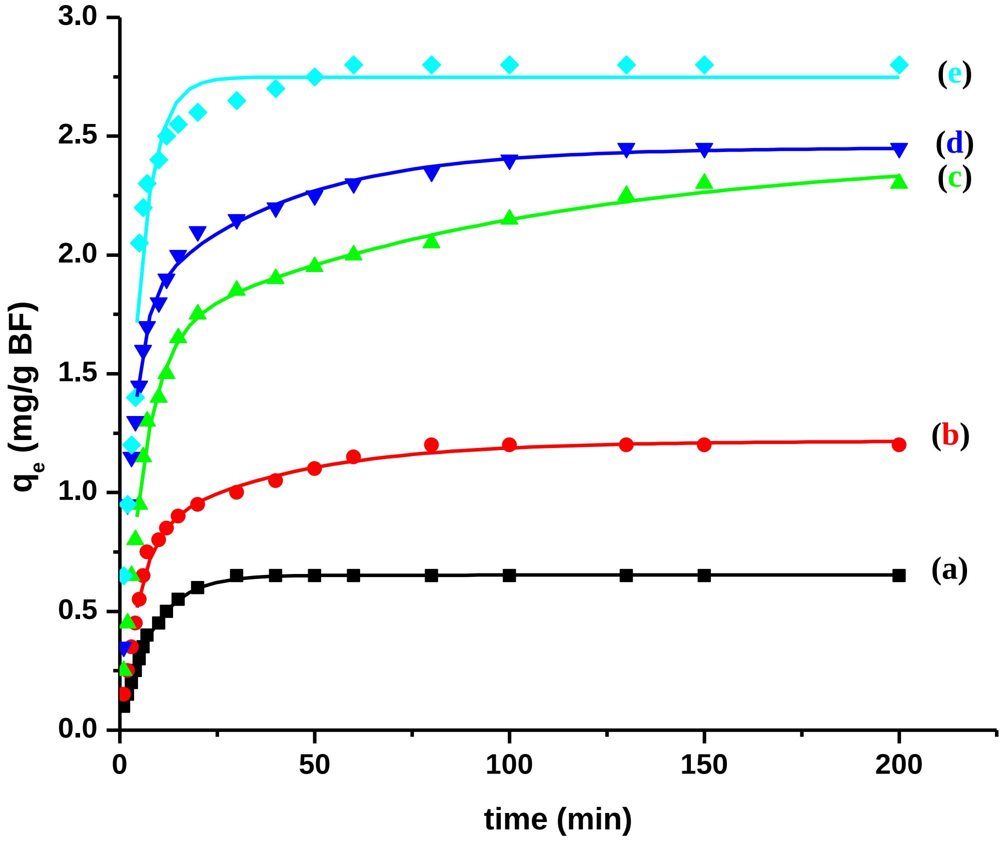


Figure 4.4 Effect of various initial concentrations (C_0) of lac dye solution on adsorption capacity of lac dye on BFs: (a) $C_0 = 50$, (b) $C_0 = 150$, (c) $C_0 = 250$, d) $C_0 = 350$ and e) $C_0 =$ 500 mg/L. Dyeing conditions are pH = 3, MLR = 1:200, dyeing time = 200 min and dyeing temperature = 30°C.

4.3.3 Effect of material to liquor ratio (MLR)

For dyeing process, the dye molecules are normally transferred from the dye liquor to the fiber in a uniform and efficient manner. The rate of dye uptake by the fiber is significantly increased by the movement of the dye liquor relative to the fiber [90]. The effect of material to liquor ratio (MLR) on the adsorption of lac dye onto bamboo fibers is shown in Figure 4.5. It is found that an increase in volume of dye solution results in an increase of the dye adsorption capacity at equilibrium. This indicates that BFs is loosely packed in the higher volume of dye solution and the dye solution readily moves onto BFs surface. In this work, the highest adsorption capacity at equilibrium of lac dye is observed for dyeing system with the MLR of 1:200. Therefore, one of the dyeing conditions of dyeing process used throughout this work is carried out at MLR = 1: 200.

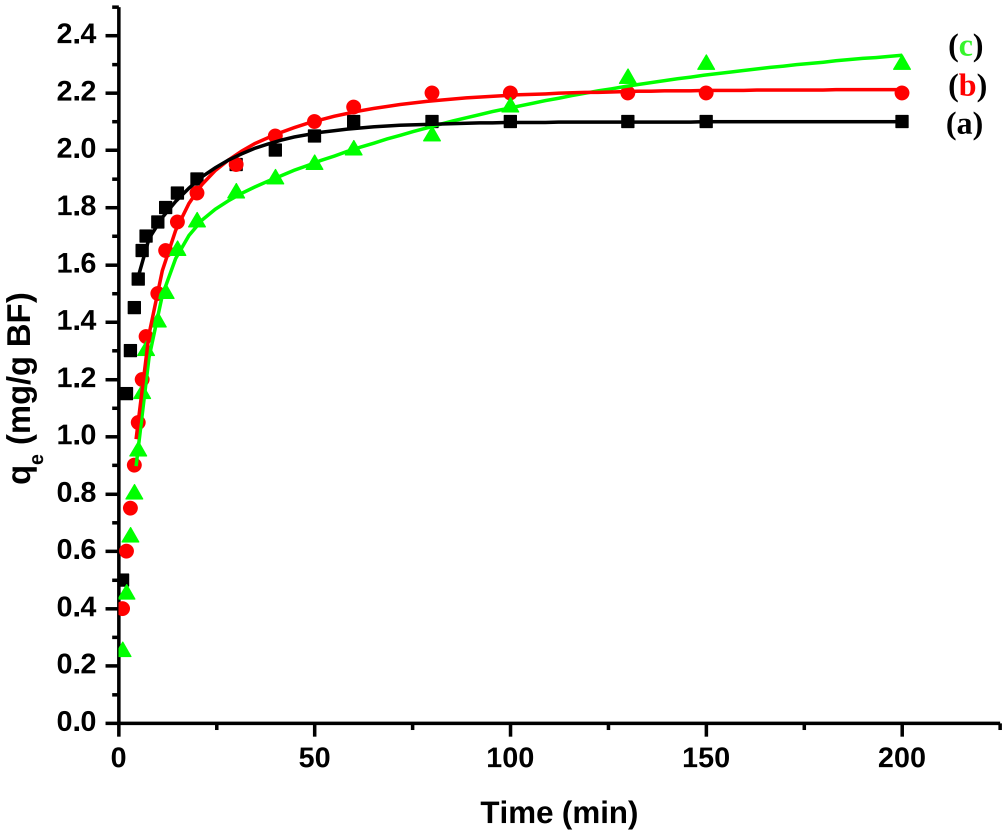


Figure 4.5 Effect of MLR of lac dye solution on adsorption capacity of lac dye on BFs: (a) MLR = 1:120, (b) MLR = 1:160, and (c) MLR = 1:200. Dyeing conditions are pH = 3, C_0 = 250 mg/L, dyeing time = 200 min and dyeing temperature = 30°C.

4.3.4 Effect of temperatures

The influence of dyeing temperatures at 30, 45 and 60 ºC on the adsorption of lac dye onto controlled and PEI-treated BFs are shown in Figures 4.6 and 4.7, respectively. For the controlled BFs dyeing system, the amount of dye adsorbed per gram BFs is different at different dyeing temperatures. At initial stage of the dyeing process, the adsorption rate increases with increasing dyeing temperature indicating a kinetically controlled process [91, 92]. Normally, the mobility of the dye molecule increase with temperature due to an increase in kinetic energy. At equilibrium, the amount of the dye adsorbed onto controlled BFs dyeing at higher temperature is lower than those of dyeing at lower dyeing temperature. This indicate the dyeing process is controlled by an exothermic process for the controlled BFs dyeing system. For PEI-treated BFs system, the increase in dyeing temperature slightly affect the adsorption capacity at temperature of 45°C and 60°C as shown in Figure 4.7. This is due to that the interaction effect between lac dye molecules and PEI-treated BFs is predominant. However, the highest adsorption capacity at equilibrium is observed at dyeing temperature of 30ºC.

In summary, the optimal conditions obtained from this study are pH = 3.0, C_0 = 250 mg/L, MLR = 1:200, dyeing time = 200 min and temperature = 30 ºC. These conditions are used for study of the kinetic and thermodynamics of lac dyeing on BFs.

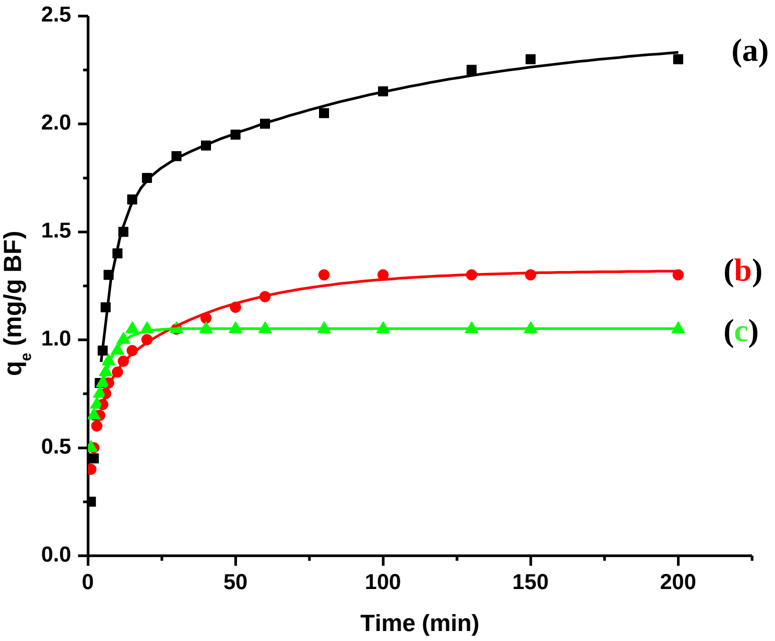


Figure 4.6 Effect of dyeing temperatures on adsorption capacity of lac dyeing on controlled BFs: (a) 30 ºC, (b) 45 ºC and (c) 60 ºC. Dyeing conditions are pH = 3, C_0 = 250 mg/L, MLR 1:200, dyeing time = 200 min.

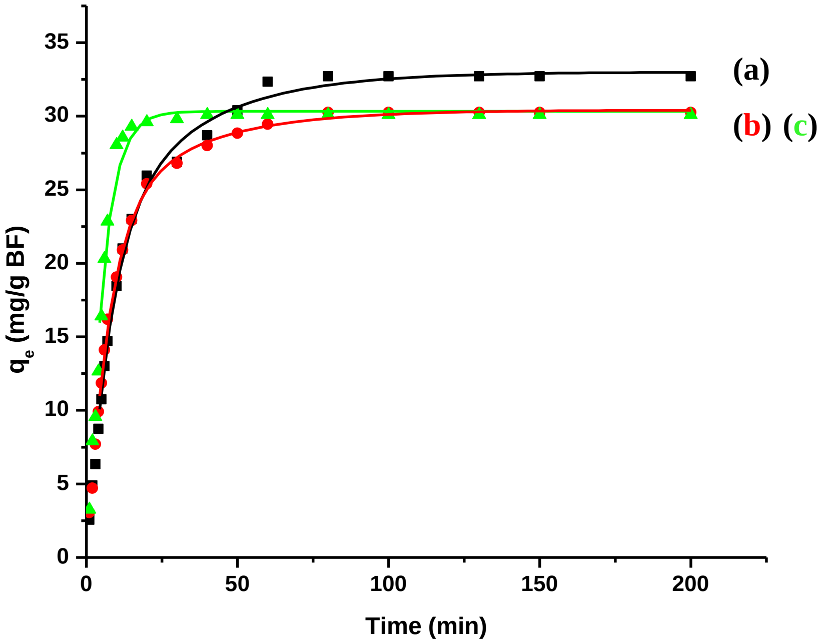


Figure 4.7 Effect of temperatures on adsorption capacity of lac dye on PEI-treated BFs: (a) 30 ºC, (b) 45 ºC and (c) 60 ºC. Dyeing conditions are pH = 3, C_0 = 250 mg/L, MLR 1:200, dyeing time = 200 min.

4.4. ATR-FTIR spectra of lac dyed BFs systems

For lac dyeing system, the FTIR spectrum of lac dyed on controlled BFs and PEI treated BFs are shown in Figure 4.8 Characteristic peaks of laccaic acids and erythrolaccin corresponding to C=O streching vibration absorption peak of ketone at 1639 cm^{-1}, O−H streching vibration absorption peak at 1421 cm^{-1} of phenol and O−H streching vibration at 3314 cm^{-1} of carboxyl grops in anthraquinone are observed. For lac dyed PEI-treated system, most of the absorption bands appears as same as those observed for controlled BFs . It is seen that the absorption peak of N-H bending group of the amine bands at 1573 cm^{-1} is diminished after dyeing (Figure 4.8b). The result indicates that the both of NH_2^+ and NH_3^+ of PEI can from the interaction with carboxyl group of lac dye electrostatic interactions schematically proposed in Figure 4.9. This interaction result in the diminution of N-H bending group as seen from no significant change in FTIR spectra of the lac dyed controlled- and PEI-treated BFs.

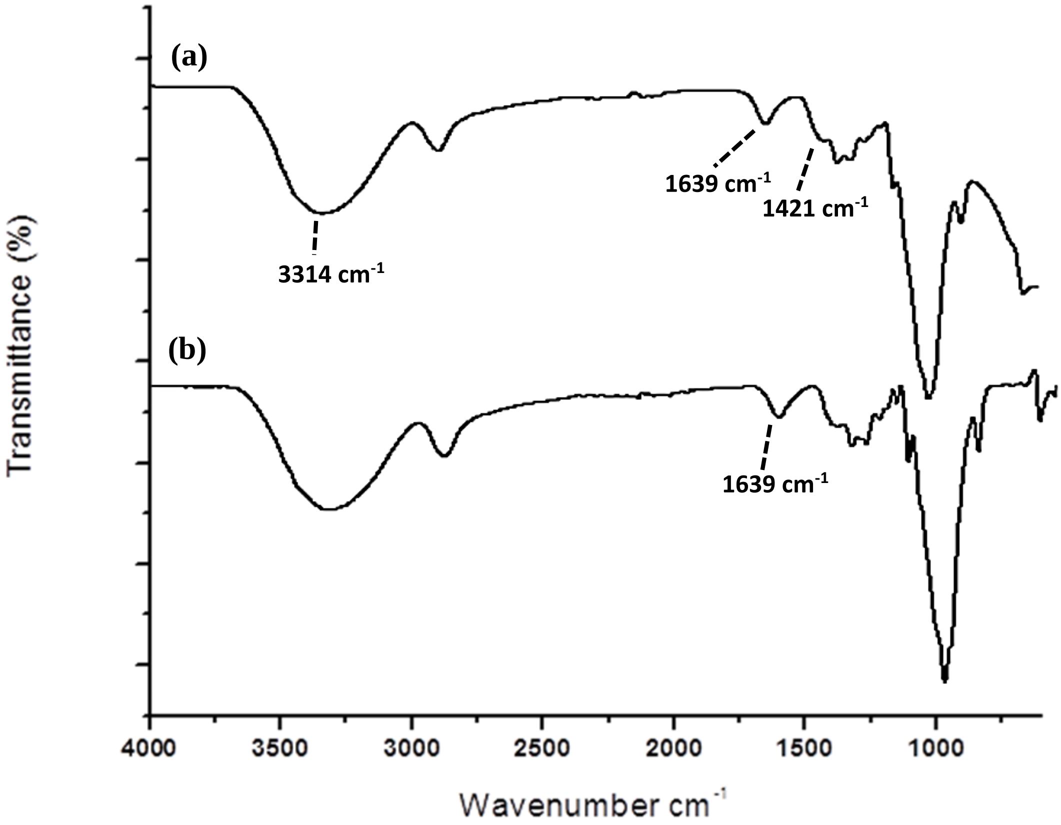


Figure 4.8 ATR-FTIR spectra of lac dyed BFs systems on (a) controlled and (b) PEI-treated BFs.

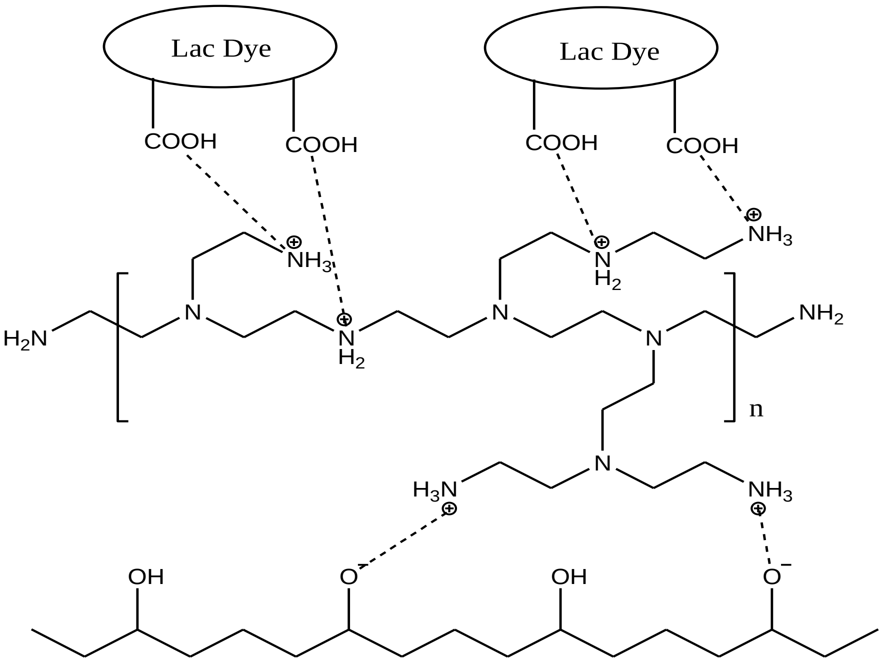


Figure 4.9 Proposed schematic diagram of BF–PEI–lac dye interaction.

