

# **Studies on Low cost Bio-Adsorbent in Wastewater Treatment**

by

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A thesis submitted in partial fulfillment of the requirements for the degree of  
Master of Philosophy  
in Chemistry



Khulna University of Engineering & Technology  
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May, 2018

# **Dedication**

To my Mother, Wife and children for their  
patience and prayers.

## Declaration

This is to certify that the thesis work entitled "*Studies on Low cost Bio-Adsorbent in Wastewater Treatment*" has been carried out by *Md.Ruhul Amin* in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above thesis work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

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## Approval

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## Abstract

Environmental pollution is a great concern in now a day. In modern time, with civilization and industrialization environmental pollution increases. Effluents of textile and dyeing industries pollute the environment directly and indirectly as well. Adsorption is one of the versatile techniques of removing waste. In the present investigation LBS Lima Bean Seed (LBS) (locally known as Rukuri in northern zone of Bangladesh) powder has been used as adsorbent for the removal of three textile reactive dyes, namely Reactive Magenta HB (RMHB), Active Orange P2R (AOP2R) and Reactive Red ME6BL (RRME6BL). It is observed that removal efficiency of RMHB, AOP2R and RRME6BL is high at lower pH (acidic medium). Though AOP2R and RRME6BL adsorbed at pH 2.0 and pH 3.0 respectively but in case of RMHB, it adsorbed relatively at higher pH, 6.0. Effect of concentration, adsorbent dose and contact time on adsorption process was observed. Removal of dyes increases with amount of adsorbent and time. But at in case of lower initial dye concentration dye removal rate was faster. Equilibrium time for the adsorption process was about 120 min. From the isotherm study it is observed that the applicability of the linear form of Langmuir and Freundlich model to LBS was confirmed by the high correlation coefficient  $R^2 > 0.97$ . This suggests that the Langmuir isotherm and Freundlich models both provide good model of the sorption system. The value of  $1/n$  was lower than 1, ( $n$  is greater than 1) indicating that studied dyes were favorably adsorbed by LBS. During the kinetics study it is seen that the plot of pseudo-first order has a high correlation coefficient than the plot of pseudo-second order. It should be mentioned, in both cases the value of  $R^2$  is close to the unity. More over the values of amount of adsorbate at equilibrium,  $q_e$  dramatically differ from the experimental values in case of pseudo-second order. So, the adsorption of tested dyes on LBS is more appropriately followed the pseudo-first order model when compared with that of the pseudo-second order model. Study of Intraparticle diffusion model suggested that Intraparticle diffusion is not only Solo Rate Limiting Step.

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## ABBREVIATION

RMHB	Reactive Magenta HB
AOP2R	Active Orange P2R
RRME6BL	Reactive Red ME6BL
LBS	Lima Bean Seed's
$\lambda_{\max}$	Maximum absorbance at wave length $\lambda$
$\epsilon$	Molar extinction coefficient
nm	nanometer
$A_0$	Initial absorbance
$A_e$	Equilibrium absorbance
$A_t$	Absorbance at time t
$C_0$	Initial concentration
$C_e$	Equilibrium concentration
$C_t$	Concentration at time t
$q_e$	Amount of adsorbed at Equilibrium
$q_t$	Amount of adsorbed at time t
$q_m$	Maximum adsorption capacity (mg/g)
V	Amount adsorbed at any pressure
$V_m$	Amount adsorbed for monolayer formation
$K_a$	Rate of adsorption
$K_d$	Rate of desorption
$K_L$	Langmuir adsorption constant
$K_F$	Freundlich adsorption constant
$\theta$	Fractional coverage of the surface
$K_1$	Pseudo first order rate constant ( $\text{min}^{-1}$ )
$K_2$	Pseudo second order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ )
$K_{id}$	Intraparticle diffusion constants ( $\text{mg g}^{-1} \text{min}^{-1}$ )
T	Absolute temperature

## CHAPTER-I

### INTRODUCTION

#### 1.1 Human Life in the earth environment:

The earth is probably the best place in the universe that can support human life. Human being is dependent on the earth's environment and its natural resources. Environment literally means surrounding and everything that affect an organism during its life time is collectively known as its environment. In another words "Environment is sum total of water, air and land interrelationships among themselves and also with the human being, other living organisms and property" [1]. The environment can vary in scale from microscopic to global in extent. It can also be subdivided according to its attributes. Examples include the marine environment, the atmospheric environment and the terrestrial environment [2]. Civilization and massive industrialization is causing the depletion of natural resources and pollution of air, water and land.

Water is essential for the survival of any form of life. On an average, a human being consumes about two liters of water every day. Water accounts for about 70% of the weight of a human body. So the quality as well as quantity of water is of vital concern for mankind since it is directly linked with human welfare. It is a matter of history that faucal pollution of drinking water caused water borne diseases wiped out entire population of a country.

Land, sometimes referred to as dry land, is the solid surface of the Earth that is not permanently covered by water. The vast majority of human activity throughout history has occurred in land areas that support agriculture, habitat, and various natural resources. The Soil contamination or soil pollution as part of land degradation is caused by the presence of xenobiotic (human-made) chemicals or other alteration in the natural soil environment. It is typically caused by industrial activity, agricultural chemicals, or improper disposal of waste. The most common chemicals involved are petroleum hydrocarbons, polynuclear aromatic hydrocarbons, solvents, pesticides, lead, and other heavy metals. Contamination is correlated with the degree of industrialization and intensity of chemical usage.

Air The atmosphere of Earth is the layer of gases, commonly known as air that surrounds the planet Earth and is retained by Earth's gravity. The atmosphere of Earth protects life on

Earth by absorbing ultraviolet solar radiation, warming the surface through heat retention and reducing temperature extremes between day and night. By volume, dry air contains 78.09% nitrogen, 20.95% oxygen, 0.93% argon, 0.04% carbon dioxide, and small amounts of other gases. Air also contains a variable amount of water vapor, on average around 1% at sea level, and 0.4% over the entire atmosphere. Air pollution occurs when harmful substances including particulates and biological molecules are introduced into Earth's atmosphere. It may cause diseases, allergies or death in humans; it may also cause harm to other living organisms such as animals and food crops, and may damage the natural or built environment. Human activity and natural processes can both generate air pollution.

### **1.1.2 Environment and its Chemistry:**

Environmental chemistry is the scientific study of the chemical and biochemical phenomena that occur in natural places. It should not be confused with green chemistry, which seeks to reduce potential pollution at its source. It can be defined as the study of the sources, reactions, transport, effects, and fates of chemical species in the air, soil, and water environments; and the effect of human activity and biological activity on these. Environmental chemistry is an interdisciplinary science that includes atmospheric, aquatic and soil chemistry, as well as heavily relying on analytical chemistry and being related to environmental and other areas of science. Environmental chemistry is the study of chemical processes occurring in the environment which are impacted by humankind's activities. These impacts may be felt on a local scale, through the presence of urban air pollutants or toxic substances arising from a chemical waste site, or on a global scale, through depletion of stratospheric ozone or global warming. The focus in our courses and research activities is upon developing a fundamental understanding of the nature of these chemical processes, so that humankind's activities can be accurately evaluated.

Environmental chemistry involves first understanding how the un-contaminated environment works, which chemicals in what concentrations are present naturally, and with what effects. Without this it would be impossible to accurately study the effects humans have on the environment through the release of chemicals.

Environmental chemists draw on a range of concepts from chemistry and various environmental sciences to assist in their study of what is happening to a chemical species in the environment. Important general concepts from chemistry include understanding chemical reactions and equations, solutions, units, sampling, and analytical techniques .

## **1.2 Environmental Pollution:**

Environmental pollution is defined as a deviation from the natural composition of a part of the environment, which results in the adverse effects on human and the plant life. Human population explosion, rapid industrialization, deforestation, unplanned urbanization scientific and technological advancement etc. are main reasons for environment pollution.

Today, pollution is a prevalent phenomenon that is caused mostly by anthropogenic activities. Pollution can be caused by the direct or indirect activity of human. Polluted water or land may be harmful to human health or the quality of aquatic ecosystems or terrestrial ecosystems directly depending on aquatic ecosystems, which result in damage to material property or interfere with amenities and other legitimate uses of the environment. Environmental pollution means any departure from a normal state of environment. Pollutant is a substance present in a nature in greater quantity than the natural substance due to human activity, which ultimately has a detrimental effect on the environment and therefore on living organism and mankind. The atmosphere, the hydrosphere, the lithosphere and the biosphere may be polluted by different reason. With increased population, ever growing urbanization and increased industrialization in urban areas the pollution problems began to have devastating effects on environment.

The major forms of pollution are listed below along with the particular contaminant relevant to each of them:

- Air pollution: the release of chemicals and particulates into the atmosphere. Common gaseous pollutants include carbon monoxide, sulfur dioxide, chlorofluorocarbons (CFCs) and nitrogen oxides produced by industry and motor vehicles. Photochemical ozone and smog are created as nitrogen oxides and hydrocarbons react to sunlight.
- Water pollution: It occurs by the discharge of wastewater from commercial and industrial waste (intentionally or through spills) into surface waters; discharges of untreated domestic sewage, and chemical contaminants, such as chlorine, from treated sewage; release of waste and contaminants into surface runoff flowing to surface waters (including urban runoff and agricultural runoff, which may contain chemical fertilizers and pesticides); waste disposal and leaching into groundwater; eutrophication and littering [ 3 - 5].

- Soil contamination occurs when chemicals are released by spill or underground leakage. Among the most significant soil contaminants are hydrocarbons, heavy metals, herbicides, pesticides and chlorinated hydrocarbons.
- Radioactive contamination, resulting from 20th century activities in atomic physics, such as nuclear power generation and nuclear weapons research, manufacture and deployment.
- Thermal pollution is a temperature change in natural water bodies caused by human influence, such as use of water as coolant in a power plant.

### **1.2.1 Pollution in Aquatic Environment:**

Saving water to save the planet and to make the future of mankind safe is what we need now. With the growth of mankind, society, science, technology, our world is reaching to new high horizons but the cost which we are paying or will pay in near future is surely to be too high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem [6]. One of the important classes of the pollutants is dyes.

When human life began on the earth, food and shelter were the two most important necessities. Immediately thereafter however came clothing which introduced textile industry. Man had been using various means to decorate the clothes such as fabrication, printing, dyeing, pasting etc. About a century ago, coloring matter had been nature in general and vegetation in particular [7, 8]. At present new developments of synthetic dyeing are greatly welcomed by all textile industry. A simple dye is a water soluble chromogen that can be firmly fixed to the fabrics by physical and chemical bonding. Color playing a dominant role in the life of a man from time immemorial, but natural color does not exist for long time, for this man tries to retain the preferable color for long period. Today coloring matter is industrially producing synthetic dyes and pigments. Dyes exhibit considerable structural diversity and are classified in several ways [9]. These can be classified both by their chemical structure and their application to the fiber type such as Reactive dyes, Direct dyes, Azo dyes, Mordant dyes, Vat dyes, etc. [10-11]

Textile industries are the major consumers of water and they release a fair amount of dyes and other impurities. The characteristics of the waste water discharges vary from location to location depending upon the population density and industrial sector working in that area, land use pattern, ground water level [12]. Textile industry is one of the most important industries in all over the world. The water consumption in textile industry,

especially in dyeing and washing processes, is too high. Therefore, large amount of waste water is produced and discharged to the receiving environment during textile production process [13]. The water used in various processes in Bangladesh textile industry is discharged to a receiving environment without treatment. Therefore, there is a large burden on the receiving water bodies. In textile industry the use of organic dyes has increased dramatically. Waste water from textile industry contains various contaminants such as dyes, surfactants and heavy metals & other impurity. Synthetic dyes are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, food, cosmetics and other industries [14]. Approximately, 10,000 different dyes and pigments are used industrially, and over  $7 \times 10^5$  tons of synthetic dyes are produced annually worldwide. In 1991, the world production of dyes was estimated 6, 68,000 tons of which azo dyes contributed 70% [15]. During dyeing process, a substantial amount of azo dye is lost in wastewater. Sen et al. [16] reported that about 10-15% of dyes were lost in effluent during dyeing process. The amount of dye lost is dependent upon type of dyes, the method of application and depth of shade required and discharge of these dyes in the environment poses serious ecological concern [17, 18]. Major classes of synthetic dyes include azo, anthraquinone and tri-aryl-methane dyes, and many of them are toxic or even carcinogenic compounds with long turn over times. With the increased use of a wide variety of dyes, wastewater is becoming increasingly alarming. Human eyes can clearly detect a concentration of 0.005mg/L of reactive dyes in water [19]. Therefore, the presence of dye exceeding this limit would not be permitted aesthetically. Textile dyes have synthetic origin and complex aromatic molecular structures that make them difficult to bio-degrade when discharged into eco-system [20-21]. Dyestuff producers and users are interested in stability and fastness of dyes on the fabric and they are continually producing dyestuffs which are more difficult to degrade after use [22]. Therefore, this also poses a problem on the degradation of dyestuffs in the environment by natural processes. Because of the diversity of dye components available for the synthesis, a large number of structurally different azo dyes exist and are used in industry. Approximately 80-95 % of all reactive dyes are based on the azo chromogen [23, 24]. Reactive dyes are colored compounds that contain one or two functional groups capable of forming covalent bonds with the active sites in fibers. A carbon or phosphorous atom of the dye molecule will bind to hydroxyl groups in cellulose, amino, thiol, and hydroxyl groups in wool, or amino groups in polyamides [25]. Most fiber-reactive Azo dyes are used for dyeing cellulosic materials,

such as cotton, and are a major source of dye waste in textile effluents. Although, many of dyes are not normally toxic, discharge of colored effluents to environment without removing the color may cause several problems in water. These can be listed as follows:

1. Depending on the exposure time and dye concentration, dyes may have acute and/or chronic effects on exposed organisms.
2. Dyes may absorb and reflect sunlight entering the water so the growth of bacteria levels sufficient to degrade impurities in the water and to start the food chain, may be interfered.
3. Abnormal coloration of surface waters captures the attention of both the public and the Authorities.

Waste water containing dyes represents massive water pollution which is harmful for mankind and also for fish, aquatic plants [20, 26]. The removal of dyestuffs from effluents is of great importance for many countries in the world, both from environmental and economic aspects. Water consumption in the textile industry is too high and water is very costly in many developed countries. Advanced treatment methods are considered for re-use of waste water generated from textile industries. For controlling water pollution it is essential to treat waste water. Waste water containing dyes become a problem. No single treatment is adequate for removing impurity from wastewater [27]. Adsorption by activated charcoal is the effective and cheap method for removing dyes from waste water [25, 28].

### **1.2.2 Water pollution due to discharge of Industrial effluents:**

Water is the most vital element among the natural resources, and is crucial for the survival of all living organisms. The environment, economic growth and development of Bangladesh are all highly influenced by water its regional and seasonal availability, and the quality of surface and groundwater. In terms of quality, the surface water of the country is unprotected from untreated industrial effluents and municipal wastewater, run off pollution from chemical fertilizers and pesticides. Water pollution is an undesirable change in the state of water, contaminated with harmful substances. It is the second most important environmental issue next to air pollution. Any change in the physical, chemical and biological properties of water that has a harmful effect on living things is water pollution. Water pollution affects all the major water bodies of the world such as lakes, rivers, oceans and groundwater. Polluted water is also unfit for drinking and for other consumption purposes. It is also not suitable for agricultural and industrial use. Polluted water also

contains viruses, bacteria, intestinal parasites and other harmful microorganisms, which can cause waterborne diseases such as diarrhea, dysentery, and typhoid. Due to water pollution, the entire ecosystem gets disturbed. Among the sources of water pollution, domestic waste (domestic sewage) and industrial waste are the most important sources contributing to water pollution [29, 30]. Under natural conditions, lakes, rivers, and other water bodies undergo eutrophication, an aging process that slowly fills in the water body with sediment and organic matter. When these sediments enter various bodies of water, fish respiration becomes impaired, plant productivity and water depth become reduced, and aquatic organisms and their environments become suffocated. Pollution in the form of organic material enters waterways in many different forms as sewage, leaves and grass clippings, or runoff from livestock feedlots and pastures. When natural bacteria and protozoan in the water breakdown this organic material, they begin to use up the oxygen dissolved in the water. Many types of fish and bottom-dwelling animals cannot survive when levels of dissolved oxygen drop below two to five parts per million. When this occurs, it kills aquatic organisms in large numbers which leads to disruptions in the food chain.