4.5. Morphology of lac dyed BFs systems

The SEM micrographs of lac dyed BFs systems are illustrated in Figure 4.10. For the controlled BFs (Figure 4.10a) after dyeing with lac dye, the rough surface is clearly observed for both lac dyed BFs systems. Especially, larger rought surface area of the PEI- treated BFs is seen as shown in Figure 4.10b indicating the better adsorption ability of controlled BFs.

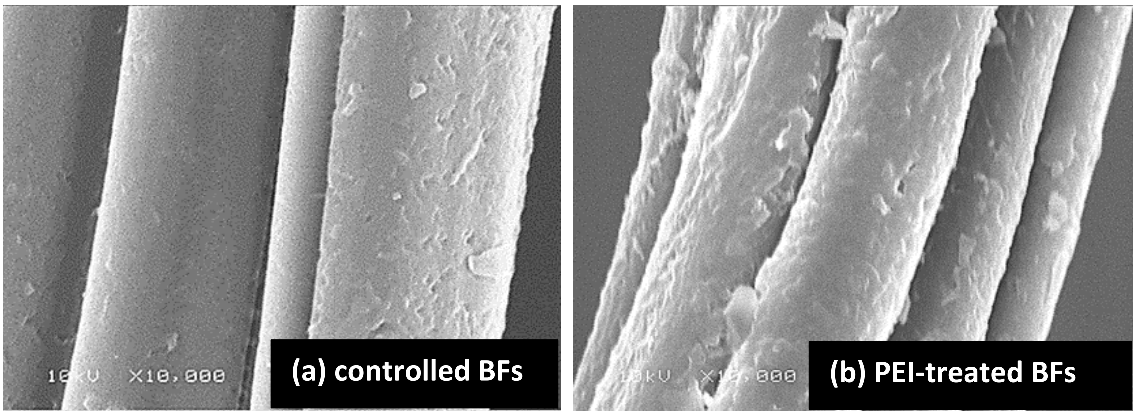


Figure 4.10 SEM micrographs of lac dyed BFs systems on (a) controlled and (b) PEI-treated BFs.

Figure 4.11 shows optical image of controlled (Figure 4.11a) and PEI treated BFs after dyeing in comparison with undyed system. For lac dyeing system, the adsorption capacity of lac dye absorb on PEI treated BFs (Figure 4.11c) significantly increases when compared with the controlled BFs (Figure 4.11b), as seen from the progressing increase in integrity of color.

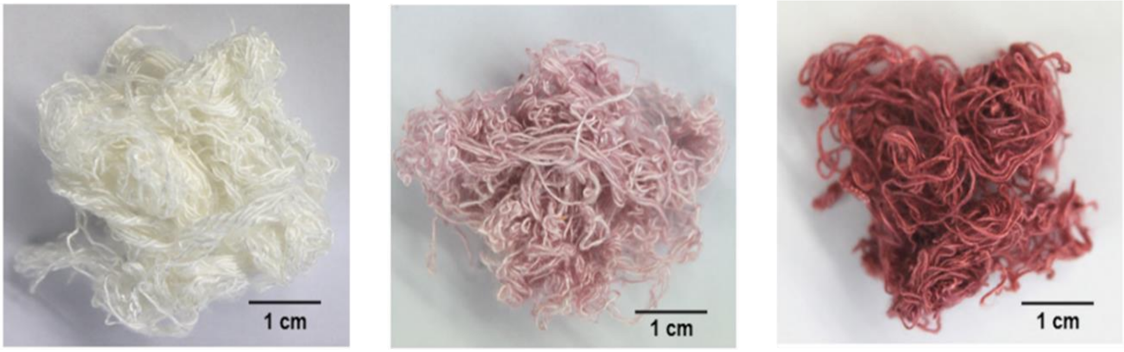


Figure 4.11 Images of controlled BFs (a), controlled BFs dyed with lac (b), and PEI-treated BFs dyed with lac (c). The dyeing conditions are C_0 = 500 mg/L, pH = 3, MLR = 1:200, dyeing temperature = 30°C and dyeing time = 200 min).

4.6 Adsorption isotherms

4.6.1 Langmuir isotherm

The equilibrium adsorption isotherm is fundamental in describing the interaction behaviour between solutes and adsorbents, and is important in the design of an adsorption system [93]. Figures 4.12 and 4.13 show the linear plots of $1/qe$ versus $1/Ce$ obtained from Langmuir equation this model for the controlled BFs and PEI treated BFs systems, respectively. The values of Q (the maximum amount of the dye per unit weight of fiber to form complete monolayer coverage on the surface) and b the Langmuir constant related to the affinity of binding sites are respectively calculated from the intercepts and slopes of different straight lines. The experimental data for the adsorption of lac dye on BFs were fitted to a linear form of Langmuir isotherm (Eq. 2.3). The data for the adsorption of lac dyeing on controlled BFs and PEI treated BFs at 30, 45 and 60 ºC are listed in Tables 4.1. From the data in shown table 4.1, it is found that the adsorption capacity (Q) of lac dye at higher temperature decreased with increasing temperature indicating that the process is exothermic. The good fit is observed for the adsorption data of lac dye onto controlled BFs and PEI treated BFs at 30, 45 and 60 ºC (correlation coefficient, $R^2 > 0.99$). As expected for exothermic process, the *Q* values decrease with increasing temperature. Morever, the *b* values indicated that the controlled BFs and PEI treated BFs has a maximum affinity for lac dye at lower temperature.

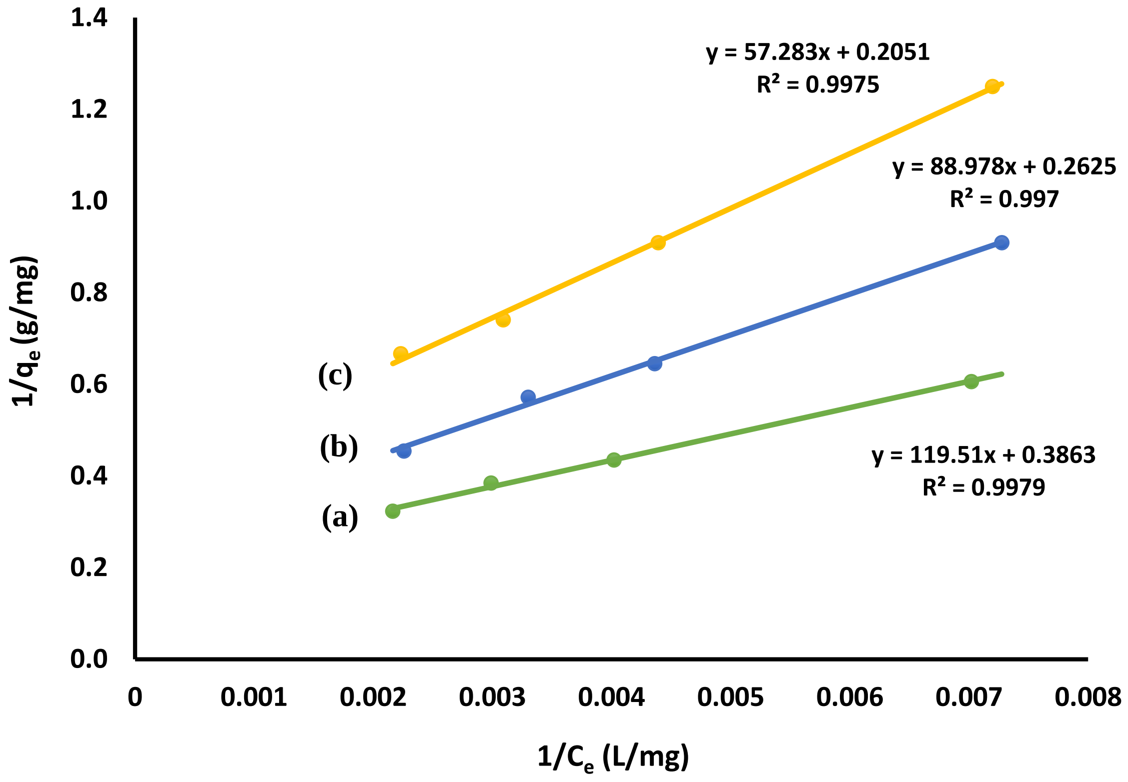


Figure 4.12 The Langmuir adsorption isotherms of lac dye onto controlled BFs under dyeing temperatures of (a) 30 ºC, (b) 45 ºC and (c) 60 ºC.

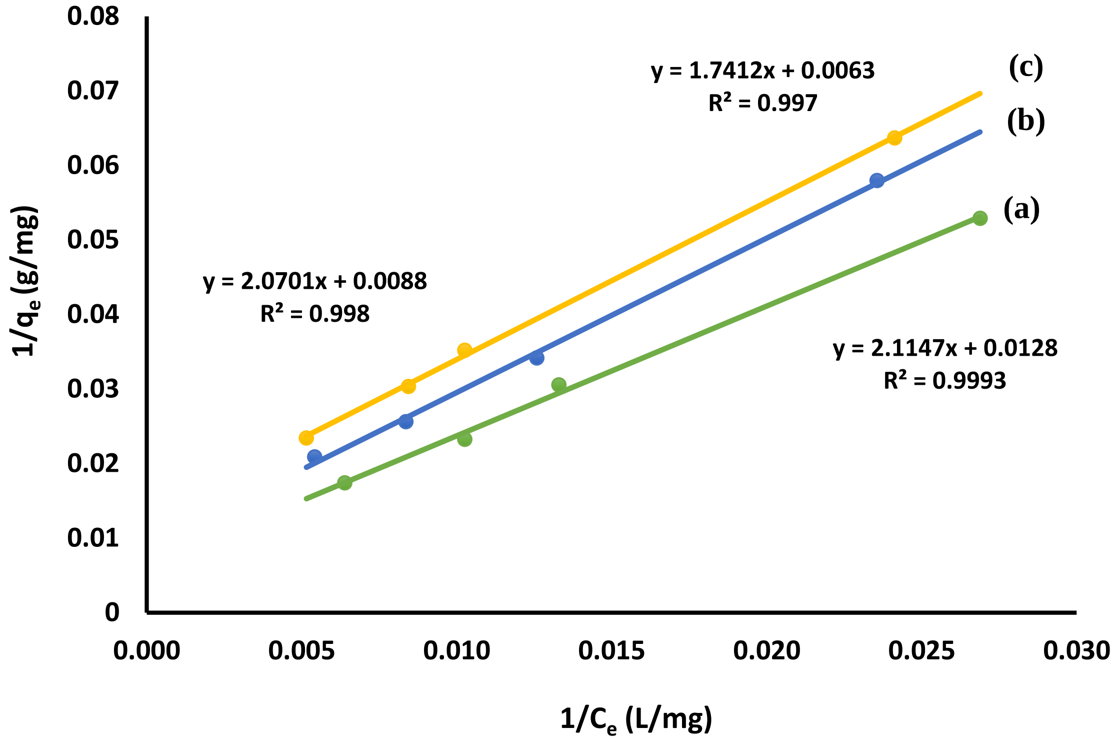


Figure 4.13 The Langmuir adsorption isotherms of lac dyed onto PEI treated BFs under dyeing temperatures of (a) 30 ºC, (b) 45 ºC and (c) 60 ºC.

Table 4.1 The Langmuir adsorption isotherm of lac dye onto PEI treated BFs.

Temperature (°C)	***Q* (mg/g)**	***b***	***R*^{2}**
Untreated system			
30	4.88	3.58×10^{-3}	0.9979
45	3.81	2.95×10^{-3}	0.9970
60	2.59	3.23×10^{-3}	0.9975
PEI-treated system			
30	158.73	3.62×10^{-3}	0.9970
45	113.64	4.25×10^{-3}	0.9980
60	78.13	6.05×10^{-3}	0.9993

4.6.2 Freundlich isotherm

The Freundlich equation was also applied for the adsorption of lac dyeing by the equation (2.6). The linear plots of ln q_e versus ln C_e is shown in Figure 4.14 for the controlled BFs and Figure 4.14 for PEI treated BFs. The Q_f and 1/*n* can be respectively determined from intercept and slope of the plot as listed in Table 4.2. The magnitude of the exponent 1/*n* gives an indication of the favourability of adsorption. Values, of $n > 1$ obtained represent favourable adsorption conditions [94]. The Q_f values decreased with increasing temperature which again supported an exothermic process. The Freundlich equation is not likely fit well with the experimental data, when compared with the Langmuir equation as seen from the lower correlation coefficient ($R^2 > 0.98$) obtained from Fruendlich isotherm.

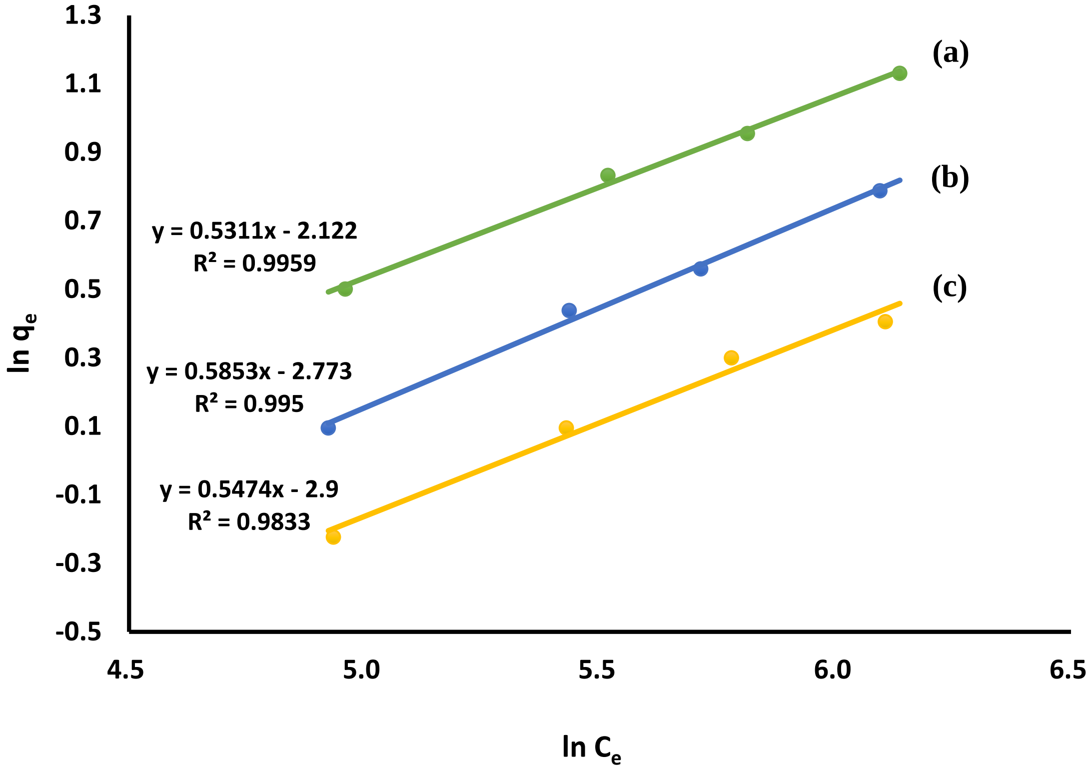


Figure 4.14 The Freundlich adsorption isotherms of lac dyed onto controlled BFs under dyeing temperatures of (a) 30 ºC, (b) 45 ºC and (c) 60 ºC.

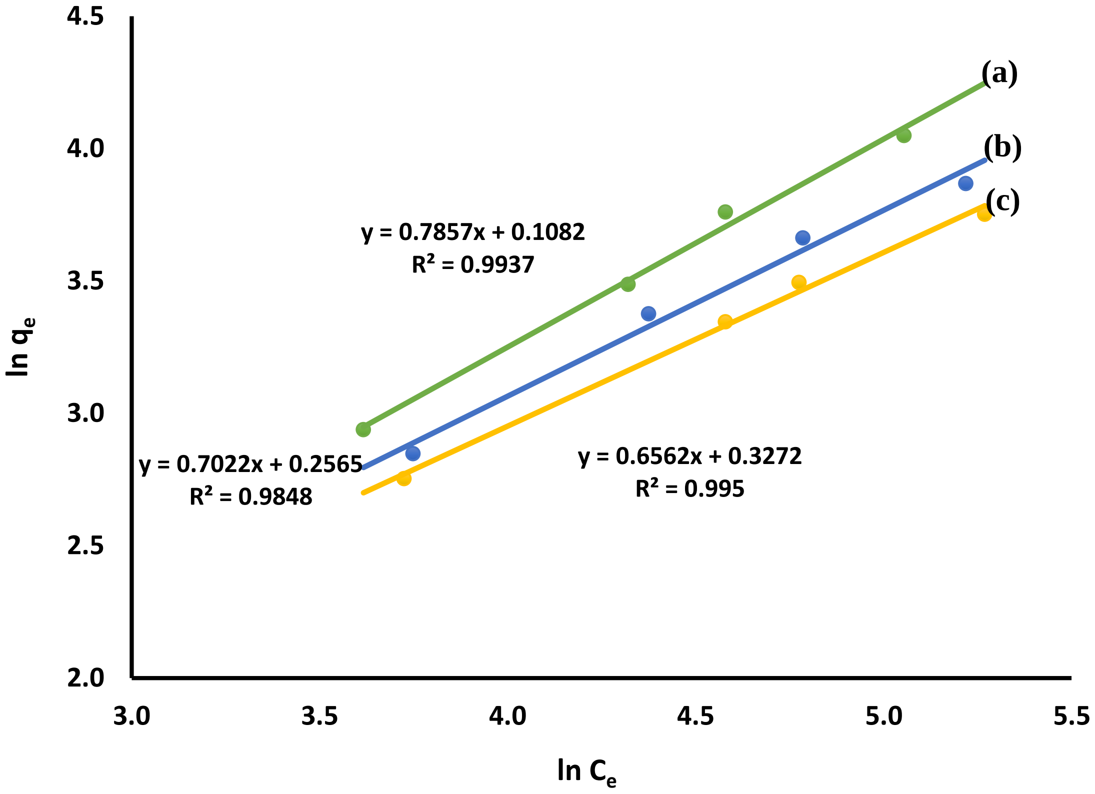


Figure 4.15 The Freundlich adsorption isotherms of lac dyed onto PEI treated BFs under dyeing temperatures of (a) 30 ºC, (b) 45 ºC and (c) 60 ºC.

Table 4.2 The Freundlich adsorption isotherm of lac dye onto PEI treated BFs.

Temperature (°C)	Q_f (mg/g)	*n*	R^2
Untreated system			
30	0.12	1.88	0.9959
45	0.06	1.71	0.9950
60	0.05	1.83	0.5883
PEI-treated system			
30	1.11	1.27	0.9937
45	1.29	1.42	0.9848
60	1.39	1.52	0.9950

4.7 Kinetics of adsorption

4.7.1 Pseudo-first-order kinetics

Lagergren's pseudo first order kinetics of adsorption [95] corresponding to equation (2.8) is firstly studied. A straight line of ln (q_e - q_t) versus t suggests the applicability of this kinetic model to fit the experimental data. The first-order rate constant k_1 and equilibrium adsorption capacity q_e (cal) at three different temperatures were calculated from the slope and intercept as shown in Figures 4.16 - 4.17. The calulated kinetic parameters are presented in table 4.3. The lac dyeing onto BFs is considered to be pseudo first-order with high correlation coefficients above 0.99 at 30°C as shown in Fig. 4.16. In addition, the q_e which is the adsorption capacity, agreed very well with both experiment and calculation as listed in Table 4.3.

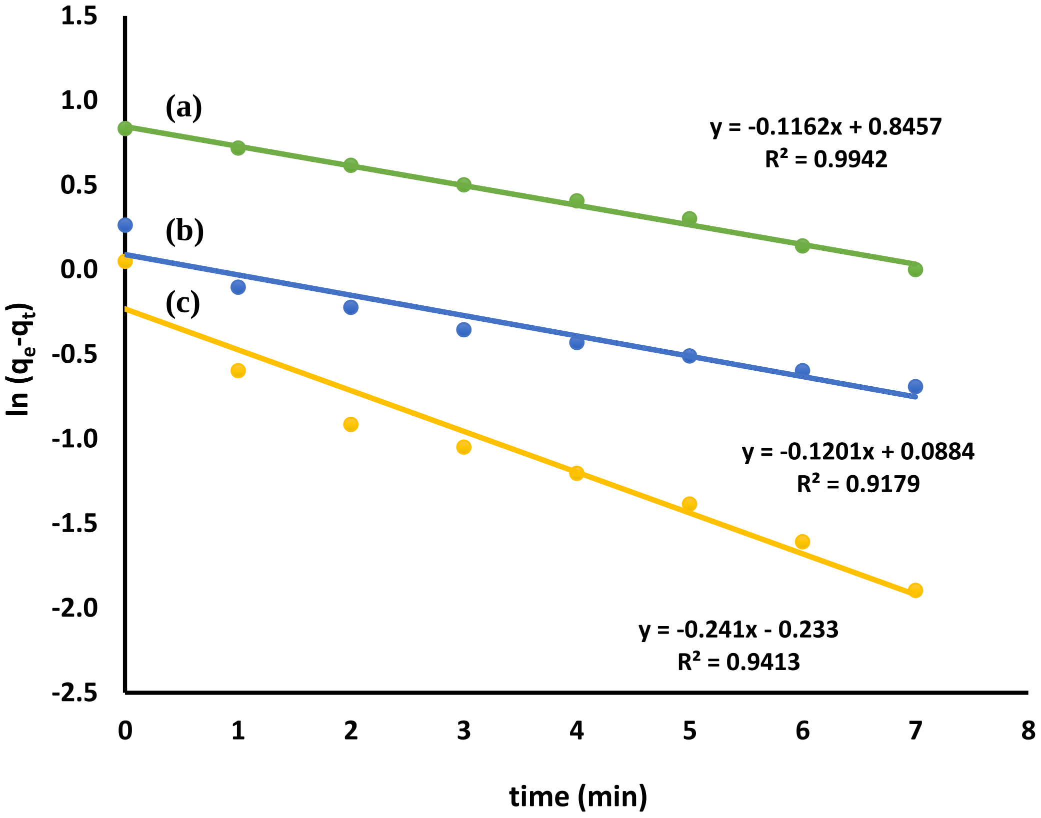


Figure 4.16 Plot of the pseudo-first-order kinetics for lac dye onto controlled BFs under dyeing temperatures of (a) 30 ºC, (b) 45 ºC and (c) 60 ºC.

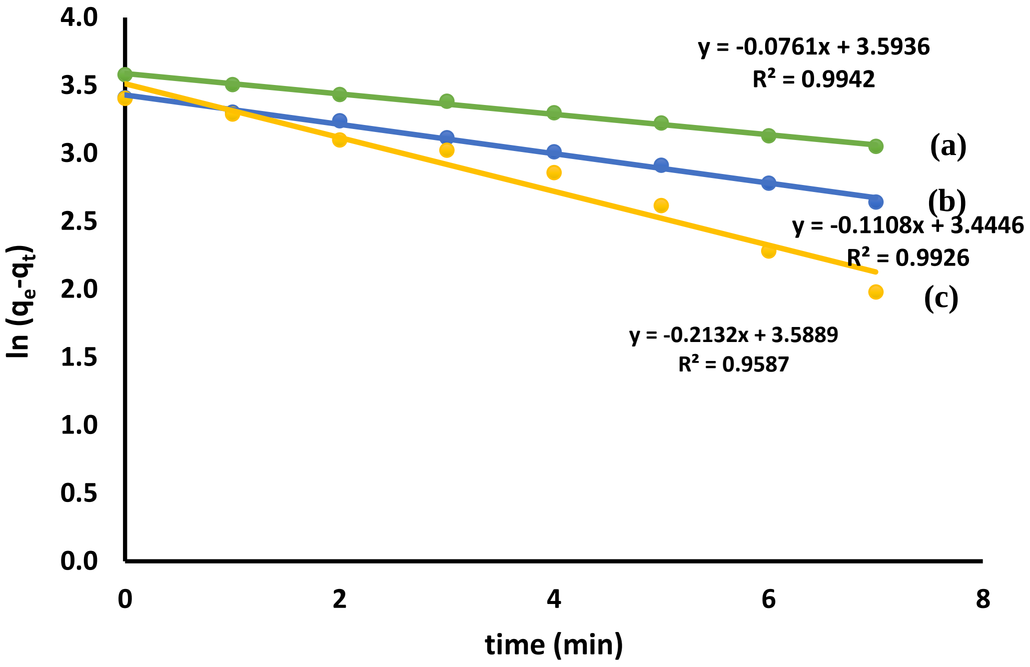


Figure 4.17 Plot of the pseudo-first-order kinetics for lac dye onto PEI treated BFs under dyeing temperatures of (a) 30 ºC, (b) 45 ºC and (c) 60 ºC.

4.7.2 Pseudo-second-order kinetics

The pseudo second-order kinetic model expressed by the equation (2.10) is also applied for kinetic investigation. The plots of pseudo second-order kinetics are shown in Figure 4.18 for controlled BFs and 4.19 for PEI treated BFs dyeing system. The slope and intercept from the plot of (t/q_t) versus t are the pseudo secondorder rate constant (k_2) and q_e, respectively [96]. The kinetic parameters obtained from the plots are shown in Table. 4.3. The correlation coefficients for the pseudo second-order kinetic model for controlled BFs and for PEI treated BFs are mostly less than those of the pseudo first-order kinetic model. However, a large difference in equilibrium adsorption capacity (q_e) between the experiment and calculation is observed, indicating that the adsorption behavior is not likely to be a pseudo second-order. The calulated kinetic are as presented in Table 4.3. Lac dyeing onto controlled BFs and PEI treated BFs is considered to be pseudo first-order as seen from high correlation coefficients for controlled BFs and PEI treated BFs. In addition, the calculated value of q_e is nearly the same as experimental value. The obtained results indicate that the adsorption behavior follows the pseudo first-order kinetics.

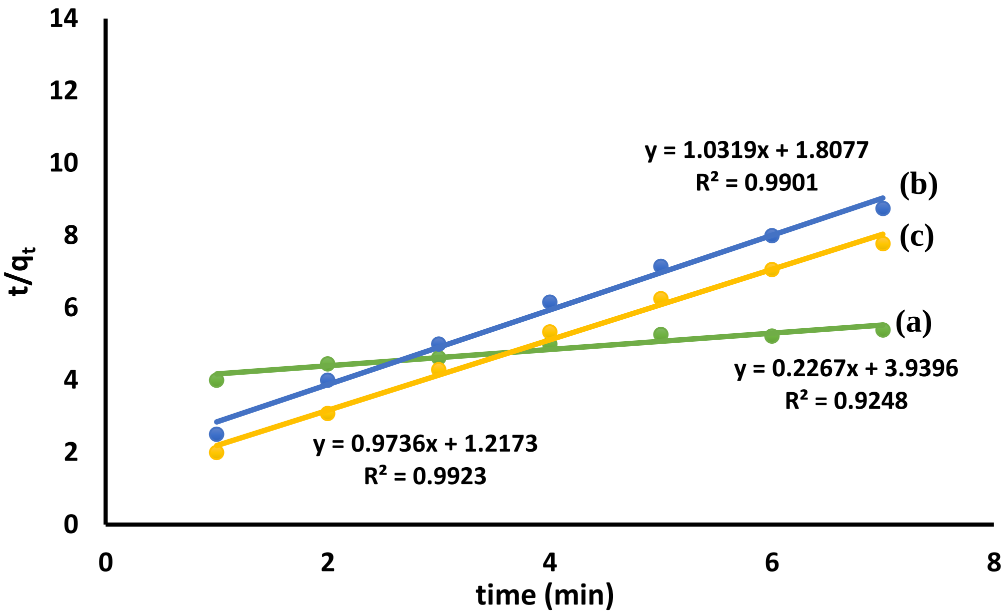


Figure 4.18 Plot of the pseudo-second-order kinetics for lac dyed onto controlled BFs under dyeing temperatures of (a) 30 ºC, (b) 45 ºC and (c) 60 ºC.

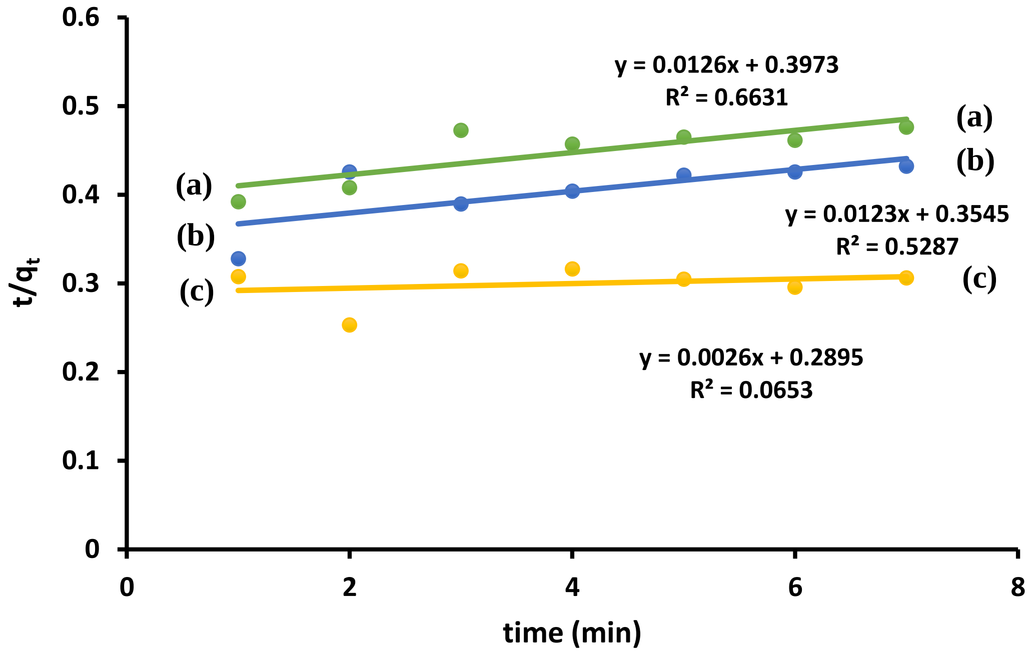


Figure 4.19 Plot of the pseudo-second-order kinetics for lac dyed onto PEI treated BFs under dyeing temperatures of (a) 30 ºC, (b) 45 ºC and (c) 60 ºC.

Table 4.3 The kinetic parameter of calculated using pseudo-first- and pseudo-second-order models.

Kinetics parameter	**Pseudo-first-order model**			**Pseudo-second-order model**		
	30 ºC	**45 ºC**	**60 ºC**	**30 ºC**	**45 ºC**	**60 ºC**
Untreated system						
q_e, exp	2.30	1.30	1.05	2.30	1.30	1.05
q_e, cal	2.24	1.03	0.74	1.00	1.07	3.23
k_1	1.01×10^{-1}	0.97×10^{-1}	2.16×10^{-1}	-	-	-
k_2	-	-	-	5.22×10^{-1}	6.52×10^{-1}	0.26×10^{-1}
R^2	0.9942	0.9179	0.9412	0.9901	0.9923	0.9248
PEI-treated system						
q_e, exp	32.70	30.25	30.10	32.70	30.25	30.10
q_e, cal	36.11	30.61	44.98	70.42	60.60	161.29
k_1	0.74×10^{-1}	1.04×10^{-1}	2.78×10^{-1}	-	-	-
k_2	-	-	-	5.15×10^{-4}	7.99×10^{-4}	1.39×10^{-4}
R^2	0.9942	0.9926	0.9587	0.8345	0.7746	0.4086

4.8 Thermodynamics of adsorption

4.8.1 Determination of activation energy

As discussed above, the adsorption behavior is likely to obey the the pseudo first-order adsorption mechanism. The rate constant (k_1) at different temperatures listed in Table 4.4 are then applied to estimate the activation energy of the adsorption of lac dyeing on bamboo fiberss by the Arrhenius equation (Equation 13). The slope of the plot of ln k_1 versus 1/T (Figure 4.17) is used to evaluate E_a. For controlled BFs and PEI treated BFs system, R^2 obtained from the calculation are high enough. So, the values of calculated activation parameters are reliable. The rate constants (k_1) are found to respectively increase with increasing temperature. The E_a of the PEI treated BFs system is much higher than that of the controlled BFs system. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5–40 kJ/mol while higher activation energies (40–800 kJ/mol) suggest chemisorption [97]. It is seen that, the value of activation energy of the treated BFs system (36.74 kJ/mol) increases as compared with the controlled system (20.94 kJ/mol). This means that the treated BF system still behave physisorption. However, the increase in E_a value of the treated system indicates that the treated system nearly approaches to the chemisorption.