**Fig.1.2.1.** Aquatic Environment pollution by Industry

### **1.2.3 Textile dyeing industries in Bangladesh and pollution:**

The textile industry has played an important role in Bangladesh's economy for a long time. Currently, the textile industry in Bangladesh accounts for appx.45 percent of all industrial employment and contributes 5 percent to the total national income. Major products exported from Bangladesh include polyester filament fabrics, man-made filament mixed fabrics, PV fabrics, viscose filament fabrics and man-made spun yarns. Major garments



exported include knitted and woven shirts and blouses, trousers, skirts, shorts, jackets, sweaters and sportswear, among other fashion apparel.

The major problem affliction to local environment around Bangladesh's textile dyeing industries is the hazards caused by dye effluents with waste water, which contain both chemical and organic pollutants [31]. The rivers of Dhaka, Narayangong, Chittagong and Khulna Districts are major receivers of the untreated effluents coming from textiles, dyeing, chemicals, etc. [32]. Discharge of effluents from textile mills into drainage have been among the most important water and soil pollution problem in this area. Local peoples have been facing many problems including health, sanitation due to pollute water of this area.



**Fig.1.2.3** Aquatic Environment pollution by Industrial dyes

### 1.3 Dyes

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is usually used as an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber. The dyes were obtained from animal, vegetable or mineral origin with no or very little processing. So dyes are

mainly organic and inorganic chemical substances. And if these substances spread out in the environment, they may cause huge adverse impact on the environment [33].

A good dye is one which when applied to the fabrics show good fastness to washing, light and heat. In the beginning of the 20th century, synthetic dyestuffs had almost completely supplanted natural dyes [34]. The worldwide high level of production and use of dye generates colored waste water which gives rise of environmental concern. The dye is generally applied in an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments appear to be colored because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate.



**Fig.1.3. Different Dyes powder and their uses in Textile Industries.**

Dyes can be classified according to their chemical structure and their application. In term of chemical structure, dyes can be inorganic or organic compounds. Again, both groups can be subdivided into natural and synthetic compounds. According to the dyeing method, dyes can be divided into anionic, direct or disperse dyes, here based on their application [10]. Azo compounds have the azo linker (two nitrogen atoms double bonded to each other:  $N=N$ ). Each nitrogen atom is bound to another group, which most often is an aryl group. There are dyes with one, two, three and even four azo groups in the molecule. The

aromatic rings usually have chloro, hydroxyl, sulphate or nitro groups attached, either to increase the solubility of the dye in water or to enhance its interactions with the substrate. Today, azo dyes are widely used because of their good performance and cost effectiveness. Anthraquinone based compounds are considered to constitute the second most important class of textile dyes after azo dyes. Nevertheless, they do not show the large variety of colors that azo dyes do. In addition, it must be noted that Anthraquinone dyes are expensive. Indigo is extensively used to color denim, popular mostly due to its characteristic of producing gradually fading blue shades. These are used for coloring acrylic fibers and paper. Within this class of dyes, a number of arylcarbenium dyes are used in the basic process, and there are neutral and anionic dyes. Copper Phthalocyanine is widely used in plastics, paints and inks, as well as in the textile industry for dyeing and printing. Sulphur compounds and sulphur containing Chromophores are prepared when sulphur is heated together with aromatic compounds, where sulphur dyes are polymers with heterocyclic rings and thiophenolic sulphur. Sulphur black is used in the textile industry with the highest tonnage of all sulphur containing dyes.

### 1.3.1 Classification of Dyes According to Their Usage

According to the application method, dyes can be classified into acidic, basic, direct, mordant, vat, reactive, and disperse dyes (**Table 1.3.1**).

Class	Principle Substrate	Application method	Chemical types
<b>Acid</b> [15, 34]	nylon, wool, silk, paper, inks, and leather	usually from neutral to acidic Dye baths.	Azo, Anthraquinone, Azine, nitro & nitroso
Azo, Anthraquinone, Azine, nitro and nitroso	cotton, rayon, cellulose acetate and polyester	fiber impregnated with coupling component and treated with Diazonium salt	Azo
<b>Basic</b> [10]	Paper, poly-acryl-nitrile, modified nylon, polyester and inks	applied from acidic dye-baths	Cyanine, azo, Azine, xanthene's, acridine, oxazine, and Anthraquinone
<b>Direct</b> [34, 35]	cotton, rayon, paper, leather and nylon	applied from neutral or slightly alkaline baths	Azo, Phthalocyanine, stilbene, and

		containing additional electrolyte	oxazine
Disperse	polyester, polyamide, acetate, acrylic and plastics	fine aqueous dispersions often applied by high temperature/ pressure	Azo, Anthraquinone, styryl, nitro, and benzodifuranone
Fluorescent brighteners	soaps and detergents, fibers, oils, paints, and plastics	from solution, dispersion or suspension in mass	Stilbene, pyrazoles, coumarin, and naphthalamides
Food, drugs, and cosmetic dyes	foods, drugs, cosmetics		Azo, Anthraquinone, carotenoid and triarylmethane
Mordant	wool, leather, and anodized aluminum	applied in conjunction with Cr salts	Azo and Anthraquinone
Oxidation Bases	hair, fur, and cotton	aromatic amines and phenols oxidized on the substrate	Aniline black and indeterminate structures
<b>Reactive</b> [36]	cotton, wool, silk, and nylon	reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, Anthraquinone, phthalocyanine, formazan, oxazine, and basic
Solvent [10]	plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes	dissolution in the substrate	Azo, tri-phenyl-methane, Anthraquinone, and Phthalocyanine
<b>Sulpher</b> [35]	cotton and rayon	aromatic substrate, vetted with sodium sulphide and re-oxidized to insoluble sulphur containing products on fiber	indeterminate structures

Vat	cotton, rayon, and wool	water-insoluble dyes solubilized by reducing with sodium hydrogen sulfite, then exhausted on fiber and Re-oxidized.	Anthraquinone (including polycyclic Quinone's) and indigoids
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**Table 1: Summary of the classes of dyes according to their application [10].**

#### 1.4 Adverse Effects of Dye-Loaded Waste Water

Wastewater from the textile industry is a complex mixture of many polluting substances ranging from Organo-chlorine-based pesticides to heavy metals associated with dyes or the dyeing process [37]. Many dyes are visible in water at concentrations as low as 1 mg/L. Textile-processing wastewaters, typically with dye content in the range (10-200) mg/L are therefore usually highly colored and discharge in open waters presents an aesthetic problem.

As dyes designed to be chemically and photolytically stable, they are highly persistent in natural environments. The majority of dyes pose a potential health hazard to all forms of life. These dyes may cause allergic responses, skin dermatomes, eczema (Su and Horton, 1998), and may affect the liver, the lungs, the immune system and the reproductive system of experimental animals as well as human systems [38, 39]. Azo Dyes are carcinogenic, causing tumors of liver and urinary bladder in experimental animals [40]. However, reduction of azo dyes, i.e. cleavage of the dye's azo linkage(s), leads to formation of aromatic amines and several aromatic amines are known mutagens and carcinogens. In mammals, metabolic activation (reduction) of azo dyes is mainly due to bacterial activity in the anaerobic parts of the lower gastrointestinal tract. Various other organs, especially the liver and the kidneys, can, however, also reduce azo dyes [41].

According to World Bank, 2012 report emissions of organic pollutants from industrial activities are a major cause of degradation of water quality. Within this context, the developing countries contribute the largest amount of textile wastewater. Moreover, about 10% of dyes used in the textile industry are lost during the dyeing process, and 2% are directly discharged as aqueous effluents into the environment. Without adequate treatment,



these compounds retain their color and structural integrity under exposure to sunlight, soil, bacteria and sweat, and exhibit a high resistance to microbial degradation in wastewater treatment systems. They remain in the environment for longer periods, if discharged without adequate treatment [42].

Thus, waste materials from textile industries are usually discharged as wastewaters, which are high in color, have decreased biochemical oxygen demand (BOD), increased chemical oxygen demand (COD), a change in pH, in temperature, and in turbidity and have toxic chemical content. Apart from this, several dyes and their metabolites have proved toxic to aquatic life (aquatic plants, microorganisms, fish and mammals). It is noteworthy that some dyes are mutagenic. Moreover, due to a decrease of light penetration into the water due to the dyes, the photosynthetic activity of the aquatic system is affected. Dye waste effluents from factories can be a direct health risk (WHO, 2000; WHO, 2002).

### **1.5 Procedures for the Separation and Elimination of Dyes from Water:**

The problematic discussed above necessitates that remnant dyes are separated from wastewater. Procedures for the separation and elimination of dyes from water have to satisfy: firstly, those organic dye-wastes are separated from water environment and secondly, that at least a partial or better yet a complete mineralization or decomposition of the organic dye wastes occurs. Separation processes can be based on fluid mechanics (sedimentation, centrifugation, filtration and flotation) or on synthetic membrane separation techniques (micro-, ultra- and Nano-filtration, and reverse osmosis). Additionally, physio-chemical processes (i.e., adsorption, chemical precipitation, coagulation flocculation, and ionic exchange processes) can be used to separate dissolved, emulsified and solid components from the water environment. Partial and complete mineralization or decomposition of dyes as pollutants can be achieved by biological and chemical processes. Biological methods are used in connection with activated sludge processes and membrane bioreactors. Chemical processes include the advanced oxidation of dyes with ozone;  $H_2O_2$  which can be run concomitantly under UV-irradiation. The biological and chemical processes can also be combined [43, 44]. Among these techniques adsorption is one of the easy and common techniques.

## **1.6 Adsorption:**

Adsorption techniques have gained favor recently due to their efficiency in the removal of pollutants. Thus, adsorption techniques have been found to be among the most effective and proven treatments of dye-loaded wastewater. It is a rapid process of separation of the adsorbate from the aqueous phase of the waste water, producing high quality water. It is a process, which is economically feasible [45]. This process consists in the transfer of soluble dyes from wastewater to the surface of a solid, highly porous material (the adsorbent). Adsorbents can be of organic or inorganic nature. Inorganic adsorbents are china clay, bentonite clays, silica gel, metal oxides, zeolites and fly ash [46-50]. Typical natural organic adsorbents that have been used are peat [51] and woodchips. One of the most used adsorbents is activated carbon.

### **1.6.1 General concept of adsorption:**

Adsorption is defined as the accumulation of a particular substance on interface. The species that is concentrated on the interface is called adsorbate and the material of the surface is called adsorbent. The reason of this accumulation is either a long-range van-der Waal's force of attraction or the electrostatic force of attraction or the unsaturation of the valence force on the surface i.e. the residual field of force [52, 53].

The adsorbent may be solid or liquid. Surface of solid or liquid have certain properties that make them different from bulk. There is no chemical distinction between molecules or atoms on the surface and the molecules or atoms in the bulk. The molecules on the surface have unbalanced forces and they have tendency to satisfy this, whenever the opportunity comes. Adsorption takes place with a decrease in free energy and entropy. As the adsorption continues, the adsorbed solute also tends to desorb. At one stage equal amount of solute is adsorbed and desorbed simultaneously. Eventually, the rates of adsorption and desorption will attain an equilibrium and the time at which such equilibrium is achieved is known as equilibrium time. Adsorption when involves the condensation of single layer of molecules on the surface is termed as monolayer and when involves the condensation of several layers is termed as multi-layer.

The factors on which the extent of adsorption depends are:

- a) The pressure of adsorbate in case of gases.
- b) The nature of the active sites on the surface.
- c) The concentration of the liquid phase.

- d) The nature of adsorbent or adsorbate.
- e) The temperature of surroundings.
- f) pH of the liquid phase.

Adsorption process usually occurs in the following steps [54]:

- a) Bulk solution transport: In this step the adsorbents travel from the bulk solution to the boundary layer of a fixed film liquid neighboring the adsorbent. The dynamic force for this step is advection and dispersion in adsorbent contactors.
- b) Film diffusion transport: In this step, adsorbents spread from inert liquid film to the entry of the pores of the adsorbent and
- c) Pore transport and adsorption: In this step, adsorbate will be attached to the adsorbent at accessible adsorption sites through grouping of molecular diffusion through the pore and/or by distribution along the surface of the adsorbent.

### **1.6.2 Adsorption mechanism:**

The resultant cohesive force is zero when a molecule inside the bulk experiences cohesive forces of equal magnitude in all directions. But the molecules on the surface are pulled downwards and sideways but no forces act on them. “The most favored approach to an investigation of the adsorption mechanism is a study of the isotherm”. The most important aspects are:

- a) The rate of adsorption.
- b) The shapes of the isotherm.
- c) The significance of the plateau found in many isotherms.
- d) The extent of solvent adsorption.
- e) Whether the adsorption is monolayer or extends over several layers
- f) The orientation of the absorbed molecules.
- g) The nature of the interaction between absorbed and adsorbent.
- h) The effect of temperature.

At the first available opportunity of these surface atom or molecules will try to satisfy the unsaturation by capturing other molecules, atoms due to the tendency for the force of energy of any stir thee to decreases, if the valence requirements of the atoms on the surface satisfied. Adsorption tends to take place simply through the van der Waal’s force of attraction, result the physisorption. On the other hand, the adsorption takes place through the chemical force for bond formation and termed as chemisorption or in some case specific adsorption. Monolayer adsorption occurs due to single adsorbate species interact



with adsorbent in chemisorption and physisorption. In some cases of physisorption, multilayer adsorption occurs to lateral van der Waal's force of interaction.

A molecule inside the bulk experiences cohesive forces of equal magnitude in all directions. The resultant cohesive forces is therefore, zero. The molecules on the surface are pulled downwards and sideways but no force act on above them. Therefore, they possess unbalanced or residual attractive force towards liquids and gases and hold adsorbed particles. At the first available opportunity these surface atom or molecules will try to satisfy the unsaturation by capturing other molecules due to the tendency for the force of energy of any surface to decrease. If the valence requirements of the atoms on the surface satisfied, adsorption tend to take simply through the van der Waal's force of attraction, result the physisorption.

### 1.6.3 Adsorption mechanisms of organic compounds:

Organic compounds can adsorb to the adsorbing surface and adsorbents, because organic compounds can be polar or nonpolar in all or part of the compound. Moreover, they may or may not be charged. The organic interactions with the surface can be different from those interactions of inorganic ions and the most important adsorption mechanisms of organic materials are illustrated in the (Table 1.6.3) [55].

Mechanism	Principal organic functional groups involve
Cation Exchange	Amines, ring NH, hetero cyclic N
Protonation	Amines, hetero cyclic N, carbonyl, carboxylate
Anion Exchange	Carboxylate
Water Bridging	Amino, carbonyl, carboxylate, alcoholic OH
Cation Bridging	Carbonylate, carboxylate ,amines, alcoholic OH
Ligand Exchange	Carbonylate
Hydrogen Bonding	Amino, carbonyl, carboxyl, phenyl hydroxyl
Van der Waals interactions	Uncharged, nonpolar organic functional groups
Covalent Bonding	Acrylamide, vinyl sulphonate

### 1.6.4 Types of adsorption:

According to the nature of the force of attraction, two types of adsorption have been distinguished:

- a) Physical adsorption.
- b) Chemical adsorption.

**(a) Physical adsorption:**

When the attractive force holding the adsorbate species on the surface arises from long range van der Waals force or London force of attraction the adsorption is called physical adsorption or van der Waals adsorption. It is similar to that of condensation of vapor on the surface of its own liquid. No electronic interaction takes place in physisorption; as a result, chemical nature of adsorbed species does not change. It is not associated with catalyst. Physical adsorption requires no activation energy and has low heat of adsorption, (~ 20 KJ mol<sup>-1</sup>) [56]. So the physical adsorption process is exothermic [57]

**(b) Chemical adsorption:**

When the attractive force acting between adsorbed species and the surface arises from electronic interaction, the adsorption is known as chemical adsorption. This interaction results to some extent due to covalent bonding or hydrogen bonding or by both. This is associated with catalyst. Chemisorption occurs at high heat of adsorption, 200 KJ mol<sup>-1</sup> [56]. So the chemical adsorption process is exothermic Chemisorption's is classified into two groups: i) Specific adsorption and ii) Exchange adsorption.