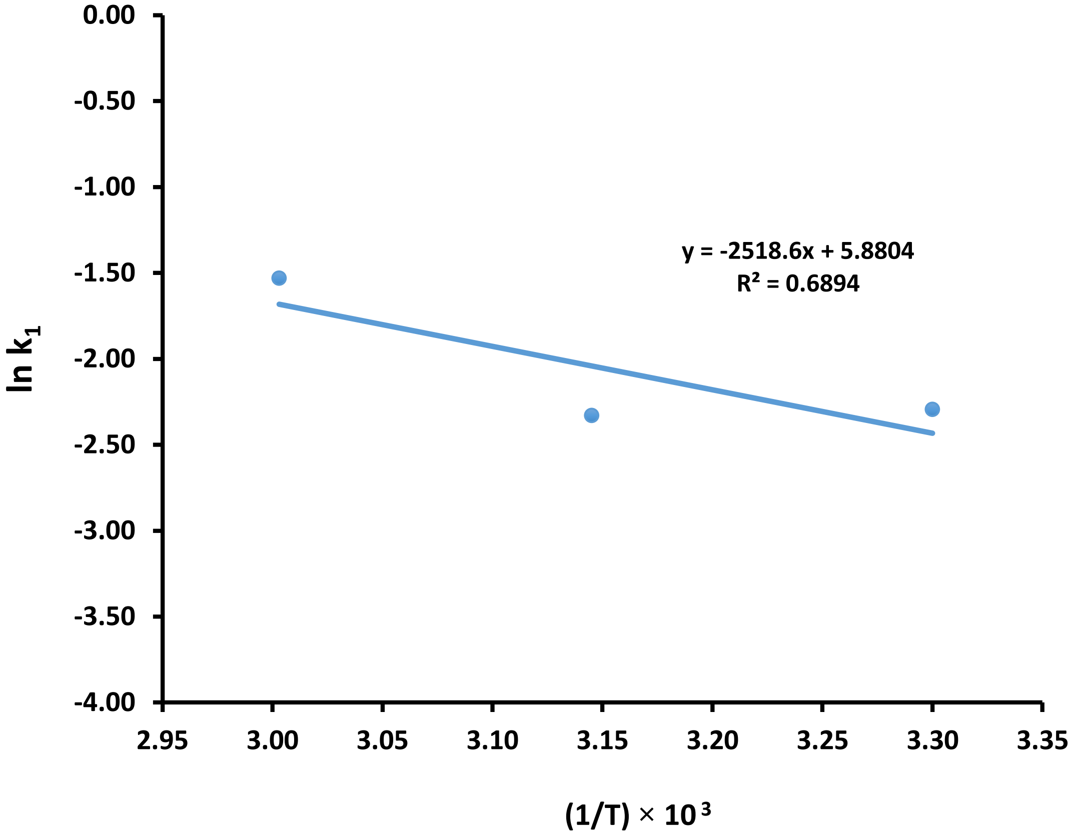


Figure 4.20 Arrhenius plots for the adsorption of lac dyed onto controlled BFs.

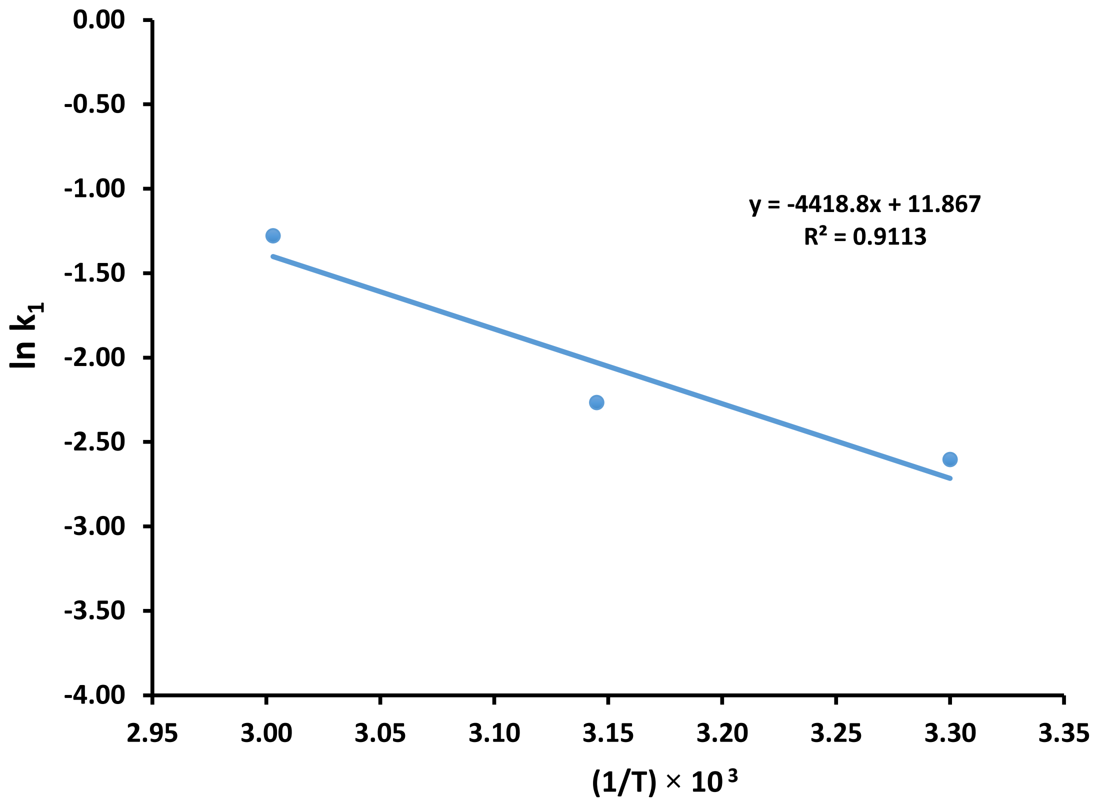


Figure 4.21 Arrhenius plots for the adsorption of lac dye onto PEI treated BFs.

Table 4.4 The activation parameters for the adsorption of lac dyeing on untreated and PEI treated BFs at 30°, 45° and 60°C.

Temperature (°C)	**Untreated BF system**			**PEI-treated BF system**		
	k_1	E_a (kJ/mol)	R^2	k_1	E_a (kJ/mol)	R^2
30°C	0.1009	20.94	0.6894	0.0740	36.74	0.9113
45°C	0.0973			0.1038		
60°C	0.2163			0.2784		

4.8.2 Determination of thermodynamics parameters

From the Eyring equation [98], the enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation can be calculated from the slope and intercept of a plot of ln (k_1/T) versus 1/T (Figure 4.20). According to equation 14, the value of $\Delta G^{\#}$ can be calculated. The results of all activation parameters are shown in Table 4.5. It is seen that for the controlled and PEI-treated systems, the negative values of $\Delta H^{\#}$ obtained indicates that lac dye adsorption is an exothermic process and the positive values of $\Delta G^{\#}$ indicates that lac dye adsorption is non spontaneous process while the negative entropy value ($\Delta S^{\#}$) reflects the interaction between lac dye and BFs.

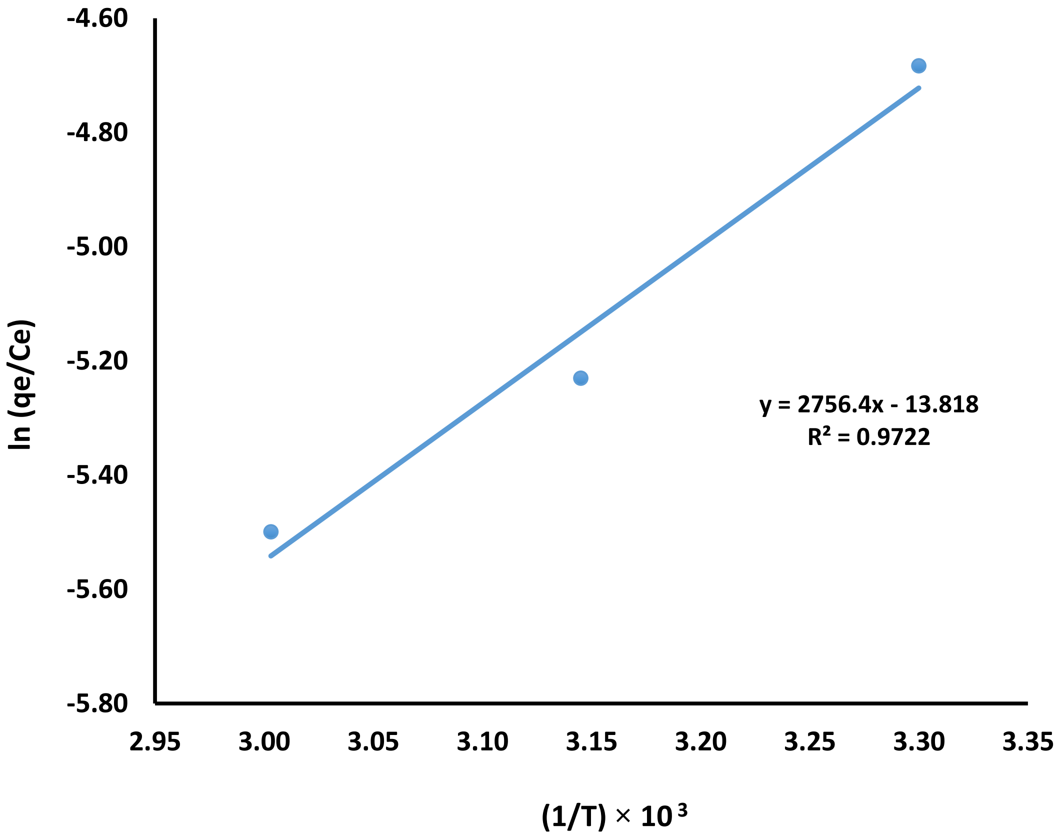


Figure 4.22 Van’t Hoff plot for the adsorption of lac dye onto controlled BFs.

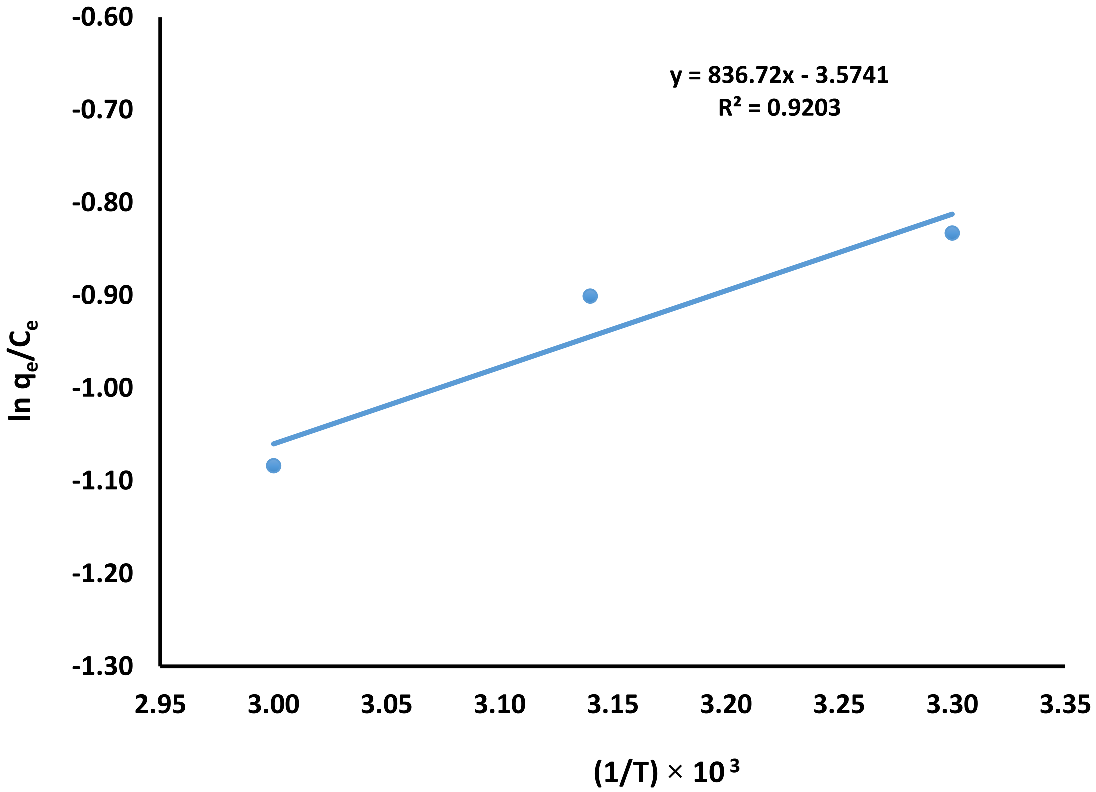


Figure 4.23 Van't Hoff plot for the adsorption of lac dye onto PEI treated BFs.

Table 4.5 Thermodynamic parameters for the adsorption of lac dyeing on untreatedand PEI treated BFs at 30°, 45° and 60°C.

T (°C)	Untreated BF system				PEI-treated BF system			
	$\Delta G^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/molK)	$\Delta H^{\#}$ (kJ/mol)	R^2	$\Delta G^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/molK)	$\Delta H^{\#}$ (kJ/mol)	R^2
30°	11.89	-114.88	-22.92	0.9722	2.05	-29.72	-6.96	0.9203
45°	13.62				2.49			
60°	15.34				2.94			

4.9 Fastness properties

Fastness testing for test the fastness properties of lac dye on controlled BFs and PEI-treated BFs were examined followed from ISO (International Organization for Standardization). The color fastness to washing ISO 105-C10 : 2006 (E) at 40 °C, 30 min used stand soap solution 5 g/L was carried out. From the result of color change as shown in table 4.6, it is found that the staining ability of lac dyed for PEI-treated BFs are slightly better than those for controlled BFs.

Table 4.6 The color fastness to water and to washing of lac dyed BFs systems for controlled and PEI-treated BFs.

	Controlled BFs		PEI-treated BFs	
	to water	to washing	to water	to washing
Color change (Rating)	4	1-2	4-5	2
Color staining (Rating)	4-5	4-5	4-5	4-5
- Acetate	4-5	4-5	4-5	4-5
- Cotton	4-5	4-5	4-5	4
- Nylon	4-5	4-5	4-5	4-5
- Polyester	4-5	4-5	4-5	4-5
- Acrylic	4-5	4-5	4-5	4-5
- Wool	4-5	4-5	4-5	4-5

* Rating for color fastness have 5 levels as the followed: 5 = No color change / staining, 4 = Slightly color change / staining, 3 = Noticeable color change / staining, 2 = Considerable color change / staining, 1 = Excessive color change / staining.

4.10 Comparision of adsorption capacity between untreated and PEI-treaeted bamboo fibers.

BFs are negatively charged due to the presence of carboxyl and hydroxyl-groups [99], whereas the lac dye has hydroxyl-groups and carboxylic group in molecule and therefore also presents a negative charge [100]. Hence, the binding of the negatively charged dye molecules to the fibers is not favoured electrostatically, attempts to improve the surface of BFs were undertaken [101]. Therefore, in this work PEI as a mordant for enhancement the adsorption capacities of lac dye on BFs was used. From the present result, it is found that the use of PEI as amordant can improve the adsorption capacities of lac dye on BFs. In order to compare the results of adsorption capacities, the dye adsorbed per gram on BFs for controlled and PEI-treated BFs are shown in Figure 4.24. The adsorption capacities with a present of PEI can be improved up to ~ 20 times that of the controlled system.

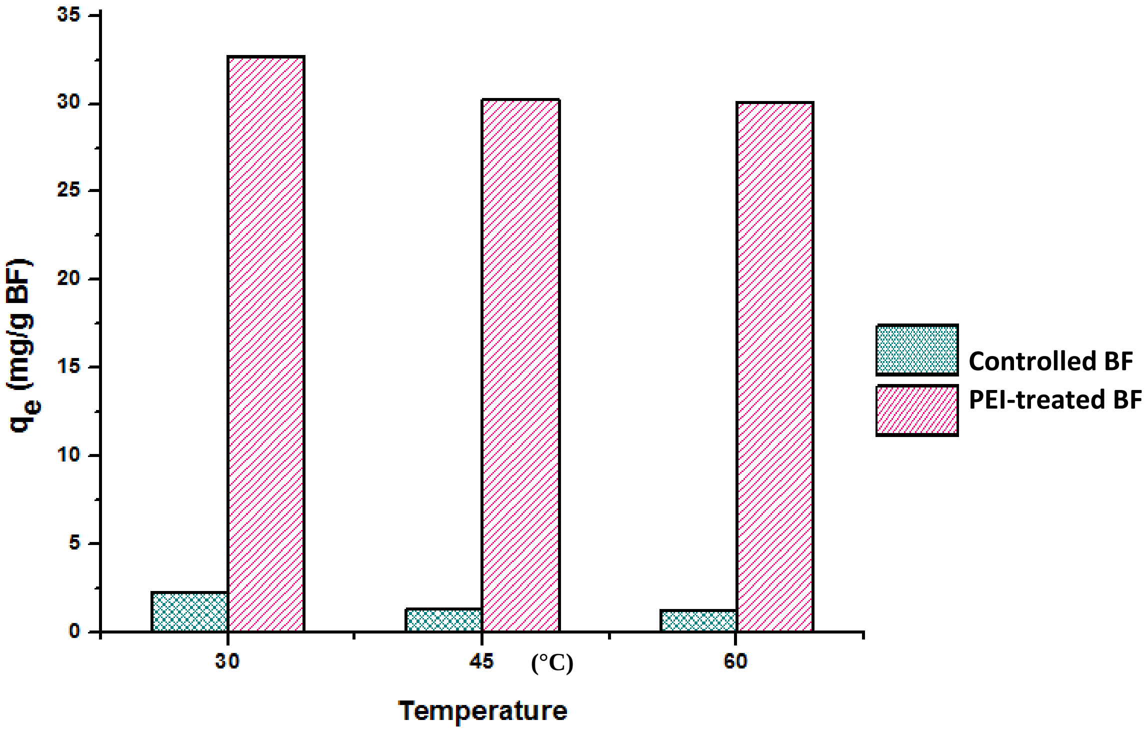


Figure 4.24 Effect of PEI on the adsorption of lac dye onto controlled BFs and PEI-treated BFs.

CHAPTER 5

CONCLUSIONS

In this work, the effect of polyethyleneimine (PEI) as a mordant on adsorption behavior of lac dyeing on bamboo fibers was investigated. The effects of pH, dyeing temperature, material to liquor ratio (MLR), contact time and initial lac dye concentration on adsorption capacity were studied. The isotherm, kinetics and thermodynamics of the adsorption were also investigated. The conclusions of the present study can be drawn as follows:

1. The optimum conditions of lac dyeing on BFs was found as pH = 3, initial dye concentration = 250 mg/L, MLR = 1:200, dyeing time = 200 min and dyeing temperature = 30°C.