**1.6.5 Adsorption equilibrium**

The adsorbed solute tends to desorb into the solution during the adsorption from solution as the adsorption continues. At one stage equal amounts of solute is adsorbed and desorbed simultaneously. Eventually, the rates of adsorption and desorption attains an equilibrium. This is called adsorption equilibrium. The corresponding time at which such equilibrium achieved is called equilibrium time  $t_e$  and the corresponding solute concentration is called equilibrium concentration. The Knowledge of equilibrium time is necessary for adsorption, which control the adsorption capacity. The position of equilibrium is the characteristics of the entire system, the adsorbate, adsorbent, solvent temperature, pH etc. [58]. A number of mathematical expressions have been developed to give quantitative relationship between the amounts adsorbed with the equilibrium concentration of the solution.

$$\frac{x}{m} = f(C_e, T) \dots\dots\dots (1)$$

Where,  $x/m$ =weight of adsorbate adsorbed per gram of adsorbent  $C_e$ = equilibrium concentration of the solution.  $T$  = absolute temperature (K)

## 1.7 Adsorption isotherm:

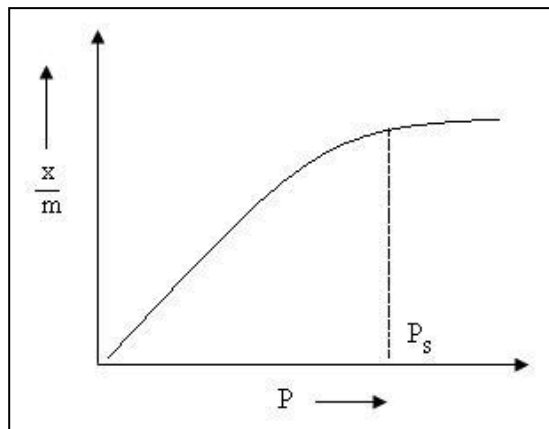
The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems. The adsorption isotherm is also an invaluable tool for the theoretical evaluation and interpretation of thermodynamic parameters such as heats of adsorption. An isotherm may fit experimental data accurately under one set of conditions but fail entirely under another [59]. The adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature. In general, the adsorption isotherm describes how adsorbate will interact with adsorbents and so is critical in optimizing the use of adsorbents.

Adsorption is usually characterized by isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials.

### 1.7.1 Type of Adsorption Isotherm:

Five different types of adsorption isotherm and their characteristics are explained below:

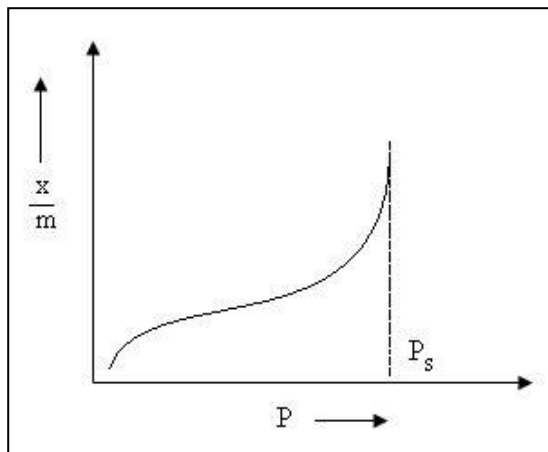
#### Type I: Adsorption Isotherm



Type I Adsorption Isotherm

- The above graph depicts Monolayer adsorption.
- This graph can be easily explained using Langmuir Adsorption Isotherm.
- If BET equation, when  $P/P_0 \ll 1$  and  $c \gg 1$ , then it leads to monolayer formation and Type I Adsorption Isotherm is obtained.
- Examples of Type-I adsorption are Adsorption of Nitrogen ( $N_2$ ) or Hydrogen ( $H_2$ ) on charcoal at temperature near to  $-180^\circ C$ .

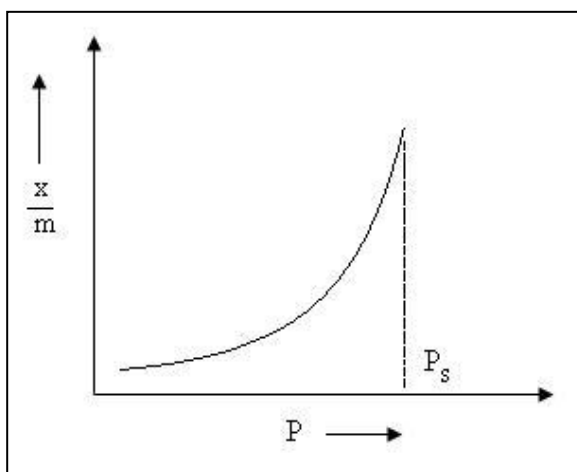
### Type II: Adsorption Isotherm



Type II Adsorption Isotherm

- Type II Adsorption Isotherm shows large deviation from Langmuir model of adsorption.
- The intermediate flat region in the isotherm corresponds to monolayer formation.
- In BET equation, value of  $C$  has to be very large in comparison to 1.
- Examples of Type-II adsorption are Nitrogen [ $N_2$  (g) adsorbed at  $-195^\circ\text{C}$  on Iron (Fe) catalyst and Nitrogen ( $N_2$  (g)) adsorbed at  $-195^\circ\text{C}$  on silica gel.

### Type III Adsorption Isotherm

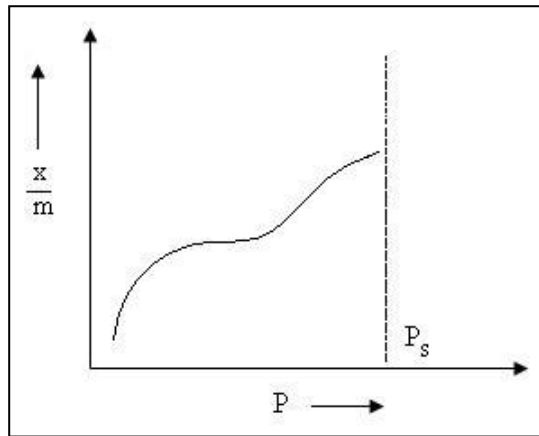


Type III Adsorption Isotherm

- Type III Adsorption Isotherm also shows large deviation from Langmuir model.

- In BET equation value if  $C \lll 1$  Type III Adsorption Isotherm obtained.
- This isotherm explains the formation of multilayer.
- There is no flattish portion in the curve which indicates that monolayer formation is missing.
- Examples of Type III Adsorption Isotherm are Bromine ( $\text{Br}_2$ ) at  $79^\circ\text{C}$  on silica gel or Iodine ( $\text{I}_2$ ) at  $79^\circ\text{C}$  on silica gel.

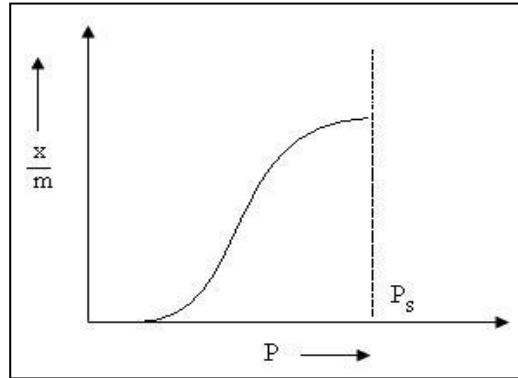
**Type IV: Adsorption Isotherm**



Type IV: Adsorption Isotherm

- At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer.
- The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure ( $P_s$ ) of the gas.
- Examples of Type IV Adsorption Isotherm are of adsorption of Benzene on Iron Oxide ( $\text{Fe}_2\text{O}_3$ ) at  $50^\circ\text{C}$  and adsorption of Benzene on silica gel at  $50^\circ\text{C}$ .

**Type V: Adsorption Isotherm**



Type V Adsorption Isotherm

- Explanation of Type V graph is similar to Type IV.
- Example of Type V Adsorption Isotherm is adsorption of Water (vapors) at 100 °C on charcoal.
- Type IV and V shows phenomenon of capillary condensation of gas.

**1.7.2 Langmuir isotherm [57]:**

The Langmuir isotherm is the best known of all isotherms. In 1916 Langmuir derived an equation based on the adsorption of gases on a solid considering the following assumption

1. The surface is homogeneous. No chemical interaction takes places between the adsorbate and adsorbent. So that the chemical and physical behavior of the adsorbate remain unchanged.
2. Each site accommodate only one adsorbate and forms a layer of one molecule thickness i.e. monolayer adsorption.
3. The dynamic equilibrium exists between adsorption and desorption. For gas-solid adsorption the Langmuir equation can be written as:

$$V = \frac{V_m bp}{1 + bp} \dots\dots\dots (2)$$

And  $\theta = \frac{bp}{1 + bp} \dots\dots\dots (3)$

Where, V = amount adsorbed at any pressure, V<sub>m</sub> = amount adsorbed for monolayer formation, b = k<sub>a</sub>/k<sub>d</sub> = equilibrium constant, K<sub>a</sub> = rate of adsorption, K<sub>d</sub> = rate of desorption, P = pressure of adsorbate, θ = fractional coverage of the surface

Rearranging equation (2), we get

$$\frac{1}{V} = \frac{1}{bpV_m} + \frac{1}{V_m} \dots\dots\dots (4)$$

This is the Langmuir equation for gas solid system. Langmuir equation is also valid for adsorption from solution. Therefore, replacing the pressure term by equilibrium concentration ( $C_e$ ), equation (4) becomes,

$$\frac{C_e}{x/m} = \frac{1}{bV_m} + \frac{C_e}{V_m} \dots\dots\dots (5)$$

This equation is known as Langmuir isotherm equation and the linear form of this equation can be written as follows

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{C_e}{q_m} \dots\dots\dots (6)$$

Where,  $K_L = bV_m =$  Langmuir adsorption constant (L/mg)

$x/m = q_e =$  equilibrium amount adsorbed (mg/g)

$q_m =$  maximum adsorption capacity (mg/g)

### 1.7.3 Freundlich isotherm [60]:

An empirical relationship was given by Freundlich when pressure is neither too high nor too low, then

$$V \propto P^{\frac{1}{n}}$$

$$\text{or, } V \propto KP^{\frac{1}{n}}$$

Where,  $V =$  amount adsorbed at any pressure,  $P =$  is the Pressure

This is the Freundlich equation and can be written as:

$$\frac{x}{m} = kC_e^{\frac{1}{n}}$$

$$\text{or, } \log \frac{x}{m} = \log k_F + \frac{1}{n} \log C_e$$

$$\text{or, } \log q_e = \log k_F + \frac{1}{n} \log C_e \dots\dots\dots (7)$$

Where,  $K_F$  is a constant for the system, related to the bonding energy.  $K_F$  can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration.  $1/n$  is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for  $1/n$  below 1 indicates a normal Freundlich isotherm while  $1/n$  above 1 is indicative of cooperative adsorption. This equation shows the variation of

adsorption with concentration at constant temperature. It has been found to be valid over a limited range of concentration. A plot of  $\log q_e$  versus  $\log C_e$  gives a straight line of slope  $1/n$ , is known as classical adsorption isotherm or Freundlich isotherm.

#### 1.7.4 BET isotherm:

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: a) gas molecules physically adsorb on a solid in layers infinitely; b) there is no interaction between each adsorption layer and c) the Langmuir theory can be applied to each layer.

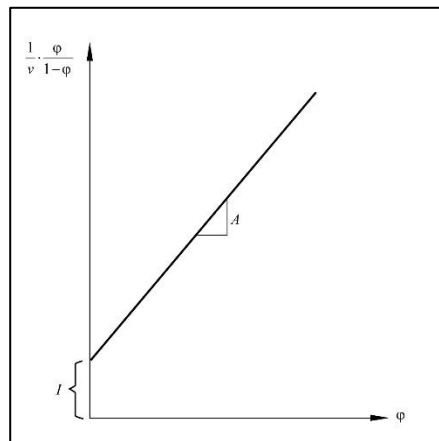
The resulting BET equation is

$$\frac{1}{v[(p_0/p) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0}\right) + \frac{1}{v_m c} \dots\dots\dots (8)$$

Where,  $p$  and  $p_0$  are the equilibrium and the saturation pressure of adsorbate at the temperature of adsorption,  $v$  is the adsorbed gas quantity (for example, in volume units), and  $v_m$  is the monolayer adsorbed gas quantity and  $c$  is the BET constant,

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right) \dots\dots\dots (9)$$

Where,  $E_1$  is the heat of adsorption for the first layer, and  $E_L$  is that for the second and higher layers and is equal to the heat of liquefaction.



BET curve

Equation (1) is an adsorption isotherm and can be plotted as a straight line with  $\frac{1}{v[(p_0/p) - 1]}$  on the y-axis and  $\varphi = \left(\frac{p}{p_0}\right)$  on the x-axis according to experimental



results. This plot is called a *BET plot*. The linear relationship of this equation is maintained only in the range of  $[0.05 < (p/p_0) < 0.35]$ . The value of the slope  $A$  and the y-intercept  $I$  of the line are used to calculate the monolayer adsorbed gas quantity  $v_m$  and the BET constant  $c$ . The following equations can be used:

$$v_m = \frac{1}{A + I}$$

$$c = 1 + \frac{A}{I}$$

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. The total surface area  $S_{total}$  and the specific surface area  $S_{BET}$  are given by

$$S_{total} = \frac{v_m N_s}{V}$$

$$S_{BET} = \frac{S_{total}}{a}$$

Where  $v_m$  is in units of volume which are also the units of the monolayer volume of the adsorbate gas,  $N$  is Avogadro's number,  $s$  is the adsorption cross section of the adsorbing species,  $V$  is the molar volume of the adsorbate gas, and  $a$  the mass of the solid sample or adsorbent [61].

## 1.8 Kinetics of adsorption

The kinetics of adsorption data was processed to understand the dynamics of adsorption process in terms of the order of rate constant. The study of adsorption kinetics describes the solute uptake rate and this rate controls the residence time of adsorbate uptake at the solid solution interface. In order to investigate the adsorption processes of studied dyes on LBS three kinetic models were used. The rate constants of chemical adsorption for studied dyes were determined using the equations of a pseudo-first-order and pseudo-second-order.

### 1.8.1 Lagergren's pseudo first order equation [62]:

The Lagergren rate equation in the following form was used when the kinetics of adsorption follow the pseudo first order rate equation. The equation is...

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \dots\dots\dots (10)$$

Where,  $q_e$  and  $q_t$  is the amounts of adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min), respectively,  $k_1$  ( $\text{min}^{-1}$ ) is adsorption rate constant. Applying conditions:

$$q_t = 0 \text{ at } t = 0$$

$$q_t = q_e \text{ at } t = t$$

Based on experimental results, linear plots of  $\log (q_e - q_t)$  versus  $q_e$  were tested the applicability of Lagergren first order equation to the adsorption of tested dyes. The rate constant was calculated from the slope.

### 1.8.2 Ho's Pseudo-second order equation [63]:

The pseudo-second order kinetics may be expressed as:

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

$$\text{or, } \frac{dq_t}{(q_e - q_t)^2} = k_2 dt$$

Where,  $q_t$  and  $q_e$  are the dye uptake ( $\text{mg/g}$ ) at time  $t$  and at equilibrium respectively and  $k_2$  is the rate constant of sorption process.

Integrating this for the condition  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  gives:

$$\frac{1}{(q_e - q_t)} = k_2 t + \frac{1}{q_e}$$

$$\text{or, } \frac{t}{q_t} = \frac{1}{2k_2 q_e^2} + \frac{1}{q_e} t \dots\dots\dots (11)$$

Plot of  $(t/q_t)$  versus time  $(t)$  give a straight line for the pseudo second order kinetics.

### 1.8.3 Intra-particle diffusion model

In the first step of adsorption the film diffusion is an important rate- Controlling step and external mass transfer or boundary layer diffusion can be characterized by the initial rate of solute sorption. Mass transfer and kinetic models have been used to test the experimental data. Adsorption kinetics is determined by the following stages [64].

- Diffusion of molecules from the bulk phase towards the interface space so called external diffusion.
- Diffusion of molecules inside the pores internal diffusion.
- Diffusion of molecules in the surface phase surface diffusion.