2. The FTIR band of PEI-treated BFs at 1573 cm^{-1} confirmed the achievement of treatment. However, the same peak is disappeared for lac-dyed PEI-treated BFs.

3. The use of PEI as a mordant significantly improved the adsorption capacity of lac dye. The adsorption capacity at equilibrium was about 20 times that of the controlled system.

4. Rough surface was clearly observed for the untreated BFs whereas the controlled BFs surfaces became smoother. After dyeing with lac dye, the rough surface using from the coating of lac dye was clearly observed.

5. The adsorption behavior was found to fit well with Langmuir isotherm. The adsorption were kinetics likely to be pseudo-first-order reaction.

6. The adsorption behavior indicated a kinetically controlled process. From thermodynamic studies, the physisorption, exothermic and non-spontaneous processed were observed.

REFERENCES

REFERENCES

[1] Yamada S, Noda N, Mikami E, Hayakawa J, Yamada M. Analysis of natural coloring matters in food: III. Application of methylation with diazomethane for the detection of lac color. *Journal of the Association of Official Analytical Chemists* 1989; 72(1): 42-51.

[2] Chairat M, Rattananaphani S, Bremner JB, Rattanaphani V. An adsorption and kinetic study of lac dyeing on silk. *Dyes and Pigments* 2005; 64: 231-241.

[3] Moeyes M. Natural dyeing in Thailand, White Lotus, Bangkok 1993.

[4] Satindarl K, Chattopadhyay DP, Varinder K. Dyeing of Bamboo with Tea as a natural Dye. *Research Journal of Engineering Sciences* 2012; 1(4): 21-26.

[5] Rathod A, Kolhatkar A. Analysis of physical characteristics of bamboo fabrics. *Research in Engineering and Technology* 2014; 3: 21-25.

[6] Vankar PS. Chemistry of natural dyes, *Resonance* 2000; 5: 73-80.

[7] Gulrajani ML. Introduction to Natural Dyes, Indian Institute of Technology, New Delhi 1992.

[8] Gulrajani ML, Gupta D. Natural Dyes and their Application to Textiles, Indian Institute of Technology, New Delhi 1992.

[9] Shanker R, Vankar PS. Ecofriendly ultrasonic natural dyeing of cotton fabric with enzyme pretreatments, *Desalination* 2008; 230: 62-69.

[10] Vankar PS, Shanker R, Verma A. Enzymatic natural dyeing of cotton and silk fabrics without metal mordants, *Journal of Cleaner Production* 2007; 15: 1441-1450.

[11] Janhom s, Griffiths P, Watanesk R, Watanesk S. Enhancement of lac dye adsorption on cotton fibres by poly(ethyleneimine), *Dyes and Pigments* 2004; 63: 231-237.

[12] Gowan JW. Polyakylene imide of high brightness and retention characteristics and low toxicity and method of increasing paper whiteness, Westvaco Corporation, New York 1991.

[13] DeMejo LP, Pavlisko JA. Polyethyleneimine containing toner compositions, Eastman Kodak Company, New York 1991.

[14] Hansen MR, Young PH. Method for densifying fibers using a dentifying agent, Eyerhaeuser Company, Washington 1996.

[15] DiStefano FV. Cellulosic nonwoven products of enhanced water and/ or solvent resistance by pretreatment of the cellulosic fibers, Air Products and Chemicals, New York 1989.

[16] Moody V, Needles HL. Tufted carpet textile fibers, dyes, finishes, and processes, William Andrew, New York 2004.

[17] Needles HL. Textile fibers, dye, finishes, and processes, Noyes Publications, New Jersey 1986.

[18] Waite M. Sustainable textiles: the role of bamboo and comparison of bamboo textile properties, *Journal of Textile and Apparel Technology and Management* 2009; 6: 1-21.

[19] Farrelly D. The book of bamboo: a comprehensive guide to this remarkable plant, its uses, and its history. Thames and Hudson, London 1984.

[20] Jain S, Kumar R, Jindal UC. Development and fracture mechanism of the bamboo/polyester resin composite. *Journal of Materials Science Letters* 1993; 12: 558-560.

[21] Rajulu AV, Baksh SA, Reddy GR, Chary KN. Chemical resistance and tensile properties of short bamboo fibre reinforced epoxy composites. *Journal of Reinforced Plastics and Composites* 1998; 17: 1507-1511.

[22] Lobovikov M, Shyam P, Piazza M, Ren H, Wu J. Non-wood forest products 18 world bamboo resources. A thematic study prepared in the framework of the Global Forest Resources Assessment. Rome: Food and Agriculture Organization of the United Nations 2007.

[23] Das M, Chakraborty D. Influence of alkali treatment on the fine structure and morphology of bamboo fibres. *Journal of Applied Polymer Science* 2006; 102: 5050-5056.

[24] Yao W, Zhang W. Research on manufacturing technology and application of natural bamboo fibre. In: 4th international conference on intelligent computation technology and automation, Guangdong 2011.

[25] Wang YP, Wang G, Cheng HT. Structures of bamboo fibre for textiles. *Textile Research Journal* 2010; 84: 334-343.

[26] Li LJ, Wang YP, Wang G, Cheng HT, Han XJ. Evaluation of properties of Natural bamboo fibre for application in summer textiles. *Journal of Fiber Bioengineering and Informatics* 2010; 3: 94-99.

[27] Wang X, Ren H, Zhang B, Fei B, Burgert I. Cell wall structure and formation of maturing fibres of moso bamboo (Phyllostachys pubescens) increase buckling resistance. *Journal of the Royal Society Interface* 2011; 9: 988-996.

[28] Murphy RJ, Alvin KL. Variation in fibre wall structure in bamboo. *The International Association of Wood Anatomists Bulletin* 1992; 13: 403-410.

[29] Gritsch CS, Kleist G, Murphy R. Developmental changes in cell wall structure of phloem fibres of the bamboo Dendrocalamus asper. *Annals of Botany* 2004; 94: 497-505.

[30] Parameswaran N, Liese W. Ultra structural aspects of bamboo cells. *Cellulose Chemistry and Technology* 1980; 14: 587-609.

[31] Parameswaran N, Liese W. On the fine structure of bamboo fibres. *Wood Science and Technology* 1976; 10: 231-246.

[32] Higuchi T. Chemistry and biochemistry of bamboo. *Journal of Bamboo Research* 1987; 4: 132-145.

[33] Ishii T, Hiroi T. Linkage of phenolic acids to cell-wall polysaccharides of bamboo shoot. *Carbohydrate Research* 1990; 206: 297-310.

[34] Osorio L, Trujillo E, Van AW, Verpoest I. Morphological aspects and mechanical properties of single bamboo fibres and flexural characterization of bamboo/epoxy composites *Journal of Reinforced Plastics and Composites* 2011; 30; 396-408.

[35] Tamizi MBM. Fundamental and characteristic study of cultivated malaysian bamboo selective genus Gigantochloa, Ph.D thesis, Universiti Sains Malaysia 2011.

[36] Das S. Properties of bamboo fiber, Textile Technology 1997.

[37] Tech M. End uses of bamboo fiber, Textile Technology 1986.

[38] Zollinger H. Colour Chemistry, (2nd ed.), New York: VCH 1991.

[39] Christie RM, Mather MM, Wardman RH. The Chemistry of Colour Application, Oxford: Blackwell Science 2000.

[40] Christie RM. Colour Chemistry, Cambride: Royal Society of Chemitry 2001.

[41] Bhattacharyya KG, Sarma A. Adsorption characteristics of the dye, Brilliant Green, on Neem leaf powder. *Dyes and Pigments* 2003; 57: 211-222.

[42] Perkins WS. Textile Coloration and Finishing, North Carolina: Carolina Academic Press 1996.

[43] Guaratini CCI, Zanoni MVB. Corantes Texteis. *Quimica Nova* 2000; 23: 71-78.

[44] Reddy, ALM, Nagarajan S, Chumyim P, Gowda, SR, Pradhan P, Jadhav SR, Dubey M, John G, Ajayan PM. Lithium storage mechanisms in purpurin based organic lithium ion battery electrodes, Scientific Reports 2012.

[45] Freeman HS, and Peters AT. Colorants for Non-Textile Applications, Amsterdam: Elsevier Science B. V. 2000.

[46] Lemmens RHMJ, Wulijarni SN. Plant Resources of South-East Asia 3: Dye and Tannin-Producing Plants. Bogor Indonesia 1992.

[47] Schweppe H. Identification of red madder and insect dyes by thin-layer chromatography. *American Chemical Society Symposium Series*1989; 410(2): 188-219.

[48] Zollinger H. Synthesis, Properties of Organic Dyes and Pigments, In: Color Chemistry, USA: VCH Publishers, New York 1987.

[49] Gregory P. Dyestuffs, In: Heaton C.A., The Chemical Industry. London: Chapman & Hall 1994.

[50] Gregory P. Dyes and Dye Intermediates. In: Kirk-Othmer (ed.) Encyclopedia of Chemical Technology. New Jersey: John Wiley & Sons 2009.

[51] Pandhare ED, Rama Rao AV, Srinivasan R, Venkataraman K. Lac pigments. *Tetrahedron Letters* 1996; 8: 229-239.

[52] Pandhare ED, Rama Rao AV, Shaikh IN. Lac pigments: Part III* e Isolation of laccaic acids A & B & the constitution of laccaic acid A. *Indian Journal of Chemistry* 1969; 7: 977-86.

[53] Pandhare ED, Rama Rao AV, Shaikh IN, Venkataraman K. The constitution of laccaic acid B. *Tetrahedron Letters* 1967; 26: 2437-2440.

[54] Bhide NS, Pandhare ED, Rama Rao AV, Shaikh IN, Srinivasan R. Lac pigments: Part IV constitution of laccaic acid B. *Indian Journal of Chemistry* 1969; 7: 987-995.

[55] Burwood R, Read G, Schofield K, Wright DE. The pigments of stick lac: Part II The structure of laccaic acid A1. *Journal of the Chemical Society* 1967; 842-851.

[56] Oka H, Ito Y, Yamasa S, Kagami T, Hayakawa J, Harada K-I, et al. Separation of lac dye components by high-speed countercurrent chromatography. *Journal of Chromatography* 1998; 813: 71-77.

[57] Oka H, Ito Y, Yamasa S, Kagami T, Hayakawa J, Harada K-I, et al. Identification of lac dye components by electrospray high performance liquid chromatography etandem mass spectrometry. *Journal of the Mass Spectrometry Society of Japan* 1998; 46(1): 63-68.

[58] Rama Rao AV, Shaikh IN, Venkataraman K. Laccaic acid C, the first natural anthraquinone with an amino acid side chain. *Indian Journal of Chemistry* 1968; 7: 188-189.

[59] Mehandale AR, Rama Rao AV, Shaikh IN, Venkataraman K. Desoxy erythrolaccin and laccaic acid D. *Tetrahedron Letters* 1968; 18: 2231-2234.

[60] Pandhare ED, Rama Rao AV, Srinivasan R, Venkataraman K. Lac pigments. *Tetrahedron Supplement* 1966; 8: 229-239.

[61] Chairat M, Rattananaphani S, Bremner JB, Rattanaphani V. Adsorption kinetic study of lac dyeing on cotton. *Dyes and Pigments* 2008; 76: 435-439.

[62] Horrocks AR, Anand SC. Handbook of Technical Textiles. Cambridge: Wood head 2000.

[63] Czajkowski W, Szymczyk M. Iron complexed afterchrome dyes. *Dyes and Pigments* 1998, 37: 197–204.

[64] Bardole HA, Freeman HS, Reife A. Iron salts in the post-metallisation of mordant dyes. *Textile Research Journal* 1998; 68: 141-149.

[65] Shanker R, Tiwari A, Vankar PS. Enhancement of dye uptake by enzymes in natural dyeing, M.Sc, Biochemistry dissertation (unpublished results) 2005.

[66] Shanker R, Vankar PS. Ecofriendly ultrasonic natural dyeing of cotton fabric with enzyme pretreatments. Desalination 2006.

[67] Correia VM, Stephenson T, Judd SJ. Characterization of textile wastewaters - a review. *Environmental Technology* 1994; 15: 917-929.

[68] Foulk JA, Akin DE, Dodd RB. Processing techniques for improving enzyme-retting of flax. Industrial Crops and Products 2001; 13: 239-248.

[69] Shore J. Colorants and Auxiliaries - Organic Chemistry and Application Properties, Society of Dyers and Colourists, West Yorkshire, England 2002.

[70] Broadbent AD. Basic principles of textile coloration, Society of Dyers and Colourists, West Yorkshire, England 2002.

[71] Ryder ML, Stephenson SK, Wool growth, Academic Press, London 1968.

[72] Fukatsu K, Formation of copper (II) wool keratin complexes. *Textile Research Journal* 1988; 58(2): 91–96.

[73] Kobayashi S, Hiroishi K, Tokunoh M, Saeguna T. *Macromolecules* 1987; 20: 1496-1500.

[74] Goethals EJ. Polymeric amines and ammonium salts. New York 1980.

[75] Chiou MS, Li HY. Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *Journal of Hazardous Materials* 2002; 93: 233-248.

[76] Sivaraj R, Namasivayam C, Kadirvelu K. Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions. *Waste Management* 2001; 21: 105-110.

[77] Lijuan W, Jian L. Adsorption of C.I. Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium, and thermodynamics. Industrial *Crops and Products* 2013; 42: 153-158.

[78] Chiou MS, Li HY. Adsorption behaviour of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere* 2003; 50: 1095-1105.

[79] Chiou MS, Ho PY, Li HY. Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. Dyes and Pigments 2004; 60: 69-84.

[80] Chen YY, Zou LY, Sheng J. Influence of oxygen plasma treatment upon mulberry silk microstructure. *Textile Research Journal* 2001; 22: 50-52.

[81] Alberty RA, Silbey RJ. Physical Chemistry, New York: John Wiley & Sons 1997.

[82] Laidler K, Meiser JH. Physical Chemistry. U.S.A., Houghton Mifflin 1999.

[83] Shih YF. Mechanical and thermal properties of waste water bamboo husk fibre reinforced epoxy composites. *Material Science Engineering: A* 2007; 7(2): 289-295.

[84] Bledzki AK, Reihmane S, Gassan JJ. Reinforcement of polypropylene by annual plant fibers: optimization of the coupling agent efficiency. *Applied Polymer Science* 1996; 59(3): 1329-1336.

[85] Puri VP, Pearce GR. Alkali-explosion pretreatment of straw and bagasse for enzymic hydrolysis. *Biotechnological and Bioengineering* 2004; 28(4): 480-485.

[86] Peng X, Zhong L, Ren J, Sun R. Laccase and alkali treatments of cellulose fibre: surface lignin and its influences on fibre surface properties and interfacial behavior of sisal fibre/phenolic resin composites. *Composites Part A: Applied Science and Manufacturing* 2010; 41(1): 1848-1856.

[87] Lu J, Askeland P, Drzal LT. Surface modification of microfibrillated cellulose for epoxy composite applications. *Polymer* 2008; 49(5):1285-1296.

[88] Chairat M, Rattananaphani S, Bremner JB, Rattanaphani V. An adsorption and kinetic study of lac dyeing on silk. *Dyes and Pigments* 2005; 64: 231-241.

[89] Chiou MS, Li HY. Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *Journal of Hazardous Materials* 2002; 93: 233-248.

[90] Christie RM, Matger RR, Wardman RH. The chemistry of colour application. United Kingdom: Blackwell Science Ltd; 2000.

[91] Chiou MS, Li HY. Adsorption behaviour of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere* 2003; 50: 1095-1105.

[92] Chiou MS, Ho PY, Li HY. Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. *Dyes and Pigments* 2004; 60: 69-84.

[93] Chiou MS, Li HY. Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *Journal of Hazardous Materials* 2002; 93: 233-248.

[94] Choy Keith KH, McKay G, Porter JF. Sorption of acid dyes from effluents using activated carbon. *Resources Conservation and Recycling* 1999; 27: 57-71.

[95] Dogan M, Alkan M. Adsorption kinetics of methyl violet onto perlite. *Chemosphere* 2003; 50: 517-528.

[96] Wu FC, Tseng RL, Juang RS. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. *Water Research* 2001; 35(3): 613-618.

[97] Oka H, Ito Y. Separation of lac dye components by high-speed counter-current chromatography. *Journal of Chromatography A* 1998; 813: 71-77.

[98] Chiou MS, Li HY. Adsorption behaviour of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere* 2003; 50: 1095-1105.

[99] Nollet H, Roels M, Lutgen P, Der MP, Verstraete W. Removal of PCBs from wastewater using fly ash. *Chemosphere* 2003, 53: 655-665.

[100] Stana KK, Ribitsch V. Electrokinetic properties of processed cellulose fibers *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 1998; 140: 127–138.

[101] DeMejo LP, Pavlisko JA. Polyethyleneimine-containing toner compositions. Eastman Kodak Company, New York 1991.