The intra-particle diffusion model is expressed as follows (Chen et al., 2010):

$$q_t = k_{id} + C \dots\dots\dots (12)$$

Where,  $k_{id}$  is the intra-particle diffusion rate constant ( $\text{mg/g min}^{1/2}$ ),  $C$  is the intercept ( $\text{mg/g}$ ). A plot of  $q_t$  versus  $t^{1/2}$  gives a linear relationship, from which the  $k_{id}$  value was determined from the slope. The intercept of the plot reflects the boundary layer effect. If the regression of the plot is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step.

## Chapter II

### Literature Review

#### 2.1 Literature Review

Color is the first pollutant to be known in wastewater. Water pollution due to discharge of colored effluents from textile dye manufacturing and textile dyeing mills are one of the major environmental concerns in the world today. The total dye consumption of the textile industry worldwide is more than 107 kg/yea. In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulphonate groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups. Many dyes may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system. The aquatic ecosystem can also be affected due to the toxicity of these dyes. A very low concentration of dye can make water unacceptable for various purposes. Various techniques have been employed for the removal of textile dyes from wastewaters which include adsorption, nano-filtration, electro kinetic coagulation, coagulation and precipitation, advanced chemical oxidation, electrochemical oxidation, ozonation, supported liquid membrane, liquid-liquid extraction and biological process. Adsorption has been shown to be one of the most promising and extensively used methods for the removal of both inorganic and organic pollutants from contaminated water. Some of the advantages of adsorption process are possible regeneration at low cost, availability of known process equipment, sludge-free operation and recovery of the sorbet. The use of activated carbon has been highlighted as an effective technique for dye removal. Activated carbon is the most widely used adsorbent for dye removal because of its extended surface area, its unique molecular structure, high porosity ,micro-pore structures, high adsorption capacity and high degree of surface reactivity. Use of bio-adsorbent like clay materials, rice husk, coconut coir, banana pith, wheat straw, bagasse, saw dust , used

tea leaves, cow dung have been found to be highly effective, cheap and eco-friendly. Some of the studies about the adsorption of dyestuffs are summarized below.

**Chincholi, M., et al. [65]** investigated “Removal of dye by adsorption on various adsorbents. In this investigation the most important parameter is the solution pH, where a high pH value is preferred for cationic dye adsorption while a low pH value is more suitable for anionic dye adsorption. For the effect of initial dye concentration, the removal efficiency will decrease with an increase in the initial dye concentration due to the saturation of adsorption sites on the adsorbent surface.

**Balarak, D., [66]** worked on adsorption Behavior of Acid Red 97 Dye on Canola Stalks. In this investigation, the mechanism of the adsorption of Acid Red 97 dye from aqueous solution using an Canola stalks was studied. Different parameters affecting dye removal were studied. The results of different experiments showed that Canola stalks have an ability to adsorb disperse AR97 dye from aqueous solutions. Different variables, such as contact time, adsorbent dose, adsorbent particle size, initial dye concentration and stirring rate influenced the adsorptive quantity. The experimental data of adsorbing disperse AR97 dye are fit well to Langmuir isotherm model more than Freundlich model and the maximum adsorptive quantity of Canola stalks was 19.8 mg/g according to Langmuir model.

**Zhang, W. X., et al. [67]** Investigated the potential application of wheat straw modified by etherification process for removal of toxic dyes. The adsorption conducts of the modified straw for acid green 25 and methyl orange removal were studied in both column and batch method. Obtained data as recorded by the researchers indicated the adsorption process were chemisorption in nature with an ion-exchange mechanism.

**Gulnaz, O., et al. [68]** investigated the adsorption of basic dyes BR18 and BB9 by dried activated sludge in a batch system. The data obtained showed that activated sludge had monolayer adsorption capacity of 285.71 and 256.41mg.g<sup>-1</sup> for BR18 and BB9, respectively, Langmuir and Freundlich isotherm models were applied to deduce and understand the adsorption mechanism of the investigated dyes.

**Anbia, M., et al. [69]** using mesoporous carbon adsorbent for removal of Malachite Green dye from wastewater was studied. Mesoporous carbon was synthesized and effects of various conditions such as dye concentration, adsorbent dose, contact time and pH were observed, the adsorption isotherms and rate kinetics were also determined.

**Mittal, A., [70]** applied hen feather as prospective adsorbent to removal malachite green, a toxic tri-phenyl methane dye from wastewater. The adsorption parameters such as adsorbent dosage, temperature, concentration of adsorbate, pH and contact time on the adsorption were examined. The adsorption isotherm constants obtained in the research were dependent on the initial concentration of the dye. The adsorption of malachite green was discovered to be intra-particle and film diffusion processes at lower and higher concentration respectively.

**Hameed, et al. [71]** studied papaya seeds a novel nonconventional low-cost adsorbent for the removal of Methylene blue. The effect of dye adsorption increased with increase in adsorbent dosage and pH. In terms of the initial rate of adsorption, the uptake of the cationic dye on to papaya seeds was found to occur more rapidly. The intra-particle diffusion indicated that more than one process affected the adsorption. The removal of Methylene blue by papaya seeds suggested that the sorption interaction obeyed the pseudo second-order kinetics.

**Mall, I.D., et al. [72]** studied the removal of malachite green dye from aqueous solution using bagasse fly ash and analyzed kinetic and adsorption isotherm models Adsorption was carried out in batch processes and the effects of various parameters were analyzed. Adsorption followed pseudo-second-order kinetics.

**Immich, A.P.S., et al. [73]** studied Neem leaf as adsorbent for reactive dyes. Neem leaf has proven to be a promising effective material for the removal of Remazol Blue RR dye from aqueous solution.

**Ho, Y. S., et al. [74]** utilized tree fern for remove of basic red 13 from wastewater. The system has variable factors includes adsorbent temperature, particle size and data detected the effort of tree fern, an agricultural product as a low cost adsorbent. The Langmuir isotherm was found to represent the studied adsorption result well. The dye adsorption capability of tree fern increased as the adsorbent particle size decreased. Maximum saturated monolayer adsorption capability of tree fern for BR13 was 408mg.g<sup>-1</sup>. Thermodynamic parameters suggested that the adsorption of BR13 was endothermic and spontaneous.

**Gupta, V. K., et al. [75]** transformed waste carbon slurries and blast furnace slag into low-cost adsorbents. The adsorbents has been described and utilized for the removal of basic red dye from aqueous solution. The adsorption results are related to Langmuir and

Freundlich isotherms in each method. The kinetics of adsorption relies on the adsorbate concentration and the chemical and physical characteristic of the adsorbent. Studies were behavior to scheme the effect of initial adsorbate concentration, particle size of the adsorbent, pH, temperature and solid to liquid ratio. The adsorption of BR was discovered to be first- order and endothermic in nature

**Shabudeen, P.S. Syed., [76]** “Removal of Malachite Green present in aqueous solution by use of solid agricultural waste, was studied Agricultural solid waste, Kapok hull was activated by Sulphuric acid (1:1 ratio) and batch kinetic and isotherm experiments were performed to determine the sorption and desorption characteristics. The experimental parameters affecting rate of adsorption were initial dye concentration, carbon dose, agitation time, particle size, and temperature and pH variation. It was found out that inter-particle diffusion is the rate limiting step.

**Wang, *et al.* [77]** reported on the capacity and mechanism of adsorption of two basic dyes, namely Malachite green and Methylene blue by rice bran and wheat bran. The adsorption of both basic dyes was pH dependent. Both the dyes are basic in nature, which upon dissociation release colored dye Cations into solution.

**Giwa, A.A., *et al.* [78]** worked on removal of basic dye From Aqueous Solution by Adsorption on Melon Husk in Binary and Ternary Systems. The effect of dye adsorption increased with increase in adsorbent dosage and pH. The intra-particle diffusion indicated that more than one process affected the adsorption.

**Ramesh, T. N., *et al.* [79]** investigated Removal of Indigo Carmine Dye from Aqueous Solution Using Magnesium Hydroxide as an Adsorbent. Langmuir and Harkin-Jura isotherms fit well at pH 7.0 indicating that monolayer and multilayer adsorption occurs simultaneously. The percentage of adsorption of indigo carmine dye from aqueous solution onto magnesium hydroxide maintained at pH 6-7 and at 333 K is 20% higher than that at pH 12-13. The results demonstrate that the process of adsorption is endothermic and spontaneous. Therefore, magnesium hydroxide is used as a low cost adsorbent for the removal of indigo carmine dye solution

**Malik, *et al.* [80]** used groundnut shell, an agricultural solid waste as an adsorbent for the removal of Malachite green from aqueous solution. Nut shell is carbonaceous, fibrous solid waste, which creates a disposal problem and is generally used for its fuel value.

**Abdullah, et al. [81]** studied the effectiveness of adsorption for dye removal from waste water and has made an ideal alternative to other expensive treatment method. This study investigates the potential use of sugarcane bagasse, pretreated with formaldehyde and sulphuric acid, for the removal of methyl red, an azo dye from simulated waste water. The effects of condition such as adsorbent dosage, initial dye concentration, pH and contact time were studied.

**Hameed, B.H., et al. [82]** studied the adsorption of Malachite green dye by rattan sawdust at 30°C. Results indicated that rattan sawdust can be used as low cost adsorbent source. Two isotherms Freundlich and Langmuir were analyzed and the best fit model was found to be Langmuir isotherm model. Adsorption kinetics was predicted by pseudo-first –order model.

**Filho, C., et al. [83]** The adsorption kinetics and equilibrium of methylene blue onto reticulated formic Lignin from sugar cane bagasse was studied by. The adsorption process is pH, temperature and ionic strength ( $\mu$ ) dependent.

**Shawabkeh, R.A., et al. [84]** performed study of adsorption of phenol and Methylene Blue by activated carbon from pecan shells. Activated carbon is prepared from pecan shells by chemical activation with phosphoric acid. Then it is treated with sodium dodecyl sulfate to prepare the surface for adsorption. The results indicated good removal of phenol and Methylene Blue dye by pecan shells.

**Dulman, et al. [85]** investigated the effect of Beech wood sawdust on the adsorption of six reactive dyes in aqueous solution, namely C.I. Direct Blue 6, C.I. Direct Brown 2, C. I. Direct Green 26, C.I. Direct Brown, C.I. Reactive Red 3. C.I. Basic Blue 86. The percentage removal of the reactive dyes Direct Brown 2 and Direct Brown decreased with increase in pH (above pH 10) and the maximum removal rate was occurred at pH 3. Consequently, the percentage color removal of Direct Brown 2 and Direct Brown dropped

from 98.6 to 34.7 % and 94.4 to 28.5 %, respectively. For Basic Blue the sorption has a maximum value of 97 % at pH 4.43–7.06. At lower pH ( $\text{pH} \setminus \text{pH}_{zpc}$ ), the percentage color removal of hydrolyzed reactive dyes was relatively high.

**Han, et al. [86]** “A Phoenix tree leaf has been studied as an adsorbent for the removal of Methylene blue from aqueous solution”. The Phoenix tree leaves contain abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen, etc., which make biosorption process possible. The leaf is a waste product with



practically no cost but its adsorption capacity is 80.90, 83.80, 89.70 mg g<sup>-1</sup> at 295, 305 and 323 K, respectively, makes it an adsorbent of a little importance for dye removal from wastewater.

**Thinakaran, *et al.* [87]** used Sunflower seed hull activated with sulphuric acid as an adsorbents for the removal of Acid violet 17. The Langmuir adsorption capacity was found to be 116.27 mg/g.

**Dawood, S., *et al.* [88]** worked on Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design. The kinetics of the process was found to be dependent on contact time, adsorbent dose and pH. It was observed that adsorption obeys both Freundlich and Langmuir isotherms and the intra-particle diffusion of dye molecule within the particle is the rate-limiting step.

**Dehghani, H.M., *et al.* [89]** worked on the adsorption of methylene blue dye (MBD) from aqueous solutions was investigated using a new composite made up of shrimp waste chitosan and zeolite as adsorbent. Response surface methodology (RSM) was used to optimize the effects of process variables, such as contact time, pH, adsorbent dose and initial MBD concentration on dye removal. The results showed that optimum conditions for removal of MBD were adsorbent dose of 2.5 g/L and pH of 9.0, and initial MBD concentration of 43.75 mg/L and contact time of 138.65 min. The initial concentration of dye had the greatest influence on MBD adsorption among other variables. The experimental data were well fitted by the pseudo-second order kinetic model, while the Freundlich isotherm model indicated a good ability for describing equilibrium data. According to this isotherm model, maximum adsorption capacity of the composite was 24.5 mg/g. Desorption studies showed that the desorption process is favored at low pH under acidic conditions.

**Ghahremani, R., *et al.* [90]** In order to enhance adsorption capacity for dye removal, mixed matrix SAPO-34/polyvinyl alcohol membrane adsorbent (MMMA) was synthesized. Mixing PVA with SAPO-34 particles provides an effective structure that leads to efficient adsorption performance and high methylene blue removal efficiency. The effect of zeolite content was also studied via synthesis of different MMMA. Morphology and intermolecular interaction of the MMMA were determined using Fourier transform infrared and scanning electron microscope. The adsorption measurements were carried out in batch mode at various operating parameters such as contact time, temperature, pH, and

initial concentration to determine the optimum experimental condition. The experimental data were closely fitted with the Freundlich adsorption isotherm model rather than the Langmuir and the Temkin isotherm models and the adsorption kinetic data were fitted in accordance with the pseudo-second-order model. The evaluated data for  $\Delta G^\circ$  indicated that the adsorption process is spontaneous at lower temperature values and non-spontaneous at higher temperature values. Estimated  $\Delta H^\circ$  and  $\Delta S^\circ$  values also exhibited an exothermic adsorption process with an increase in orderliness at the solid–solution interface.

## **2.2 Objective of the work:**

Reactive Magenta HB, Active Orange P2R and Reactive Red ME6BL are reactive dyes frequently supplemented into environment from discharge of textile, tannery, paper, plastics etc. industries. From discharge of these industrial wastes pollutants enter into soil and aquatic environment.

The presence of toxic chemicals on earth is threat for living beings. It is necessary to treat effluents containing mentioned dyes prior to the discharge into the receiving water. Various methods are currently used for removal of dyes from aquatic media including precipitation, coagulation, filtration, flotation, sedimentation, membrane process, electrochemical technique, ion-exchange and adsorption on solids. Among these techniques, the adsorption is the most easiest and efficient methods of removal these pollutants. Lima bean seed's powder having a very high surface area is widely used as an adsorbent in different industries. In this research work, adsorption study of Reactive Magenta HB, Active Orange P2R and Reactive Red ME6BL has been done on Lima bean seed's powder. The specific aims of this study are to:

- a) study the kinetics of adsorption of Reactive Magenta HB, Active Orange P2R, Reactive Red ME6BL has been done on Lima bean seed's powder
- b) determine the effect of pH on adsorption
- c) investigate the effect of concentration
- d) investigate the effect of contact time and
- e) Study the adsorption isotherms
- f) Study the kinetics of adsorption.

## CHAPTER III

### Methodology

### 3. MATERIALS AND METHODS

#### 3.1 Apparatus and Reagents

##### a) Glass and plastic wares

- Graduated Pipette, (2.0 mL and 1.0 mL), England
- Pipettes (25.0 mL and 10.0mL), England
- Volumetric Flasks, (1000 mL, 250 mL and 50 mL), England
- Reagent Bottles (125 mL and 250 mL), England
- Beakers (2000 mL, 1000 mL, 500 mL, 100 mL and 50 mL), China
- Polypropylene shaking bottle for adsorption ( 125 mL, Poly-lab, India)
- Funnels, China
- Centrifuge Tubes, China

##### b) Reagents and Chemicals

- Sodium hydroxide, NaOH ( E-Merck, Germany)
- Hydrochloric acid, HCl ( E-Merck, Germany)

##### c) Solvents

- Di-ionized water
- Distilled water

##### d) Instrument

- pH meter (HANNA instrument, Taiwan)
- Electric oven (HOT AIR STERILIZER, NO: YCO-010 Series, GEMMY 888)
- Electric Balance (NAFAO TRADERS)
- A double beam UV-visible spectrophotometer ( UV-160A, Shimadzu Japan)
- Electric shaker ( GEMMY Orbit shaker, Model: VRN-480)
- Laboratory test sieve (MIC-200)

### 3.1.2 Adsorbate

Reactive Magenta HB, Active Orange P2R, Reactive Red ME6BL



Figure 3.1.2: Photograph of dyes

### 3.1.3 Adsorbent

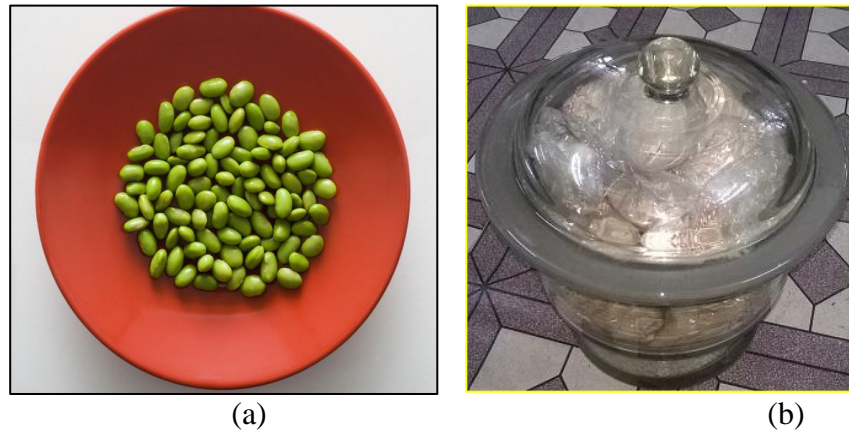
Lima Bean Seed's powder



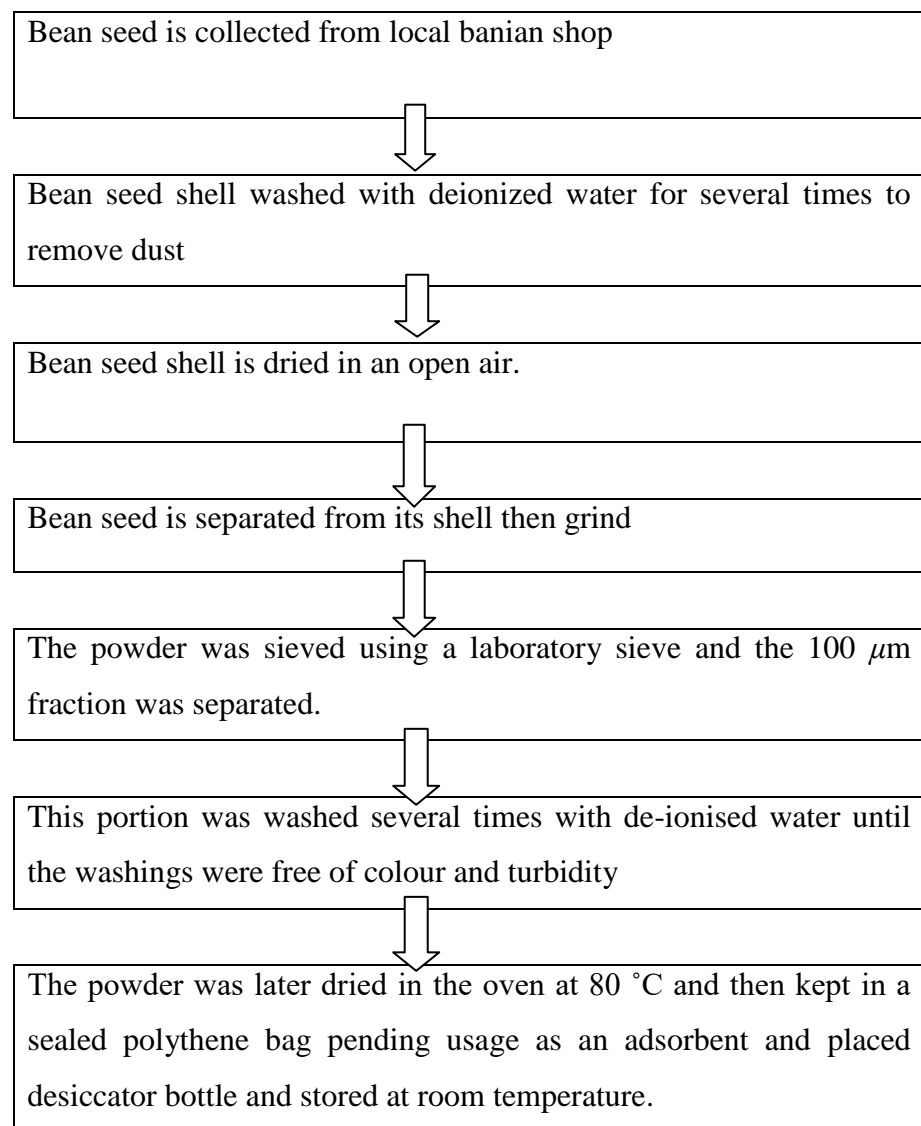
Figure 3.1.3: Photograph of adsorbent

## 3.2 Adsorbent Preparation

Dried and fresh Lima bean seed's powder was used as adsorbent. Seeds were collected from local herbal shop. They were washed with de-ionized water to remove dust like impurities and dries in the sun. Then seeds were crushed in a grinder. Then the powder were air-dried, ground and sieved to a desired mesh size. The prepared sample was placed in a desiccator bottle and stored at room temperature.



**Figure 3.2-1 (a) Bean seed's and (b) Seed's powder stored in desiccator**



**Figure 3.2-2: Flow diagram of preparation of lima bean seed's powder.**

### 3.3 Composition of Lima bean seed's

Lima bean is a tropical and subtropical legume cultivated for its edible seeds. The proximate composition of Lima Bean (*Phaseolus lunatus*) seeds is presented in Table 3.3.1. The moisture content is 6.63 %; which is lower than 10.39% reported for cowpea and 8.30% for Mung bean (Masood and Rizwana, 2010). The sample shows crude protein content (24.5%) higher than what is obtainable in most cereal crops. The high protein contents of the seeds underline its potential as protein supplements in cereals to improve protein quality. The crude fibre is (5.2%), above what is obtainable in most plant foods such as 4.61% found in Mung bean (Masood and Rizwana, 2010). The fat content is 0.61% which is lower than 1.8% reported for cowpea and 1.3% for Mung bean, while carbohydrate is 40.10%.

<b>Table 3.3.1: % Composition of Lima Bean Seeds</b>			
<b>Main analysis</b>	<b>%</b>	<b>Amino acids</b>	<b>%</b>
Dry Matter	88.4	Histidine	2.8
Crude protein	24.5	Isoleucine	4.6
Crude fibre	5.2	Leucine	8.0
Ash	4.6	Lysine	6.0
Moisture	6.63	Methionine	1.4
Starch	40.1	Phenylalanine	5.5
Total sugars	8.3	Serine	4.9
Gross energy	18.4	Threonine	4.7
Fat	0.61	Tryptophan	1.0
<b>Amino acids</b>	<b>%</b>	Tyrosine	3.6
Alanine	3.6	Valine	4.9
Arginine	5.6	<b>Minerals</b>	<b>%</b>
Aspartic acid	9.1	Calcium	4.0
Cystine	1.1	Phosphorus	5.5
Glutamic acid	12.8	Potassium	17.9
Glycine	4.8	Magnesium	2.0
<b>Source: Feedipedia-Animal feed resources information system</b>			

### 3.3.1 Characterization of bean seed's powder

The following characteristic properties of seed's powder were studied:

#### Proximate Analysis

ASTM International defines proximate analysis as the determination by prescribed methods of moisture, volatile matter, ash & fixed carbon. The proximate analysis of the given seeds powder sample will be followed by the procedure given below.

##### a) Moisture Content-

A small amount of the sample was put in a petri-dish or crucible, covered with a lid & weighed using a weighing balance. The crucible was placed in the hot air oven at 105° C with its lid removed & dried for 1.30 hrs. The crucible was taken out, immediately covered with the lid, cooled in desiccators & weighed.

% of moisture content  $M = 100(B-F) / (B-G)$

Here,

G = Weight of empty dish

B = Weight of empty dish + sample (before heating)

F = Weight of empty dish + moisture free sample (after heating)

##### b) Ash content

The crucible was ignited in the muffle furnace at (500+ 25) ° C for 1.5 hours. The Crucible was placed in the desiccator, cooled to room temperature & weighed. A known amount of the sample which was dried in the hot air oven at 150°C for 3 hours was put in the crucible & the crucible was placed back in the muffle furnace at (500+10) ° C for 1.5hours. The crucible was taken out of the furnace, placed in the desiccator, cooled to room temperature & weighed.

% of ash content,  $A = (\text{weight of ash} \times 100) / \text{Weight of sample}$

##### c) Volatile matter content

A known amount of sample was put in the crucible. The crucible was placed in a muffle furnace at (450+10) ° C, covered with lid, & placed for exactly 7 minutes. The crucible was taken out, allowed to cool & weighed.

% of volatile matter content,  $VM = [(A-B)/A] \times 100$

Here,

A = Weight of empty crucible + lid + sample (before heating)

B = Weight of empty crucible + lid + sample (after heating)

d) Fixed carbon determination:

The Fixed Carbon content (FC) is determined as:

$$\% \text{ of fixed carbon} = 100 - (M + A + VM)$$

Here,

VM = Volatile Matter content in %

M = Moisture content in %

A = Ash content in %

### **3.4 Preparation of 1.0 M HCl Solutions**

100 mL of 37.5 % of HCl was taken into 1000 mL volumetric flask and was diluted up to the mark with distilled water.

### **3.5 Preparation of 1.0 M NaOH Solutions**

44.0 g NaOH was taken into 1000 mL volumetric flask and was diluted up to the mark with distilled water.

## **3.6 Experimental portfolio for adsorption study**

### **3.6.1. Batch kinetics studies**

Adsorption experiments were carried out by agitating 100 mg of adsorbent with 25 mL of dye solutions of desired concentration and pH in a 50 mL screw type Erlenmeyer flask at room temperature. A good contact was made between the adsorbent and dye by agitating at 169 rpm in GEMMY Orbit Shaker. Dye concentration was determined spectrophotometrically by monitoring the absorbance at 400-600 nm using a double beam UV-visible spectrophotometer (UV-160A, Shimadzu, Japan) and two 1 cm cells. The wavelength of the maximum absorbance for dye was selected. The pH of dye solutions was determined using pH meter (model HANNA instrument, Taiwan). The samples were withdrawn from the shaker at pre-determined time intervals and the dye solution was separated from the adsorbent by filtration using filter paper. The absorbance of supernatant solution was measured. The effect of pH was studied by adjusting the pH of dye solutions using dilute HCl and NaOH solutions. The effect of adsorbent dosage was studied with different adsorbent doses (50–500 mg) and the effect of dye concentration at equilibrium time was studied at fixed adsorbent dose. The effect of time was studied at a fixed adsorbent dose and dye concentration.

The amount of adsorption at time  $t$  and at equilibrium time and the percentage of dye removal were calculated by the following two equations...



$$q_t = \frac{(C_0 - C_t)V}{W}$$

Where,  $C_0$  and  $C_t$  ( $\text{mg L}^{-1}$ ) are the liquid phase concentrations of dye at initial time and at any time  $t$ , respectively,  $V$  is the volume of the solution (L) and  $W$  is the mass of dry adsorbent used (g).

$$\text{removal \%} = \frac{(C_0 - C_e)}{C_0} \times 100$$

Where,  $C_e$  is the equilibrium concentration of dyes in solution ( $\text{mg L}^{-1}$ ).

### 3.6.2 Preparation of stock solution of dyes

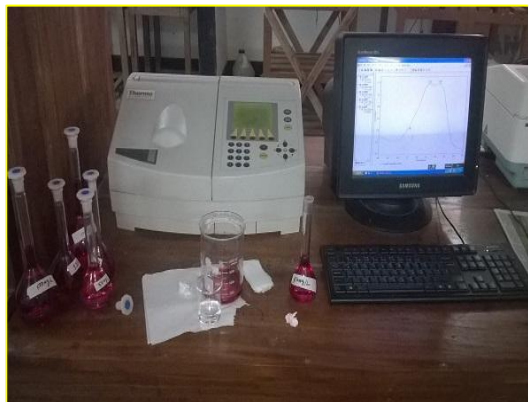
1000 mg of RMHB, AOP2R and RRME6BL were taken in three 1000 mL volumetric flask separately and dissolved in double de-ionized water to make 1000 mg/L stock solution. The volumes of the flasks were then topped up to the mark. Further dilution was made whenever it is necessary. The concentration range used for experiments was 25 mg/L to 500 mg/L.



**Figure 3.6.2 (a) Different concentrated solution of RMHB (b) Different concentrated Solution of AOP2R and RRME6BL**

### 3.6.3 Adsorption spectrum of stock solution

The adsorption spectra of three dye solutions of different concentrations at pH 6.0, pH 3.0 and pH 2.0 showed that the  $\lambda_{\text{max}}$  is independent of concentration and it was found to be 555 nm, 480 nm and 555nm for RMHB, AOP2R and RRME6BL respectively. Adsorption spectrum was recorded by a double beam UV-visible spectrophotometer (UV-160A, Shimadzu Japan) at 30° C using DDW as reference solution.



**Figure 3.6.3 UV-visible spectrophotometer (UV-160A, Shimadzu Japan)**

### **3.6.4 Determination of molar extinction coefficient**

The calibration curve was constructed by plotting the absorbance of solutions versus the different concentration of dye solutions within the range of 4 mg/L to 500 mg/L at pH 2.0, pH 3.0 and pH 6.0. From this calibration curve the molar absorption coefficient was calculated.

### **3.6.5 Optimization of pH for the adsorption experiments**

To determine the optimum pH for adsorption experiments 30 ml of 250 mg/L RMHB, AOP2R and RRME6BL solution were taken in each of ten shaking bottles in every dye. Then the pHs of the solutions was adjusted within the range from 2 to 11.0. In all case, the pH of the solution was adjusted by using acid or alkali without affecting the volume of the solution. Then 2.0 ml solution from each of the bottles were pipetting out for taking initial absorbance spectrophotometrically at  $\lambda_{\max}$  555.0 nm for RMHB and RRME6BL but 480 nm for AOP2R. Then 164 mg LBS were taken in each of ten bottles for each dye separately. The bottles were placed in Electric shaker (GEMMY Orbit shaker, Model: VRN-480) maintained at 30°C and were shaken continuously for 3.0 hours with the agitation rate 180 rpm. The reagent bottles were successively withdrawn after definite time and certain volume of each of the solution was filtrate. After filtration, the pH of the solution was measured. This pH was different than the initial value. The difference is expressed by  $\Delta\text{pH}$ . The plot of  $\Delta\text{pH}$  vs. initial pH produces a curve which intercepts the X-axis on one point as shown in figure 4.3.1-1, figure 4.3.1-3 and figure 4.3.1-5. The absorbance of the clear solution at different pH was measured spectrophotometrically at  $\lambda_{\max}$  555.0 nm for RMHB and RRME6BL but 480 nm for AOP2R. The percentage removal of dyes solution against initial pH of the solution was plotted.



**Figure 3.6.5 (a) Adjustment of pH of dye solution using HCl and NaOH, (b) Dye Solution after adsorption.**

### **3.6.6 Effect of amount of adsorbent on adsorption**

To study the effect of amount of adsorbent (LBS) on adsorption process, the following experiments were carried out using the conditions described in section (IV). Various amount such as 0.010, 0.050, 0.075, 0.100, 0.200, 0.250, 0.300, 0.450, 0.600, 0.700 and 0.840 g of LBS were used for the study. The results are presented in Table 4.3.2-1, Table 4.3.2-2 and Table 4.3.2-3.



(a)

(b)

**Figure 3.6.6 Different amount of adsorbent apply to the adsorption bottles (a) before shaking (b) after shaking.**

### **3.6.7 Effect of initial dye concentration on adsorption**

In order to investigate the effect of initial dye concentration 164 mg of Lima bean seed powder (LBS) was added to 50 ml of different studied dyes concentrations. All of the samples bottles were placed in Electric shaker (GEMMY Orbit shaker, Model: VRN-480) maintained at 30°C and were shaken continuously for 3.0 hours with the agitation rate 180

rpm. The reagent bottles were successively withdrawn after definite time and certain volume of each of the solution was filtrate, at the end of the experiment, UV/VIS spectrophotometer was utilized for measuring the absorbance of clear solution.