APPENDICES

Appendix A

The calibration curve of lac dye solution

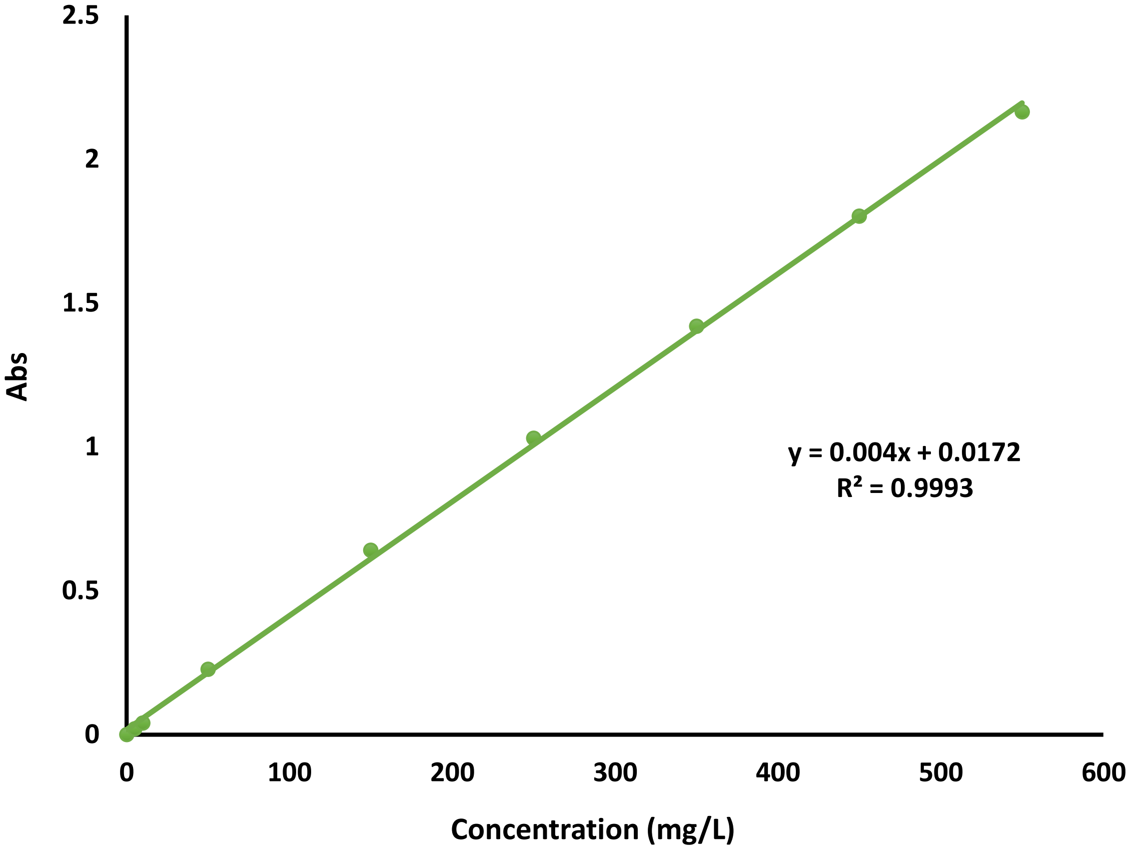


Figure A1 The calibration curve of lac dye solution, used for determination of absolute concentration on lac dye solution.

Appendix B

The calibration curve of PEI + $CuSO_4$ solution

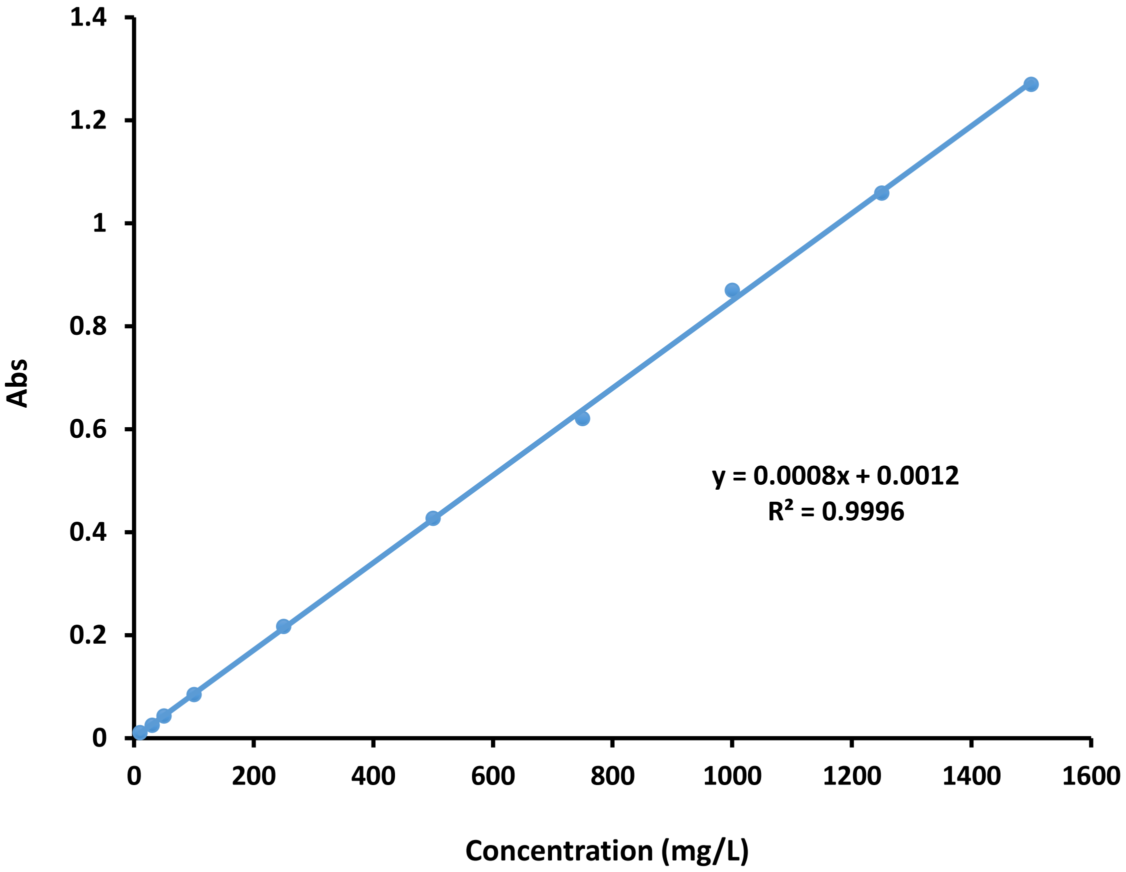


Figure B1 The calibration curve of PEI + $CuSO_4$ solution, used for determination of absolute concentration on PEI solution.

Appendix C

Amount of PEI adsorbed on BFs

Table C1 Amount of PEI adsorbed on BFs at equilibrium (mg/g BFs).

Temperature (°C)	**PEI adsorbed on bamboo fibers at equilibrium (mg/g fibers)**
30	1.25 (± 0.25)
45	1.42 (± 0.38)
60	1.33 (± 0.29)

The amount of initial concentration for PEI solution were 1000 mg/L, $CuSO_4$ 0.5 % w/v, MLR 1:200, 12 h on bamboo fibers.

Appendix D

Effect of pH on adsorption of lac dye on BF$_s$

Table D1 The adsorption data of amount of dye adsorbed per gram at equilibrium of controlled BF_s by different pH are dyeing concentration = 250 mg/L, MLR = 1:200, dyeing temperature = 30°C and dyeing time = 200 min.

pH	**C_0**	**C_e**	**(C_0 – C_e)**	**q_e (mg/g BF_s)**
1	264.70	264.2	0.50	0.1
2	254.45	249.7	4.75	0.95
3	254.45	245.95	8.50	1.7
4	229.20	224.7	4.50	0.9

Appendix E

Effect of initial concentration on adsorption of lac dye on BF$_s$

Table E1 The adsorption data of amount of dye adsorbed per gram at equilibrium of controlled BF$_s$ by different initial concentration are pH = 3, MLR = 1:200, dyeing temperature = 30°C and dyeing time = 200 min.

Dyeing time (min)	**Dye adsorbed per gram of BF$_s$**				
	50 mg/L	**150 mg/L**	**250 mg/L**	**350 mg/L**	**500 mg/L**
1	0.1	0.15	0.25	0.35	0.65
2	0.15	0.25	0.45	0.95	0.95
3	0.2	0.35	0.65	1.15	1.2
4	0.25	0.45	0.8	1.3	1.4
5	0.3	0.55	0.95	1.45	2.05
6	0.35	0.65	1.15	1.6	2.2
7	0.4	0.75	1.3	1.7	2.3
10	0.45	0.8	1.4	1.8	2.4
12	0.5	0.85	1.5	1.9	2.5
15	0.55	0.9	1.65	2	2.55
20	0.6	0.95	1.75	2.1	2.6
30	0.65	1	1.85	2.15	2.65
40	0.65	1.05	1.9	2.2	2.7
50	0.65	1.1	1.95	2.25	2.75
60	0.65	1.15	2	2.3	2.8
80	0.65	1.2	2.05	2.35	2.8
100	0.65	1.2	2.15	2.4	2.8
130	0.65	1.2	2.25	2.45	2.8
150	0.65	1.2	2.3	2.45	2.8
200	0.65	1.2	2.3	2.45	2.8

Appendix F

Effect of MLR on adsorption of lac dye on BF$_s$

Table F1 The adsorption data of amount of dye adsorbed per gram at equilibrium of controlled BF$_s$ by different MLR are pH = 3, dyeing concentration = 250 mg/L, dyeing temperature = 30°C and dyeing time = 200 min.

Dyeing time (min)	**Dye adsorbed per gram of BF$_s$**		
	MLR 1:120	**MLR 1:160**	**MLR 1:200**
1	0.50	0.40	0.25
2	1.15	0.60	0.45
3	1.30	0.75	0.65
4	1.45	0.90	0.80
5	1.55	1.05	0.95
6	1.65	1.20	1.15
7	1.70	1.35	1.30
10	1.75	1.50	1.40
12	1.80	1.65	1.50
15	1.85	1.75	1.65
20	1.90	1.85	1.75
30	1.95	1.95	1.85
40	2.00	2.05	1.90
50	2.05	2.10	1.95
60	2.10	2.15	2.00
80	2.10	2.20	2.05
100	2.10	2.20	2.15
130	2.10	2.20	2.25
150	2.10	2.20	2.30
200	2.10	2.20	2.30

Appendix G

Effect of temperature on adsorption of lac dye on BF_s

Table G1 The adsorption data of amount of dye adsorbed per gram at equilibrium of controlled BF$_s$ and PEI treated BF$_s$ by different temperature are pH = 3, dyeing concentration = 250 mg/L, MLR = 1:200 and dyeing time = 200 min.

Dyeing time (min)	**Dye adsorbed per gram of BF$_s$**					
	Controlled BF$_s$			**PEI treated BF$_s$**		
	30°C	**45°C**	**60°C**	**30°C**	**45°C**	**60°C**
1	0.25	0.40	0.50	2.55	3.05	3.25
2	0.45	0.50	0.65	4.90	4.70	7.90
3	0.65	0.60	0.70	6.35	7.70	9.55
4	0.80	0.65	0.75	8.75	9.90	12.65
5	0.95	0.70	0.80	10.75	11.85	16.40
6	1.15	0.75	0.85	13.00	14.10	20.30
7	1.30	0.80	0.90	14.70	16.20	22.85
10	1.40	0.85	0.95	18.45	19.05	28.05
12	1.50	0.90	1.00	21.00	20.90	28.55
15	1.65	0.95	1.05	23.00	22.90	29.30
20	1.75	1.00	1.05	25.95	25.40	29.60
30	1.85	1.05	1.05	26.90	26.80	29.80
40	1.90	1.10	1.05	28.70	28.00	30.10
50	1.95	1.15	1.05	30.40	28.85	30.10
60	2.00	1.20	1.05	32.35	29.45	30.10
80	2.05	1.30	1.05	32.70	30.25	30.10
100	2.15	1.30	1.05	32.70	30.25	30.10
130	2.25	1.30	1.05	32.70	30.25	30.10
150	2.30	1.30	1.05	32.70	30.25	30.10
200	2.30	1.30	1.05	32.70	30.25	30.10

Appendix H

Adsorption isotherm

Table H1 Langmuir adsorption isotherm of lac dyeing on controlled and PEI-treated BFs by different temperature are pH = 3, dyeing concentration = 250 mg/L, MLR = 1:200 and dyeing time = 200 min

C_0	**Controlled BF$_s$**				**PEI treated BF$_s$**			
	C_e	**$1/C_e$**	**q_e**	**$1/q_e$**	**C_e**	**$1/C_e$**	**q_e**	**$1/q_e$**
Temperature = 30°C								
150	142.45	0.0070	1.65	0.61	37.20	0.0269	18.90	0.0529
250	248.70	0.0040	2.30	0.43	75.20	0.0133	32.70	0.0306
350	334.45	0.0030	2.60	0.38	97.45	0.0103	43.00	0.0233
500	462.20	0.0022	3.10	0.32	156.70	0.0064	57.40	0.0174
Temperature = 45°C								
150	137.45	0.0073	1.10	0.91	42.45	0.0236	17.25	0.0580
250	229.20	0.0044	1.55	0.65	79.45	0.0126	29.25	0.0342
350	302.95	0.0033	1.75	0.57	119.70	0.0084	39.00	0.0256
500	443.20	0.0023	2.20	0.45	184.70	0.0054	47.85	0.0209
Temperature = 60°C								
150	138.95	0.0072	0.80	1.2500	41.45	0.0241	15.70	0.0637
250	227.70	0.0044	1.10	0.9091	97.45	0.0103	28.40	0.0352
350	323.45	0.0031	1.35	0.7407	118.45	0.0084	32.95	0.0303
500	448.20	0.0022	1.50	0.6667	194.20	0.0051	42.65	0.0234

Table H2 Fruendlich adsorption isotherm of lac dyeing on controlled and PEI-treated BFs by different temperature are pH = 3, dyeing concentration = 250 mg/L, MLR = 1:200 and dyeing time = 200 min

C_0	**Controlled BF$_s$**				**PEI treated BF$_s$**			
	C_e	**$\ln C_e$**	**q_e**	**$\ln q_e$**	**C_e**	**$\ln C_e$**	**q_e**	**$\ln q_e$**
Temperature = 30°C								
150	142.45	4.9590	1.65	0.5008	37.20	3.6163	18.90	2.9392
250	248.70	5.5162	2.30	0.8329	75.20	4.3202	32.70	3.4874
350	334.45	5.8125	2.60	0.9555	97.45	4.5793	43.00	3.7612
500	462.20	6.1360	3.10	1.1314	156.70	5.0543	57.40	4.0500
Temperature = 45°C								
150	137.45	4.9233	1.10	0.0953	42.45	3.7483	17.25	2.8478
250	229.20	5.4346	1.55	0.4383	79.45	4.3751	29.25	3.3759
350	302.95	5.7136	1.75	0.5596	119.70	4.7850	39.00	3.6636
500	443.20	6.0940	2.20	0.7885	184.70	5.2187	47.85	3.8681
Temperature = 60°C								
150	138.95	4.9341	0.80	-0.2231	41.45	3.7245	15.70	2.7537
250	227.70	5.4280	1.10	0.0953	97.45	4.5793	28.40	3.3464
350	323.45	5.7790	1.35	0.3001	118.45	4.7745	32.95	3.4950
500	448.20	6.1052	1.50	0.4055	194.20	5.2689	42.65	3.7530

Appendix I

Kinetics adsorption

Table I1 The pseudo-first-order kinetics of lac dyeing on controlled and PEI-treated BFs by different temperature are pH = 3, dyeing concentration = 250 mg/L, MLR = 1:200 and dyeing time = 200 min.

Time	**Controlled BF$_s$**				**PEI treated BF$_s$**			
	q_e	q_t	q_e-q_t	ln (q_e-q_t)	q_e	q_t	q_e-q_t	ln (q_e-q_t)
Temperature = 30°C								
0	2.3	0.00	2.30	0.8329	35.85	0.00	35.85	35.85
1	2.3	0.25	2.05	0.7178	35.85	2.55	33.30	33.30
2	2.3	0.45	1.85	0.6152	35.85	4.90	30.95	30.95
3	2.3	0.65	1.65	0.5008	35.85	6.35	29.50	29.50
4	2.3	0.80	1.50	0.4055	35.85	8.75	27.10	27.10
5	2.3	0.95	1.35	0.3001	35.85	10.75	25.10	25.10
6	2.3	1.15	1.15	0.1398	35.85	13.00	22.85	22.85
7	2.3	1.30	1.00	0.0000	35.85	14.70	21.15	21.15
Temperature = 45°C								
0	1.3	0.00	1.30	0.2624	30.25	0.00	30.25	3.4095
1	1.3	0.40	0.90	-0.1054	30.25	3.05	27.20	3.3032
2	1.3	0.50	0.80	-0.2231	30.25	4.70	25.55	3.2406
3	1.3	0.60	0.70	-0.3567	30.25	7.70	22.55	3.1157
4	1.3	0.65	0.65	-0.4308	30.25	9.90	20.35	3.0131
5	1.3	0.70	0.60	-0.5108	30.25	11.85	18.40	2.9124
6	1.3	0.75	0.55	-0.5978	30.25	14.10	16.15	2.7819
7	1.3	0.80	0.50	-0.6931	30.25	16.20	14.05	2.6426
Temperature = 60°C								
0	1.05	0.00	1.05	0.0488	30.1	0.00	30.10	3.4045
1	1.05	0.50	0.55	-0.5978	30.1	3.25	26.85	3.2903
2	1.05	0.65	0.40	-0.9163	30.1	7.90	22.20	3.1001
3	1.05	0.70	0.35	-1.0498	30.1	9.55	20.55	3.0229
4	1.05	0.75	0.30	-1.2040	30.1	12.65	17.45	2.8593
5	1.05	0.80	0.25	-1.3863	30.1	16.40	13.70	2.6174
6	1.05	0.85	0.20	-1.6094	30.1	20.30	9.80	2.2824
7	1.05	0.90	0.15	-1.8971	30.1	22.85	7.25	1.9810

Table I2 The pseudo-second-order kinetics of lac dyeing on controlled and PEI-treated BFs by different temperature are pH = 3, dyeing concentration = 250 mg/L, MLR = 1:200 and dyeing time = 200 min.

Time	**Controlled BF$_s$**		**PEI treated BF$_s$**	
	q_t	**t/q_t**	**q_t**	**t/q_t**
Temperature = 30°C				
1	0.25	4.00	2.55	0.3922
2	0.45	4.44	4.90	0.4082
3	0.65	4.62	6.35	0.4724
4	0.80	5.00	8.75	0.4571
5	0.95	5.26	10.75	0.4651
6	1.15	5.22	13.00	0.4615
7	1.30	5.38	14.70	0.4762
Temperature = 45°C				
1	0.40	2.50	3.05	0.3279
2	0.50	4.00	4.70	0.4255
3	0.60	5.00	7.70	0.3896
4	0.65	6.15	9.90	0.4040
5	0.70	7.14	11.85	0.4219
6	0.75	8.00	14.10	0.4255
7	0.80	8.75	16.20	0.4321
Temperature = 60°C				
1	0.50	2.00	3.25	0.3077
2	0.65	3.08	7.90	0.2532
3	0.70	4.29	9.55	0.3141
4	0.75	5.33	12.65	0.3162
5	0.80	6.25	16.40	0.3049
6	0.85	7.06	20.30	0.2956
7	0.90	7.78	22.85	0.3063

Appendix J

Activation parameter

Table J1 The activation parameters for the adsorption of lac dyeing on untreated and PEI treated BFs at 30°, 45° and 60°C.

Temperature (T)	**1/T**	**Controlled BFs**		**PEI treated BFs**	
°K		***k_1***	***$\ln k_1$***	***k_1***	***$\ln k_1$***
303	0.0033	0.1009	-2.2936	0.0740	-2.6037
318	0.0031	0.0973	-2.3300	0.1038	-2.2653
333	0.0030	0.2163	-1.5311	0.2784	-1.2787

Appendix K

Thermodynamics parameter

Table K1 Thermodynamic parameters for the adsorption of lac dyeing on untreated and PEI treated BFs at 30°, 45° and 60°C.

T (°**K**)	1/T	**Controlled BF$_s$**				**PEI treated BF$_s$**			
		q_e	C_e	q_e/C_e (K_c)	lnK_c	q_e	C_e	q_e/C_e (K_c)	lnK_c
303	0.0033	2.30	248.70	0.0092	-4.6833	32.70	75.20	0.4348	-0.8328
318	0.0031	1.30	242.95	0.0054	-5.2305	30.25	74.45	0.4063	-0.9006
333	0.0030	1.05	256.70	0.0041	-5.4991	30.10	88.95	0.3384	-1.0835

Appendix L

FTIR Spectrum

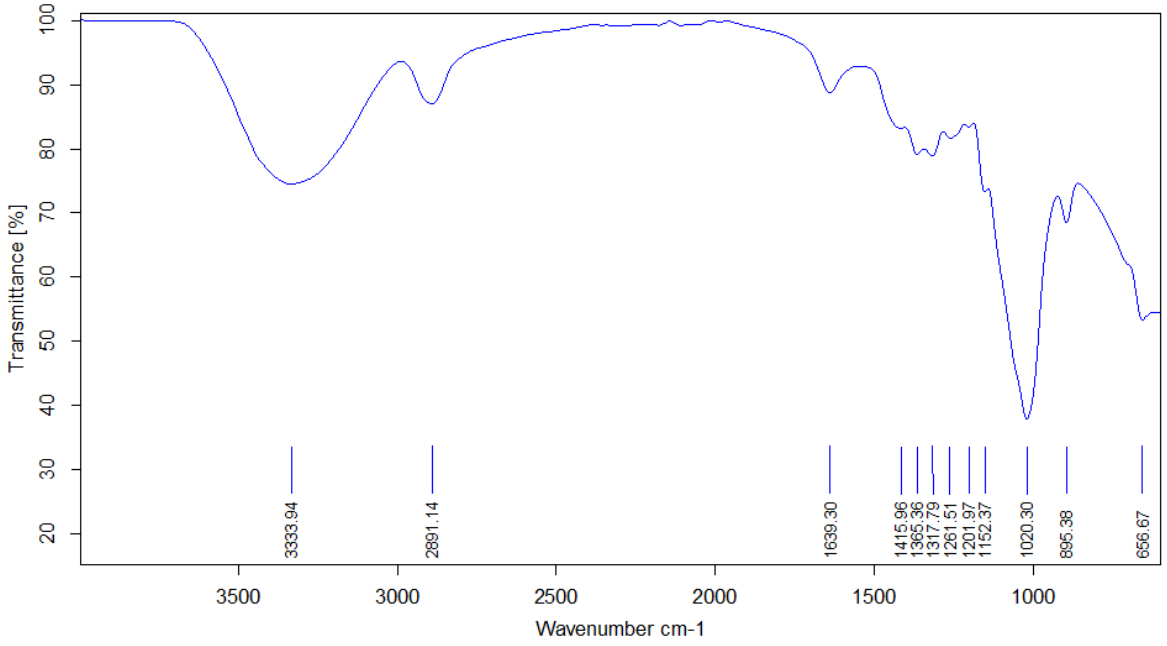


Figure L1 ATR-FTIR spectra of BFs.

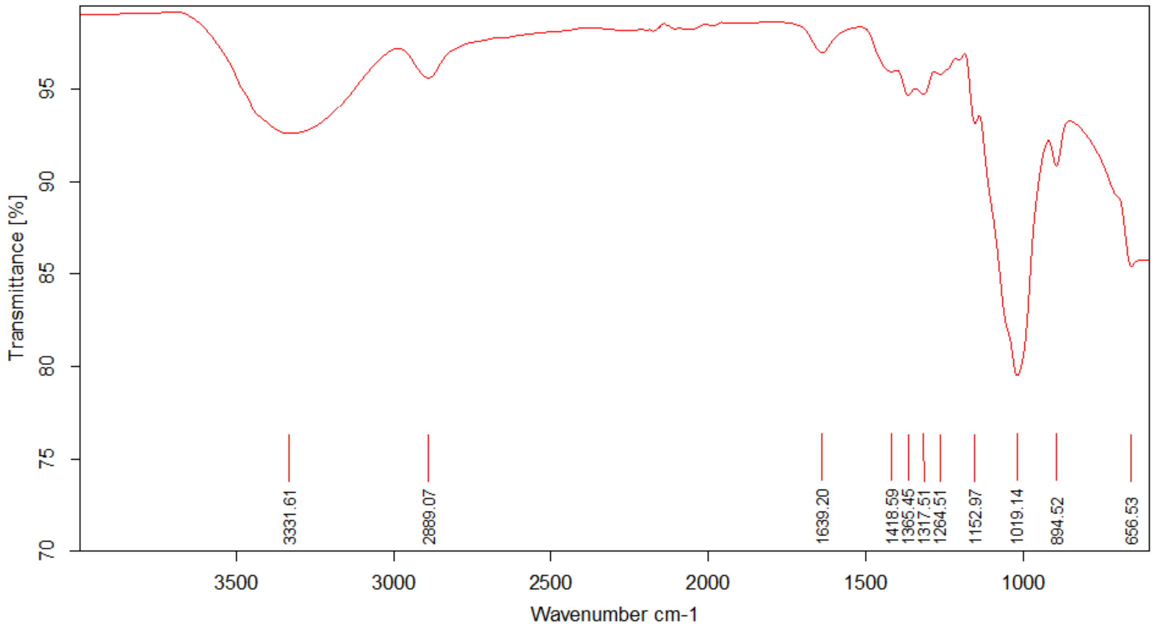


Figure L2 ATR-FTIR spectra of Controlled BFs.

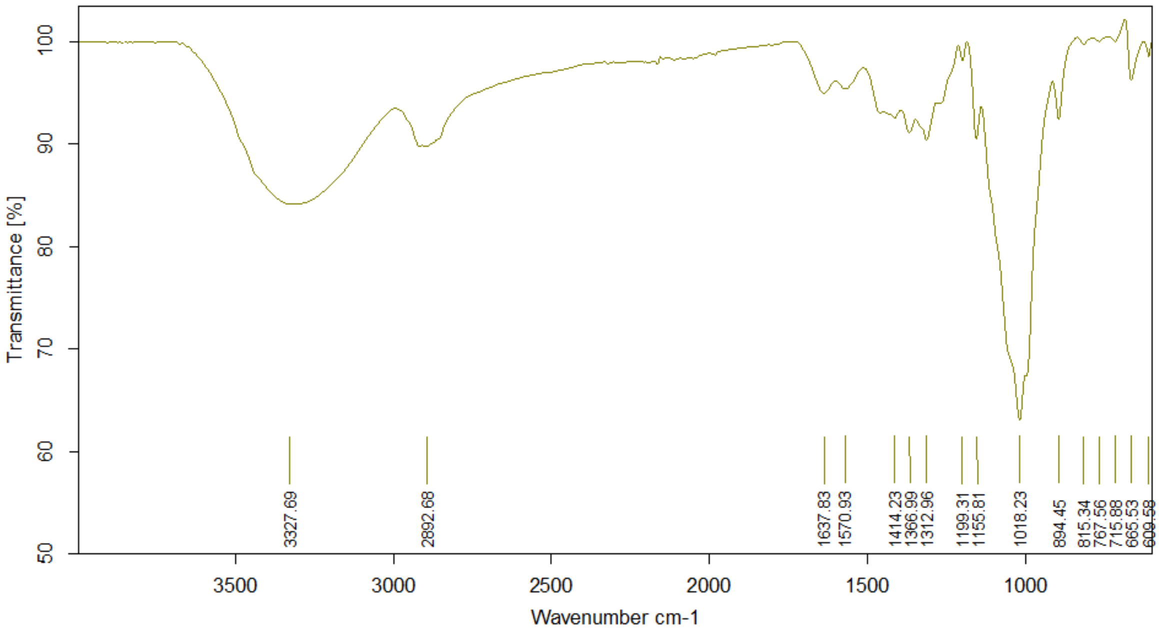


Figure L3 ATR-FTIR spectra of PEI.

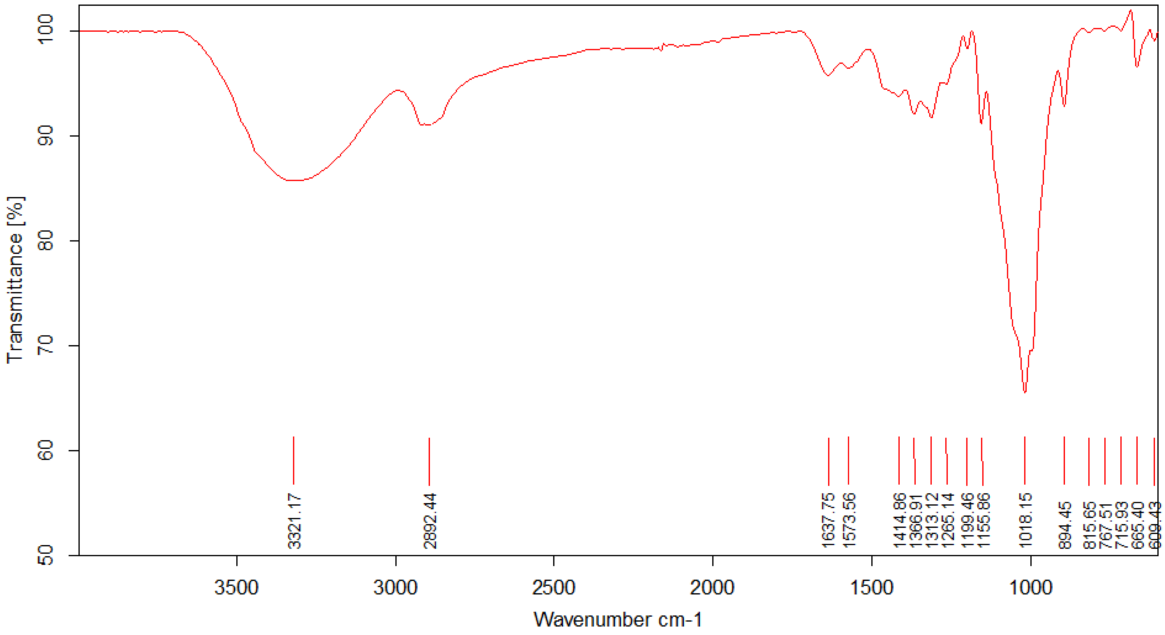


Figure L4 ATR-FTIR spectra of PEI-treated BFs.

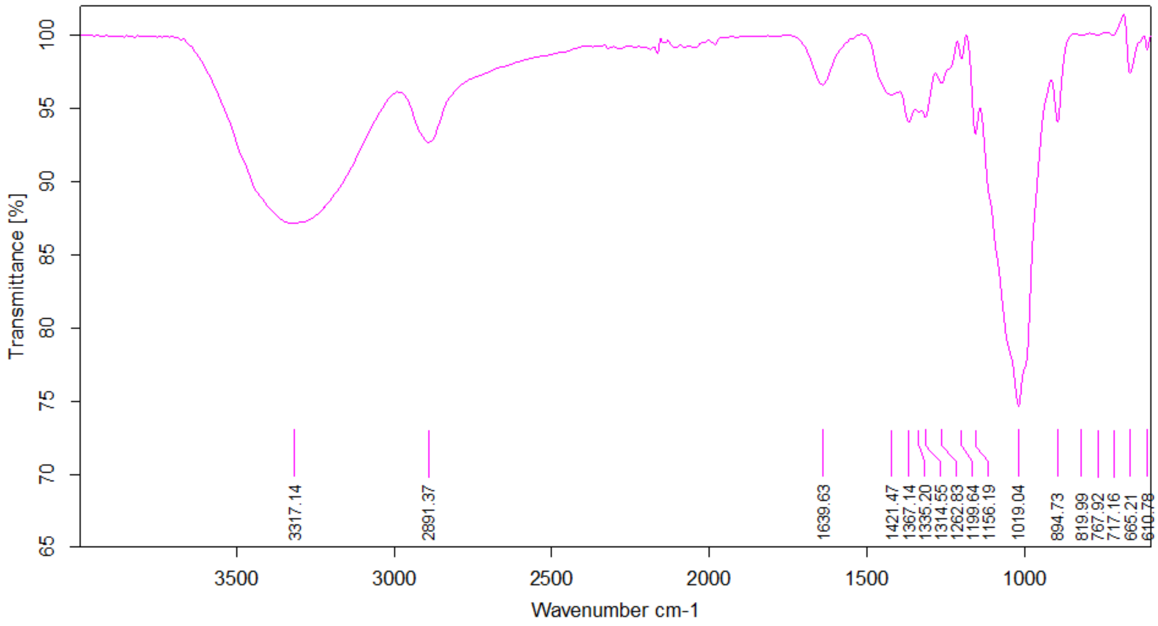


Figure L5 ATR-FTIR spectra of Lac.

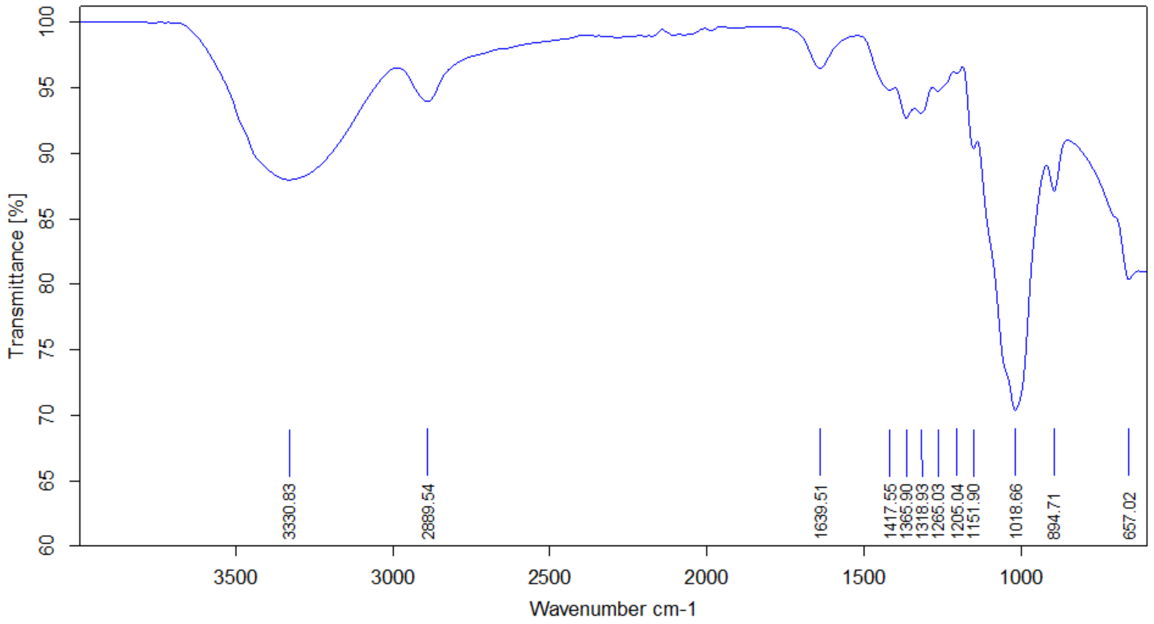


Figure L6 ATR-FTIR spectra of Lac dyed BFs.