**Figure 3.6.7 taking absorbance of different concentrated solution of dyes**

### **3.6.8 Effect of contact time on adsorption**

To find out the effect of contact time on adsorption process, 120 mg/L concentrated solution of dyes were prepared. From this 50 mL solution were taken in ten bottles and 100 mg LBS was added to each bottle. Then all of the samples bottles were placed in Electric shaker (GEMMY Orbit shaker, Model: VRN-480) maintained at 30°C for shaking with the agitation rate 190 rpm. The reagent bottles were successively withdrawn one by one after definite time and certain volume of each of the solution was filtrate, at the end of the experiment, UV/VIS spectrophotometer was utilized for measuring the absorbance of clear solution.



**Figure 3.6.8 Bottles were placed in shaker to study the contact time.**

### 3.6.9 Adsorption Isotherm

Adsorption isotherm experiments were carried out on LBS using different initial concentration of RMHB, AOP2R and RRME6BL solutions from 25 to 500 mg/L at pH 6.0 for RMHB, pH 2.0 for AOP2R and pH 3.0 for RRME6BL. The amount of LBS was 164 mg and 50 mL of different initial dyes concentrated solution were taken in each of the ten bottles. The bottles were withdrawn at the stipulated time from the shaker and supernatant were filtrate by filtration process (using filter paper). The absorbance of the clear solution was measured spectrophotometrically.



Figure 3.6.9 taking AOP2R solution inside the sample bottles

### 3.6.10 Adsorption kinetic studies

To study the kinetics of adsorption three models was used.

- a) Lagergren pseudo-first-order equation
- b) Ho's pseudo second-order equation
- c) The intra-particles diffusion model

### 3.6.11 Error Analysis

The evaluation of the best fit for which isotherms to the obtained experimental equilibrium values in this present work was done by statistical error functions to determine the most convenient kinetic and isotherm equation to represent the experimental data using the linearized correlation coefficient  $R^2$ . The closer the value of  $R^2$  to unity the more confident and favorable the experimental data is considered.

## Chapter IV

### Result and Discussion

#### 4.1 Proximate Analysis data of Lima bean seed's powder

Table-4.1.1: Proximate analysis of Lima bean seed's powder

Proximate Analysis (wt. %)		
Sl. No.	Heading	Amount
1	Moisture content	6.63
2	Ash content	17.85
3	Volatile matter content	61.95
4	Fixed Carbon	13.56

#### 4.1.1 Determination of absorbance maxima ( $\lambda_{\max}$ ) of dyes

4.1.2. Absorbance maxima ( $\lambda_{\max}$ ) of RMHB in aqueous media at pH 6.0 were determined spectrophotometrically from UV absorption spectra. The maximum absorbance of RMHB at pH 6.0 was found to be 555 nm.

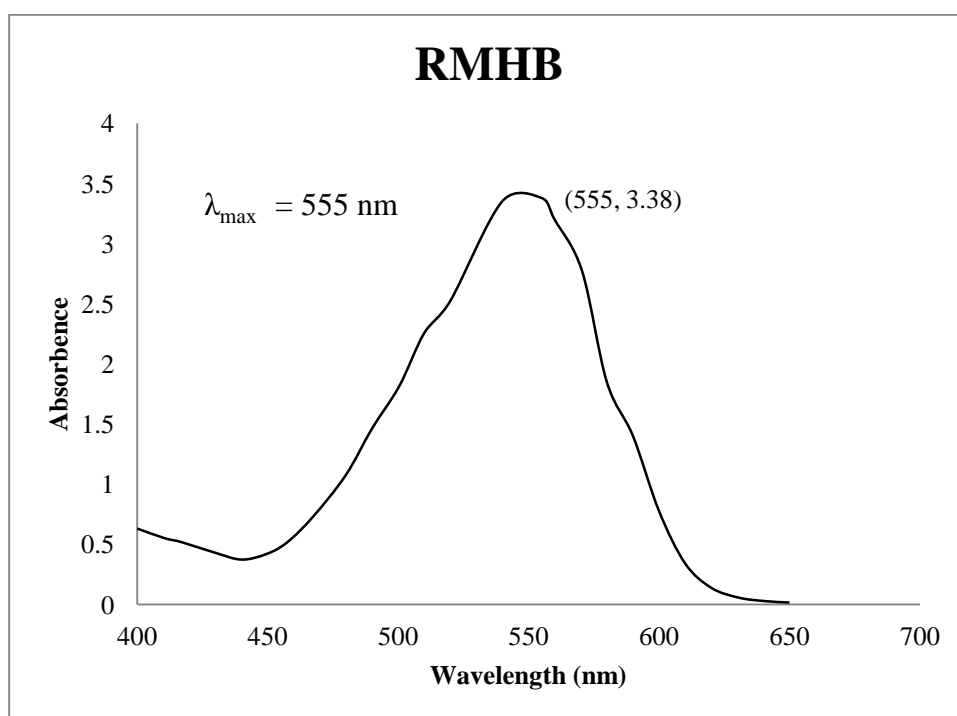
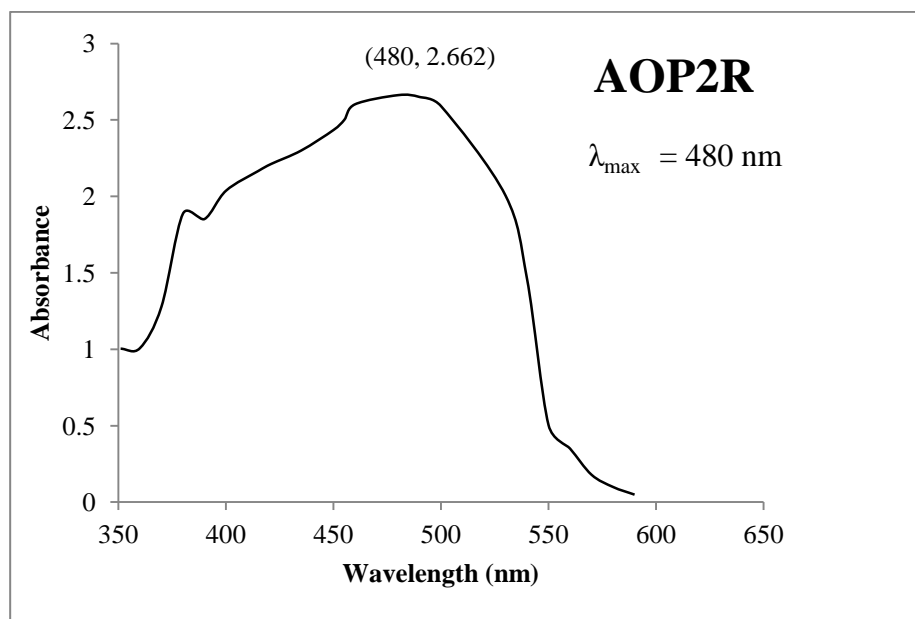


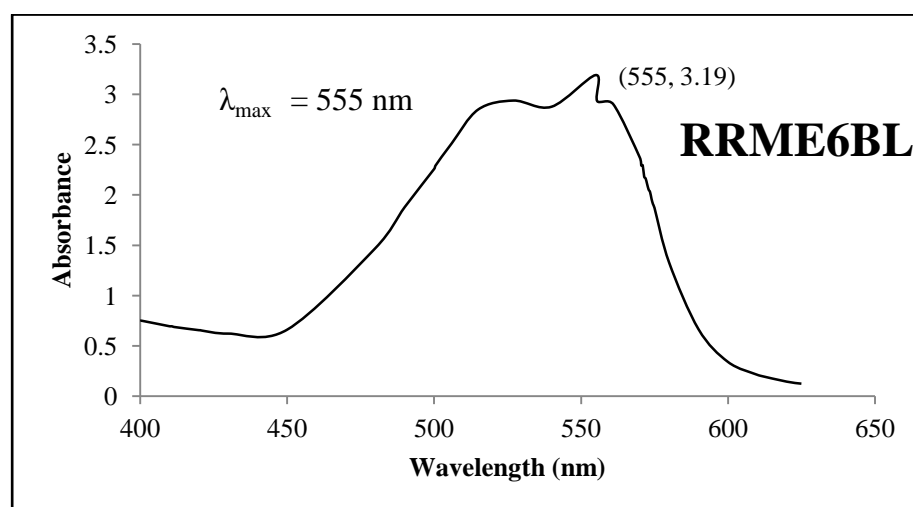
Figure 4.1.1 : UV-Vis spectrum of aqueous RMHB at pH 6.0

**4.1.3.** Absorbance maxima ( $\lambda_{\max}$ ) of AOP2R in aqueous media at pH 2.0 were determined spectrophotometrically from UV absorption spectra. The maximum absorbance of AOP2R at pH 2.0 was found to be 480 nm.



**Figure 4.1.2: UV-Vis spectrum of aqueous AOP2R at pH 2.0**

**4.1.4.** Absorbance maxima ( $\lambda_{\max}$ ) of RRME6BL in aqueous media at pH 3.0 were determined spectrophotometrically from UV absorption spectra. The maximum absorbance of RRME6BL at pH 3.0 was found to be 555 nm.



**Figure 4.1.3: UV-Vis spectrum of aqueous RRME6BL at pH 3.0**



## 4.2 Calibration Curve Determination of molar extinction coefficient using $\lambda_{\max}$

### 4.2.1 Determination of Molar Extinction Coefficient of RMHB

The absorption spectrums of RMHB solution in aqueous media of pH 6.0 were recorded. A calibration plot was prepared by plotting absorbance versus different concentration of RMHB at pH 6.0 shown in table 4.2.1-1. The curve was a straight line passing through the origin shown in (figure 4.2.1-1, figure 4.2.1-2 and figure 4.2.1-3). From the slope the value of molar extinction coefficient ( $\epsilon$ ) of RMHB was estimated. The values of molar extinction coefficient ( $\epsilon$ ) of different concentrated solution of RMHB are

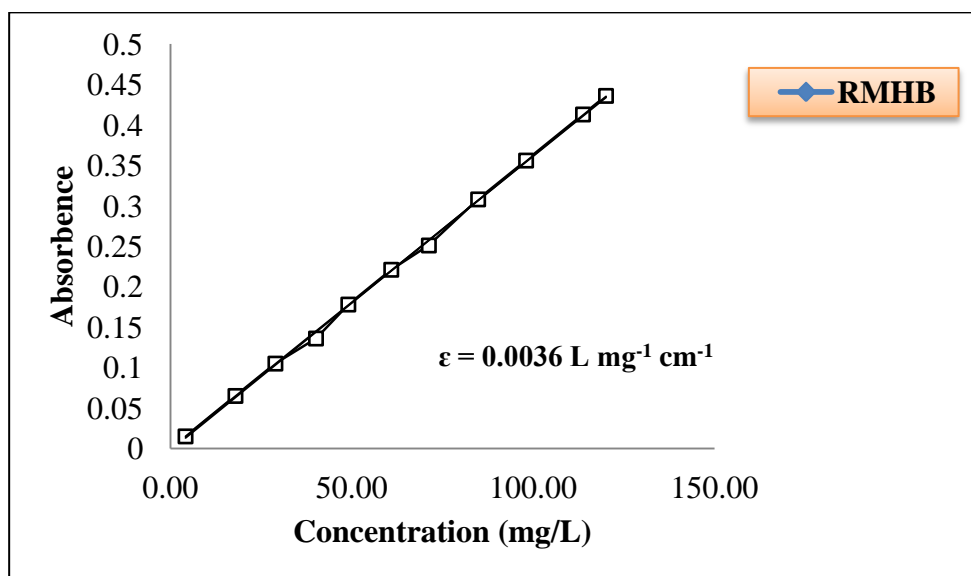
Sl. No.	Concentration of RMHB sol <sup>n</sup> .(mg/L)	Value of molar extinction coefficient ( $\epsilon$ ) (L mg <sup>-1</sup> cm <sup>-1</sup> )
1	120.00	0.0036
2	264.40	0.0035
3	500.00	0.0034

#### **Experimental Conditions:**

- Solvent Media: Deionized water
- Concentration of stock RMHB Solution: 120 mg/L, 264.4 mg/L and 500 mg/L
- pH of prepared RMHB Solution: 6.0
- Reference: Deionized water of pH 6.0

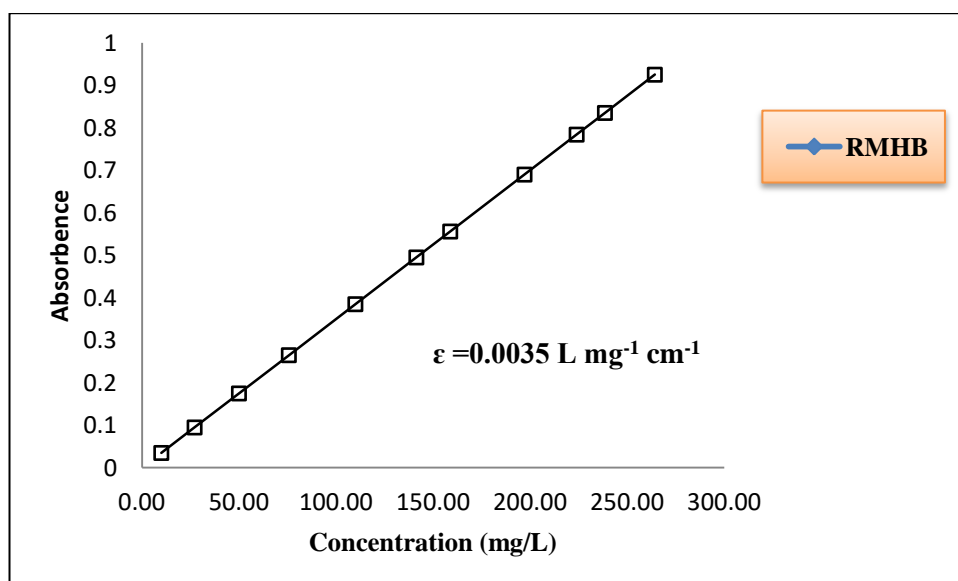


<b>Table 4.2.1-2: Determination of molar extinction coefficient of RMHB (Concentration 120 mg/L) at pH 6.0</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	4.13	0.0150
(5.00 + 45.00)	17.91	0.0650
(10.00 + 40.00)	28.93	0.1050
(15.00 + 35.00)	40.12	0.1360
(20.00 + 30.00)	49.04	0.1780
(25.00 + 25.00)	60.88	0.2210
(30.00 + 20.00)	71.25	0.2510
(35.00 + 15.00)	84.85	0.3080
(40.00 + 10.00)	98.07	0.3560
(45.00 + 5.00)	113.77	0.4130
Stock Solution	120.11	0.4360



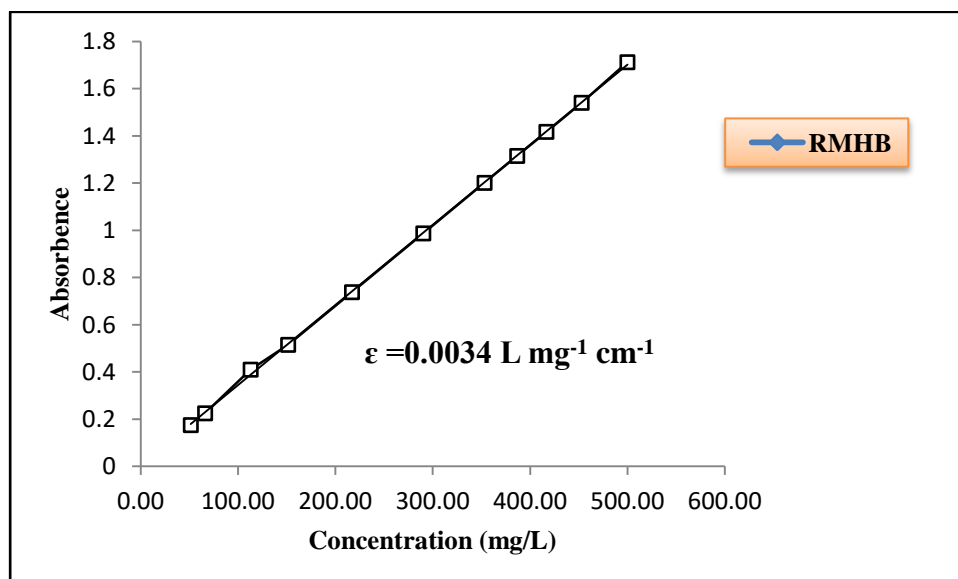
**Figure 4.2.1-1: Concentration vs. Absorbance curve of RMHB (120 mg/L) at pH 6.0**