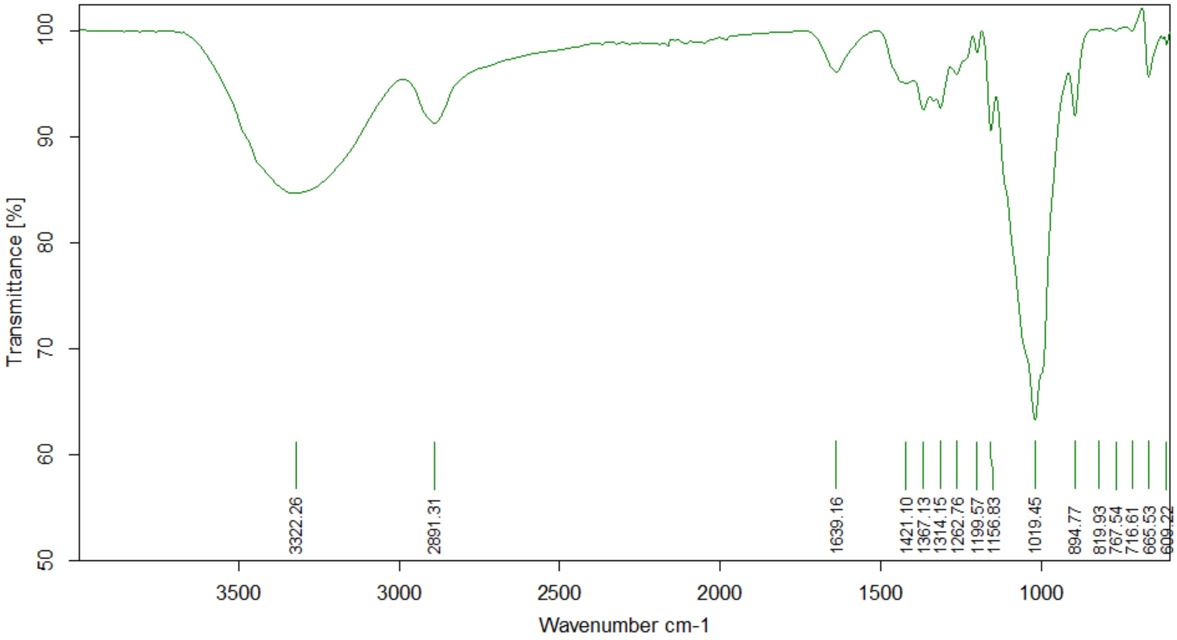
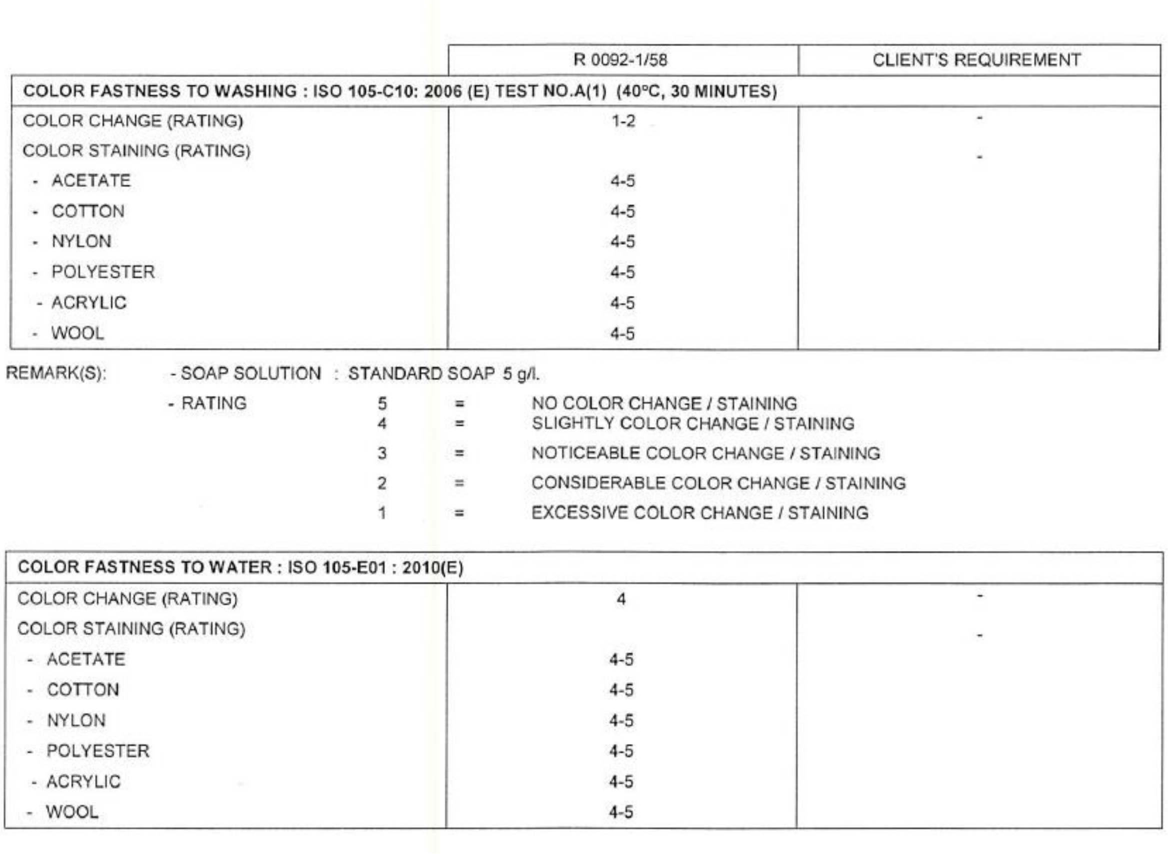


Figure L7 ATR-FTIR spectra of PEI-lac dyed BFs.

Appendix M

Fastness tester

Table M1 The color fastness to water and to washing of lac dyed controlled-BFs.



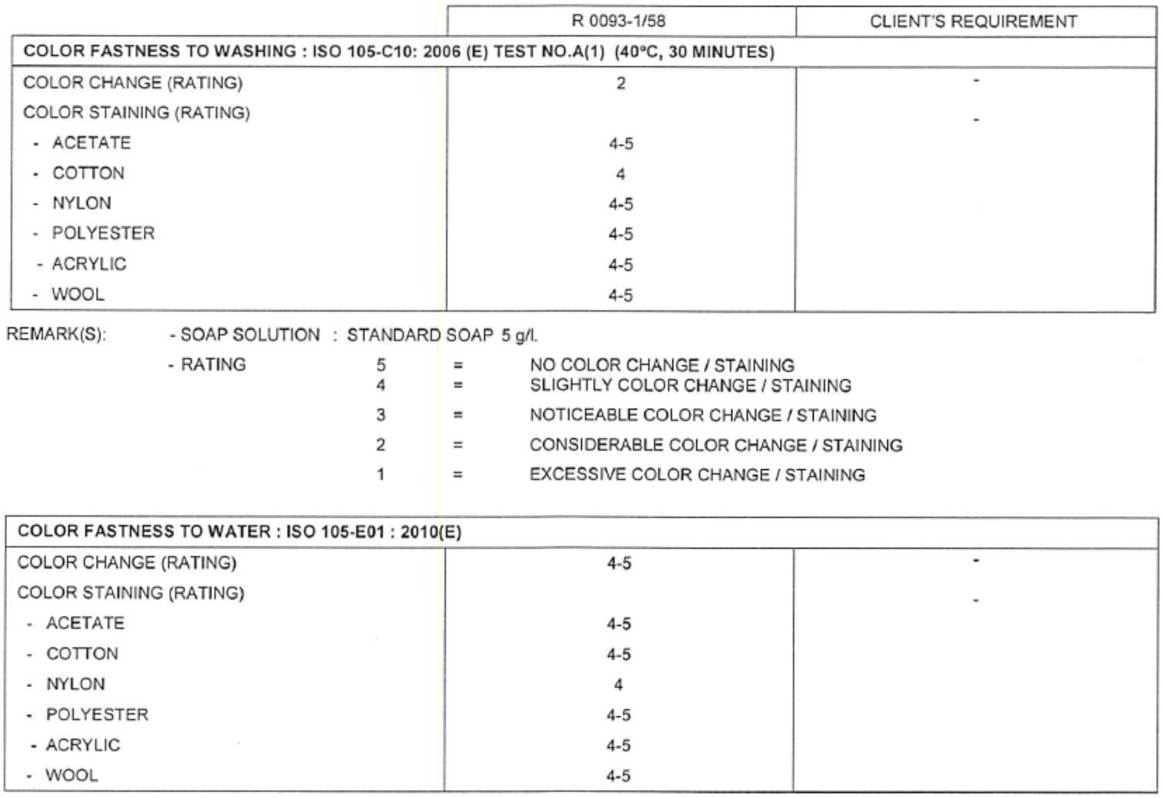
	R 0092-1/58	CLIENT'S REQUIREMENT
COLOR FASTNESS TO WASHING : ISO 105-C10: 2006 (E) TEST NO.A(1) (40°C, 30 MINUTES)		
COLOR CHANGE (RATING)	1-2	-
COLOR STAINING (RATING)		-
- ACETATE	4-5	
- COTTON	4-5	
- NYLON	4-5	
- POLYESTER	4-5	
- ACRYLIC	4-5	
- WOOL	4-5	

REMARK(S): - SOAP SOLUTION : STANDARD SOAP 5 g/l.

- RATING
  - 5 = NO COLOR CHANGE / STAINING
  - 4 = SLIGHTLY COLOR CHANGE / STAINING
  - 3 = NOTICEABLE COLOR CHANGE / STAINING
  - 2 = CONSIDERABLE COLOR CHANGE / STAINING
  - 1 = EXCESSIVE COLOR CHANGE / STAINING

COLOR FASTNESS TO WATER : ISO 105-E01 : 2010(E)		
COLOR CHANGE (RATING)	4	-
COLOR STAINING (RATING)		-
- ACETATE	4-5	
- COTTON	4-5	
- NYLON	4-5	
- POLYESTER	4-5	
- ACRYLIC	4-5	
- WOOL	4-5	

Table M2 The color fastness to water and to washing of lac dyed PEI-treated BFs.



	R 0093-1/58	CLIENT'S REQUIREMENT
COLOR FASTNESS TO WASHING : ISO 105-C10: 2006 (E) TEST NO.A(1) (40°C, 30 MINUTES)		
COLOR CHANGE (RATING)	2	-
COLOR STAINING (RATING)		-
- ACETATE	4-5	
- COTTON	4	
- NYLON	4-5	
- POLYESTER	4-5	
- ACRYLIC	4-5	
- WOOL	4-5	

REMARK(S): - SOAP SOLUTION : STANDARD SOAP 5 g/l.

- RATING
5 = NO COLOR CHANGE / STAINING
4 = SLIGHTLY COLOR CHANGE / STAINING
3 = NOTICEABLE COLOR CHANGE / STAINING
2 = CONSIDERABLE COLOR CHANGE / STAINING
1 = EXCESSIVE COLOR CHANGE / STAINING

COLOR FASTNESS TO WATER : ISO 105-E01 : 2010(E)		
COLOR CHANGE (RATING)	4-5	-
COLOR STAINING (RATING)		-
- ACETATE	4-5	
- COTTON	4-5	
- NYLON	4	
- POLYESTER	4-5	
- ACRYLIC	4-5	
- WOOL	4-5	

Appendix N

Outputs of the research

โครงการนำเสนอผลงานของนิสิตชั้นปีที่ 4
และวิทยานิพนธ์ระดับบัณฑิตศึกษา ครั้งที่ 14 ประจำปี 2557
ในวันที่ 8 พฤษภาคม 2558 ณ ห้อง SC1-200

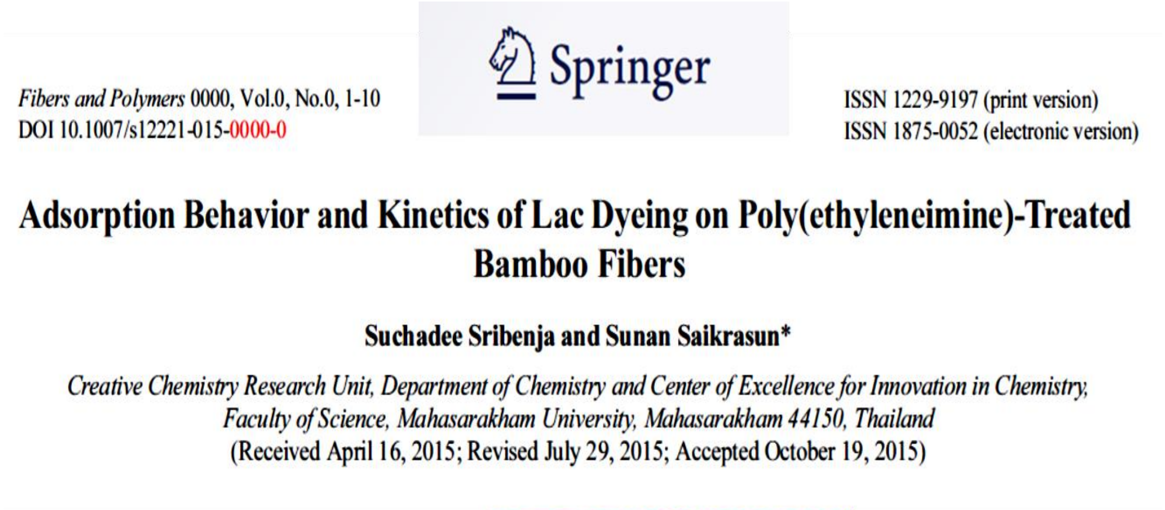
คณะวิทยาศาสตร์ มหาวิทยาลัยมหาสารคาม
ปีการศึกษา 2557

คณะวิทยาศาสตร์ มหาวิทยาลัยมหาสารคาม
ขอมอบเกียรติบัตรฉบับนี้ให้ไว้เพื่อแสดงว่า

นางสาวสุชาดี ศรีเบ็ญจา

ได้เข้าร่วมนำเสนอผลงานแบบปากเปล่า
โครงการนำเสนอผลงานโครงงานของนิสิตชั้นปีที่ ๔ และวิทยานิพนธ์นิสิตระดับบัณฑิตศึกษา
ในวันที่ ๘ พฤษภาคม ๒๕๕๘ ณ คณะวิทยาศาสตร์ มหาวิทยาลัยมหาสารคาม
ประจำปีการศึกษา ๒๕๕๗

(ศาสตราจารย์ ดร.วิเชียร มากตุ่น)
คณบดีคณะวิทยาศาสตร์ มหาวิทยาลัยมหาสารคาม



Fibers and Polymers 0000, Vol.0, No.0, 1-10
DOI 10.1007/s12221-015-0000-0

Springer

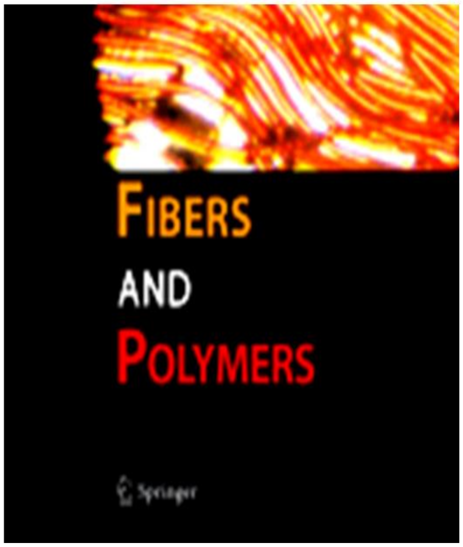
ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Adsorption Behavior and Kinetics of Lac Dyeing on Poly(ethyleneimine)-Treated Bamboo Fibers

Suchadee Sribenja and Sunan Saikrasun*

Creative Chemistry Research Unit, Department of Chemistry and Center of Excellence for Innovation in Chemistry,
Faculty of Science, Mahasarakham University, Mahasarakham 44150, Thailand

(Received April 16, 2015; Revised July 29, 2015; Accepted October 19, 2015)



Biography

Biography

Name	Miss Suchadee Sribenja
Date of brith	November 28, 1990
Place of birth	Nakhonphanom, Thailand

Institution attended

2012 Bachelor of Science degree in Chemistry Mahasarakham University

2016 Master of Science degree in Chemistry Mahasarakham University

Position and Work Place

Mahasarakham University

Contact address

26 Samutbanhan Road, Tambon Naimaung, Amphoe Maung, Nakhonphanom 48000, Thailand

Research grants & awards

Division of research Facilitation and Dissemination Mahasarakham University, fiscal year 2015,

Office of the Higher Education Commission Mahasarakham University, fiscal year 2015,

Center of Excellence for Innovation in Chemistry (*PERCH-CIC*)