<b>Table 4.2.1-3: Determination of molar extinction coefficient of RMHB (Concentration 264.29mg/L) at pH 6.0.</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	10.00	0.0350
(5.00 + 45.00)	27.14	0.0950
(10.00 + 40.00)	50.00	0.1750
(15.00 + 35.00)	75.71	0.2650
(20.00 + 30.00)	110.00	0.3850
(25.00 + 25.00)	141.43	0.4950
(30.00 + 20.00)	158.86	0.5560
(35.00 + 15.00)	197.14	0.6900
(40.00 + 10.00)	224.00	0.7840
(45.00 + 5.00)	238.57	0.8350
Stock Solution	264.29	0.9250



**Figure 4.2.1-2: Concentration vs. Absorbance curve of RMHB (264.29 mg/L) at pH 6.0**

<b>Table 4.2.1-4: Determination of molar extinction coefficient of RMHB (Concentration 500 mg/L) at pH 6.0</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	51.47	0.1750
(5.00 + 45.00)	66.18	0.2250
(10.00 + 40.00)	112.94	0.4100
(15.00 + 35.00)	151.47	0.5150
(20.00 + 30.00)	217.06	0.7380
(25.00 + 25.00)	290.29	0.9870
(30.00 + 20.00)	353.24	1.2010
(35.00 + 15.00)	386.76	1.3150
(40.00 + 10.00)	416.76	1.4170
(45.00 + 5.00)	452.94	1.5400
Stock Solution	500.00	1.7120



**Figure 4.2.1-3: Concentration vs. Absorbance curve of RMHB (500.0 mg/L) at pH 6.0**

#### 4.2.2 Determination of Molar Extinction Coefficient of AOP2R

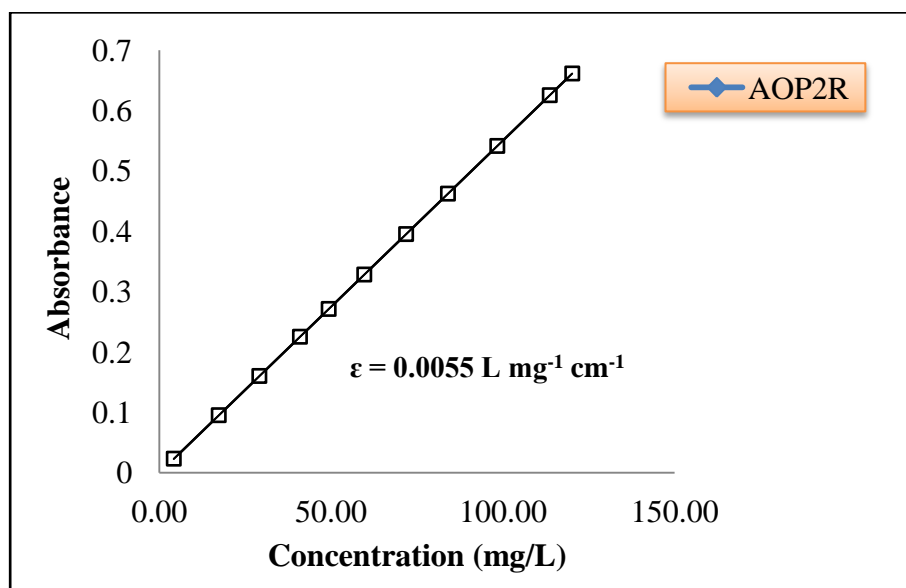
The absorption spectrums of AOP2R solution in aqueous media of pH 2.0 were recorded. A calibration plot was prepared by plotting absorbance versus different concentration of AOP2R (table 4.2.2-2, table 4.2.2-3 and table 4.2.2-4) at pH 2.0. The calibration curve was a straight line passing through the origin shown in (figure 4.2.2-1, figure 4.2.2-2, and figure 4.2.2-3). From the slope the value of molar extinction coefficient ( $\epsilon$ ) of AOP2R was estimated. The values of molar extinction coefficient ( $\epsilon$ ) of different concentrated solution of AOP2R are...

Sl. No.	Concentration of AOP2R solution (mg/L)	Value of molar extinction coefficient ( $\epsilon$ ) ( $L\ mg^{-1}\ cm^{-1}$ )
1	120.00	0.0055
2	262.59	0.0054
3	500.85	0.0047

#### **Experimental Conditions:**

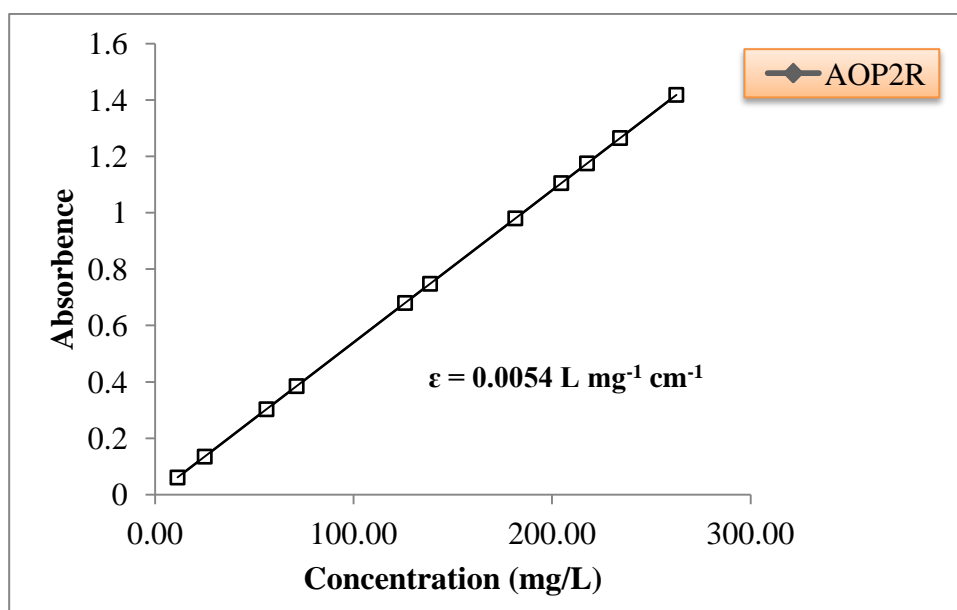
- Solvent Media: Deionized water
- Concentration of stock AOP2R Solution: 120.0 mg/L, 262.59 mg/L and 500.85 mg/L
- pH of prepared AOP2R Solution: 2.0
- Reference : Deionized water of pH 2.0

<b>Table 4.2.2-2: Determination of molar extinction coefficient of AOP2R (Concentration 120.0 mg/L) at pH 2.0.</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	4.18	0.0230
(5.00 + 45.00)	17.27	0.0950
(10.00 + 40.00)	29.09	0.1600
(15.00 + 35.00)	40.91	0.2250
(20.00 + 30.00)	49.27	0.2710
(25.00 + 25.00)	59.64	0.3280
(30.00 + 20.00)	71.82	0.3950
(35.00 + 15.00)	84.00	0.4620
(40.00 + 10.00)	98.36	0.5410
(45.00 + 5.00)	113.64	0.6250
Stock Solution	120.18	0.6610



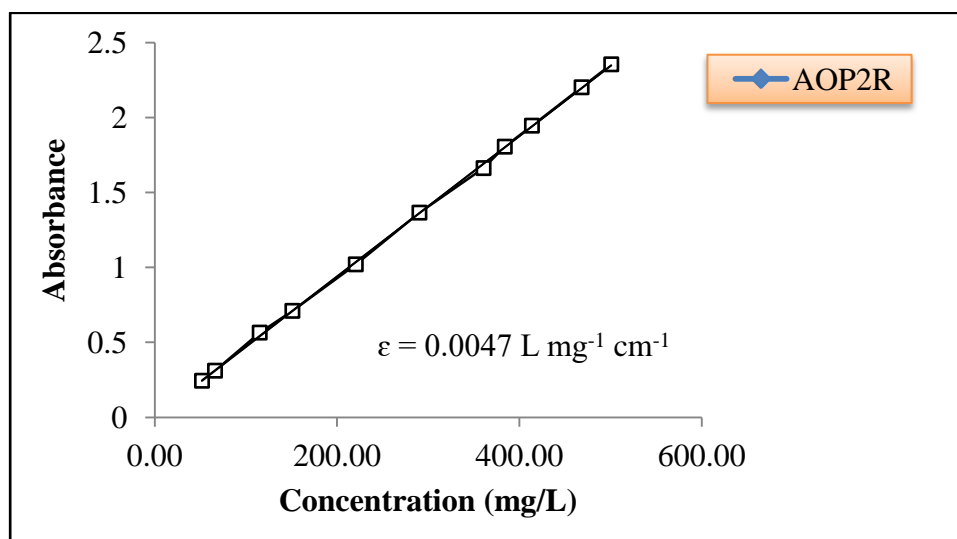
**Figure 4.2.2-1: Concentration vs. Absorbance curve of AOP2R (120.0 mg/L) at pH 2.0**

<b>Table 4.2.2-3: Determination of molar extinction coefficient of AOP2R (Concentration 262.9 mg/L) at pH 2.0.</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	11.30	0.0610
(5.00 + 45.00)	25.00	0.1350
(10.00 + 40.00)	56.11	0.3030
(15.00 + 35.00)	71.30	0.3850
(20.00 + 30.00)	125.93	0.6800
(25.00 + 25.00)	138.52	0.7480
(30.00 + 20.00)	181.48	0.9800
(35.00 + 15.00)	204.63	1.1050
(40.00 + 10.00)	217.59	1.1750
(45.00 + 5.00)	234.26	1.2650
Stock Solution	262.59	1.4180



**Figure 4.2.2-2: Concentration vs. Absorbance curve of AOP2R (262.59 mg/L) at pH 2.0**

<b>Table 4.2.2-4: Determination of molar extinction coefficient of AOP2R (Concentration 500.85 mg/L) at pH 2.0.</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	51.91	0.2440
(5.00 + 45.00)	66.17	0.3110
(10.00 + 40.00)	115.20	0.5650
(15.00 + 35.00)	151.06	0.7100
(20.00 + 30.00)	220.60	1.0200
(25.00 + 25.00)	290.43	1.3650
(30.00 + 20.00)	360.80	1.6620
(35.00 + 15.00)	384.04	1.8050
(40.00 + 10.00)	413.83	1.9450
(45.00 + 5.00)	468.30	2.2010
Stock Solution	500.85	2.3540



**Figure 4.2.2-3: Concentration vs. Absorbance curve of AOP2R (500.85 mg/L) at pH 2.0**

### 4.2.3 Determination of Molar Extinction Coefficient of RRME6BL

The absorption spectrums of RRME6BL solution in aqueous media of pH 3.0 were recorded. A calibration plot was prepared by plotting absorbance versus different concentration of RRME6BL (table 4.2.3-2, table 4.2.3-3 and table 4.2.3-4) at pH 3.0. The calibration curve was a straight line passing through the origin shown in (figure 4.2.3-1, figure 4.2.3-2, and figure 4.2.3-3). From the slope the value of molar extinction coefficient ( $\epsilon$ ) of RRME6BL was estimated. The values of molar extinction coefficient ( $\epsilon$ ) of different concentrated solution of RRME6BL are

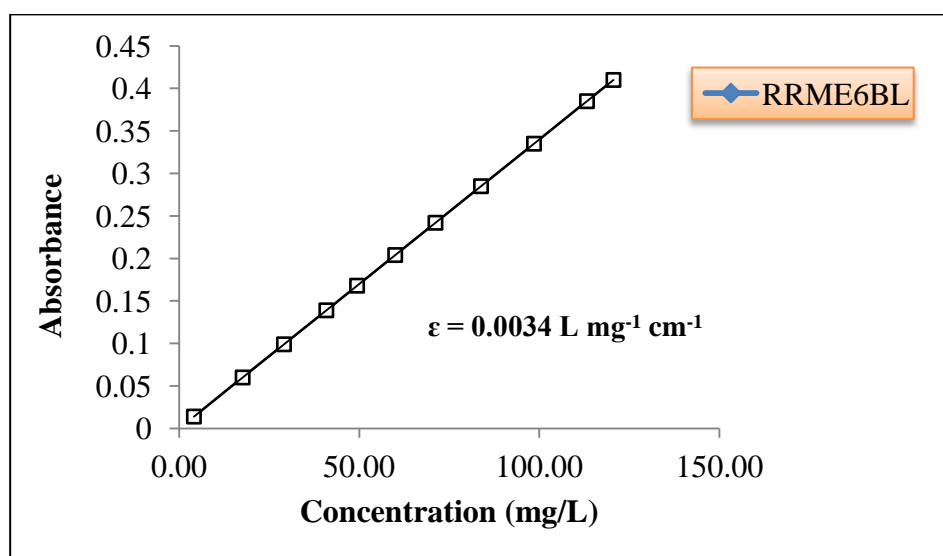
Sl. No.	Concentration of RRME6BL sol <sup>n</sup> .(mg/L)	Value of molar extinction coefficient ( $\epsilon$ ) (L mg <sup>-1</sup> cm <sup>-1</sup> )
1	120.00	0.0034
2	264.12	0.0034
3	500.00	0.0033

#### **Experimental Conditions:**

- Solvent Media: Deionized Water
- Concentration of stock RRME6BL Solution: 120.00 mg/L , 264.12 mg/L and 500.0 mg/ L
- pH of prepared RRME6BL Solution: 3.0
- Reference : Deionized water of pH 3.0

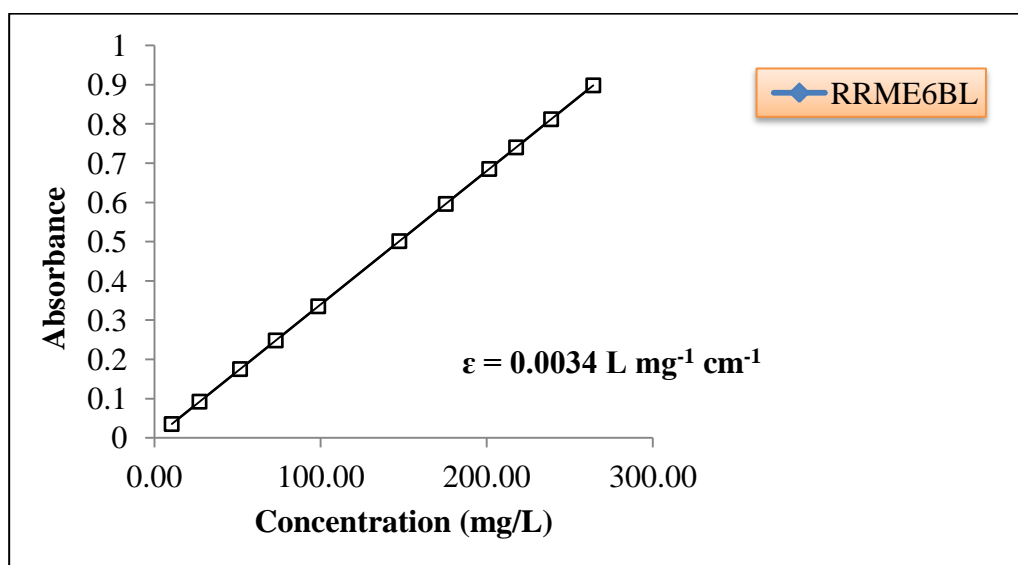


<b>Table 4.2.3-2: Determination of molar extinction coefficient of RRME6BL (Concentration 120.59 mg/L) at pH 3.0.</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	4.12	0.014
(5.00 + 45.00)	17.65	0.060
(10.00 + 40.00)	29.12	0.099
(15.00 + 35.00)	40.88	0.139
(20.00 + 30.00)	49.41	0.168
(25.00 + 25.00)	60.00	0.204
(30.00 + 20.00)	71.18	0.242
(35.00 + 15.00)	83.82	0.285
(40.00 + 10.00)	98.53	0.335
(45.00 + 5.00)	113.24	0.385
Stock Solution	120.59	0.410



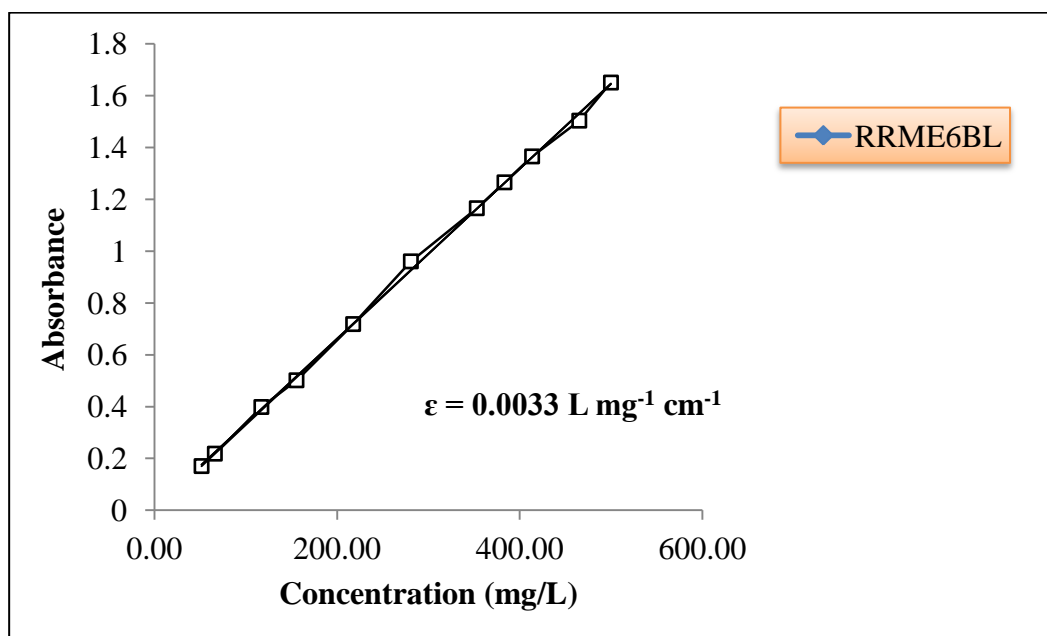
**Figure 4.2.3-1: Concentration vs. Absorbance curve of RRME6BL (120.00 mg/L) at pH 3.0**

<b>Table 4.2.3-3: Determination of molar extinction coefficient of RRME6BL (Concentration 264.12 mg/L) at pH 3.0.</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	10.29	0.0350
(5.00 + 45.00)	27.06	0.0920
(10.00 + 40.00)	51.47	0.1750
(15.00 + 35.00)	72.94	0.2480
(20.00 + 30.00)	98.53	0.3350
(25.00 + 25.00)	147.35	0.5010
(30.00 + 20.00)	175.29	0.5960
(35.00 + 15.00)	201.47	0.6850
(40.00 + 10.00)	217.65	0.7400
(45.00 + 5.00)	238.74	0.8117
Stock Solution	264.12	0.8980



**Figure 4.2.3-2: Concentration vs. Absorbance curve of RRME6BL (264.12 mg/L) at pH 3.**

<b>Table 4.2.3-4: Determination of molar extinction coefficient of AOP2R (Concentration 500.0 mg/L) at pH 3.0.</b>		
Stock solution and water taken in 50 mL volumetric Flask (mL)	Concentration (mg L <sup>-1</sup> )	Absorbance
(1.00 + 49.00)	51.52	0.1700
(5.00 + 45.00)	66.06	0.2180
(10.00 + 40.00)	117.05	0.3980
(15.00 + 35.00)	155.50	0.5010
(20.00 + 30.00)	217.58	0.7180
(25.00 + 25.00)	280.80	0.9600
(30.00 + 20.00)	353.03	1.1650
(35.00 + 15.00)	383.33	1.2650
(40.00 + 10.00)	413.64	1.3650
(45.00 + 5.00)	465.30	1.5030
Stock Solution	500.00	1.6500



**Figure 4.2.3-3: Concentration vs. Absorbance curve of RRME6BL (500.0 mg/L) at pH 3.0**

## 4.3 Adsorption studies

### 4.3.1 Optimization of pH

The effects of initial pH on dye solution of three dyes removal were investigated by varying the pHs. The pH is a significant parameter affecting the removal uptake of toxic pollutants from wastewater because Hydrogen and hydroxyl ions are usually adsorbed quite strongly on the surface of the adsorbents due to their smaller size as compared to the dye molecules and therefore adsorption of other ions is affected by pH of the solution. The pH primarily affects the degree of ionization of the dye as well as surface properties of the adsorbents. Adsorption capacities for adsorption of RMHB, AOP2R and RRME6BL solutions of various initial pHs were found different at 30° C. From the plot  $\Delta$ pH against pH (Figure 4.3.1-1, Figure 4.3.1-3 and Figure 4.3.1-5) the curve is cross to the zero line. Equilibrium pHs was greater than at lower initial pH (pH 2.0 to pH 7.0) but less at higher initial pH value (pH 8.0 to pH 11.0).

From figure it was observed that the percentage removal of RMHB, AOP2R and RRME6BL are high at different pH values. The obtained results indicated that adsorption process of three dyes were favorable in acidic medium as shown in bellow table.

Sl. No	pH	Dyes Name	Initial Concentration of Dyes (mg/L)	Highest % removal
1	6.0	RMHB	250.0	81.25
2	2.0	AOP2R		92.71
3	3.0	RRME6BL		97.19

Adsorption of RMHB, AOP2R and RRME6BL decreased with increase in pH. It is evident that the maximum removal of dye adsorbed at pH 6.0 and bellow (Figure 4.3.1-2, Figure 4.3.1-4, Figure 4.3.1-6, Figure 4.3.1-7 and Figure 4.3.1-8). This can be explained on the basis that positively charged surface is formed on the adsorbents at lower pH due to adsorption of hydrogen ions on the surface of adsorbents. It has been reported that the positively charged ions prefer to adsorb at higher pH value and negatively charged ions prefer lower pH. As pH of the system increases, number of positively charged site on the surface of adsorbents decreases. As the dye is in dissociated form of the anion, adsorption of dye decreases at higher pH values. The reason for RMHB removal at higher (but acidic

pH 6.0) than the others is may be depends on its structural formula or group presents in its structure. A negatively charged surface site on the LBS does not favour the adsorption of anionic dyes molecule due to the electrostatic repulsion. Further, lower adsorption of the dyes in alkaline medium is also due to the competition between excess OH<sup>-</sup> ions and the anionic dye molecules for the adsorption sites.

**Experimental Conditions:**

- Temperature: 30±1° C
- Concentration of RMHB, AOP2R and RRME6BL solution: 250 mg/L
- Volume of the solution taken: 30 mL
- Amount of Adsorbent (LBS): 164 mg
- Agitation rate: 180 rpm
- Shaking Time: 3 hours
- Reference: Deionized water

**Table 4.3.1-2: Observed data of percentage removal of aqueous RMHB by adsorption on LBS at various pH**

Initial pH	$\lambda_{\max}$ (nm)	Initial Absorbance (A <sub>0</sub> )	Equilibrium pH	Equilibrium Absorbance (A <sub>e</sub> )	$\Delta$ pH	% of Absorbance [A <sub>0</sub> - A <sub>e</sub> ]/A <sub>0</sub> ×100	% removal
2.0	555.0	0.602	3.20	0.148	1.20	75.42	75.42
3.0		0.679	5.10	0.156	2.10	77.03	77.03
4.0		0.750	6.80	0.215	2.80	71.33	71.33
5.0		0.835	7.20	0.245	2.20	70.66	70.66
<b>6.0</b>		<b>0.880</b>	<b>7.30</b>	<b>0.165</b>	<b>1.30</b>	<b>81.25</b>	<b>81.25</b>
7.0		0.845	7.50	0.375	0.50	55.62	55.62
8.0		0.865	7.50	0.445	-0.50	48.55	48.55
9.1		0.910	7.40	0.703	-1.70	22.75	22.75
10.0		0.870	7.60	0.810	-2.40	6.90	6.90
11.0		0.865	9.60	0.815	-1.40	5.78	5.78

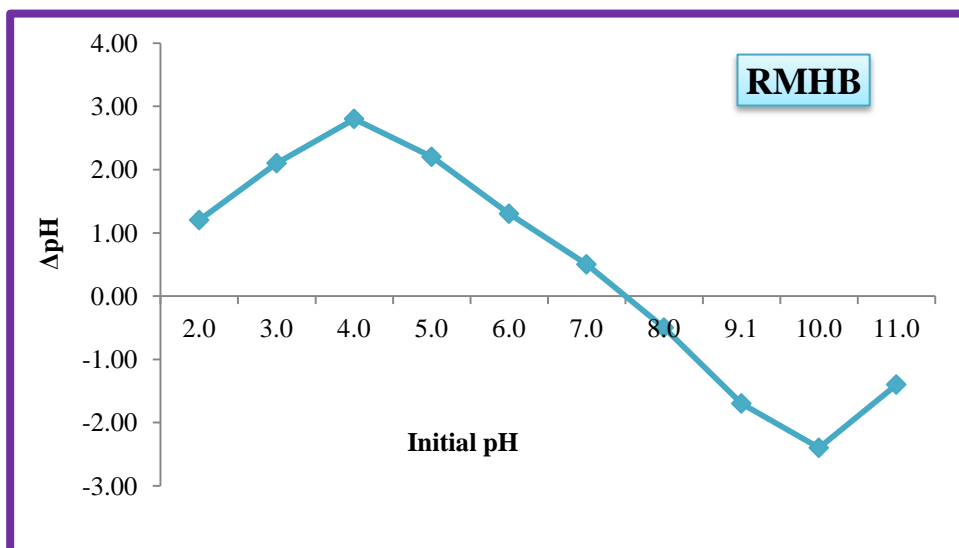


Figure 4.3.1-1: Initial pH vs.  $\Delta$ pH curve for adsorption of aqueous RMHB on LBS.

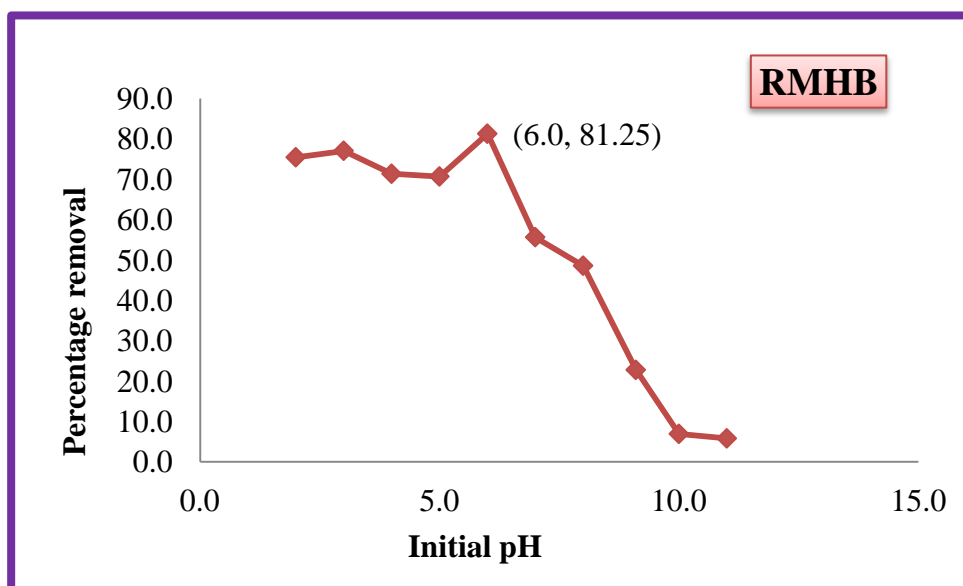
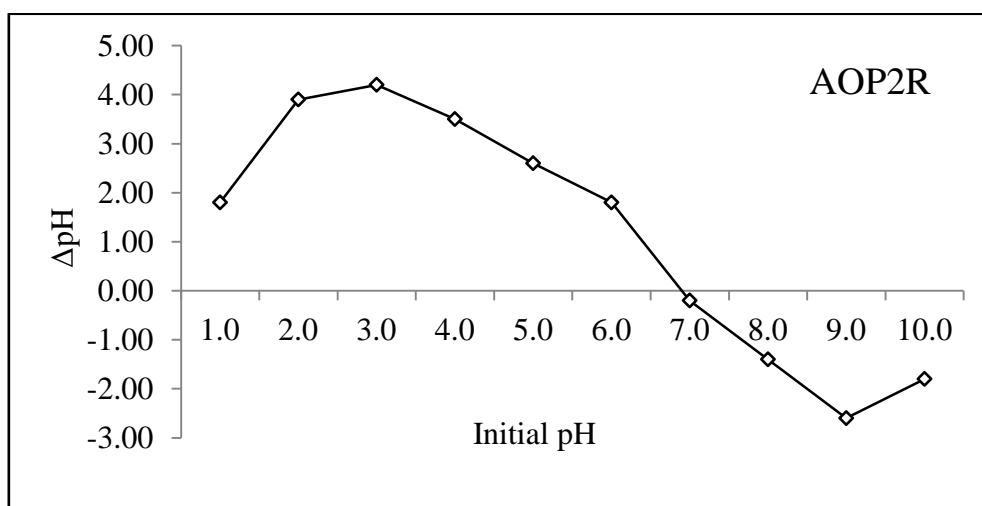
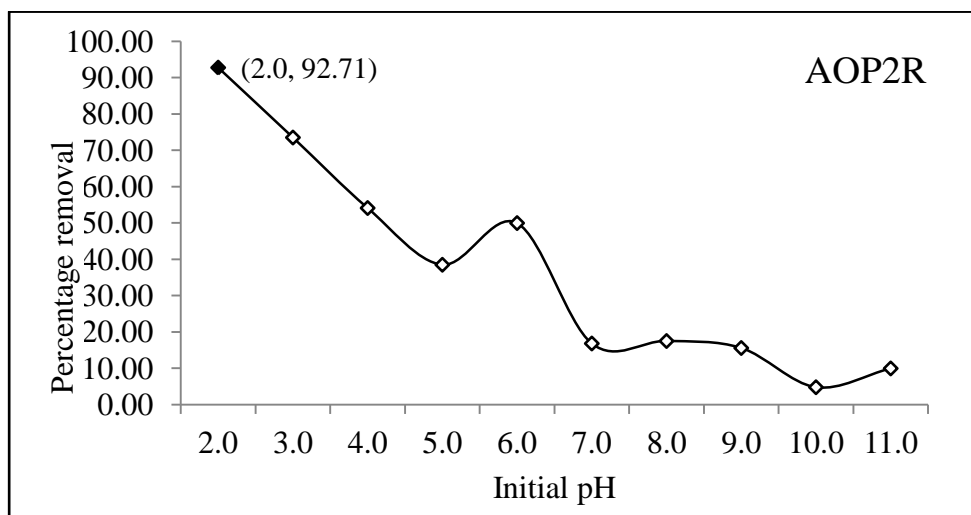


Figure 4.3.1-2: Initial pH vs. % removal for adsorption of aqueous RMHB on LBS.

<b>Table 4.3.1-3: Observed data of percentage removal of aqueous AOP2R by adsorption on LBS at various pH</b>							
Initial pH	$\lambda_{\max}$ (nm)	Initial Absorbance ( $A_0$ )	Equilibrium pH	Equilibrium Absorbance ( $A_e$ )	$\Delta$ pH	% of Absorbance $[A_0 - A_e]/A_0 \times 100$	% removal
<b>2.0</b>	<b>480.0</b>	<b>1.303</b>	<b>3.80</b>	<b>0.095</b>	<b>1.80</b>	<b>92.71</b>	<b>92.71</b>
3.0		1.320	6.90	0.350	3.90	73.48	73.48
4.0		1.350	8.20	0.620	4.20	54.07	54.07
5.0		1.365	8.50	0.840	3.50	38.46	38.46
6.0		1.378	8.60	0.690	2.60	49.93	49.93
7.0		1.382	8.80	1.150	1.80	16.79	16.79
8.0		1.345	7.80	1.110	-0.20	17.47	17.47
9.0		1.338	7.60	1.130	-1.40	15.55	15.55
10.0		1.370	7.40	1.305	-2.60	4.74	4.74
11.0		1.310	9.20	1.180	-1.80	9.92	9.92



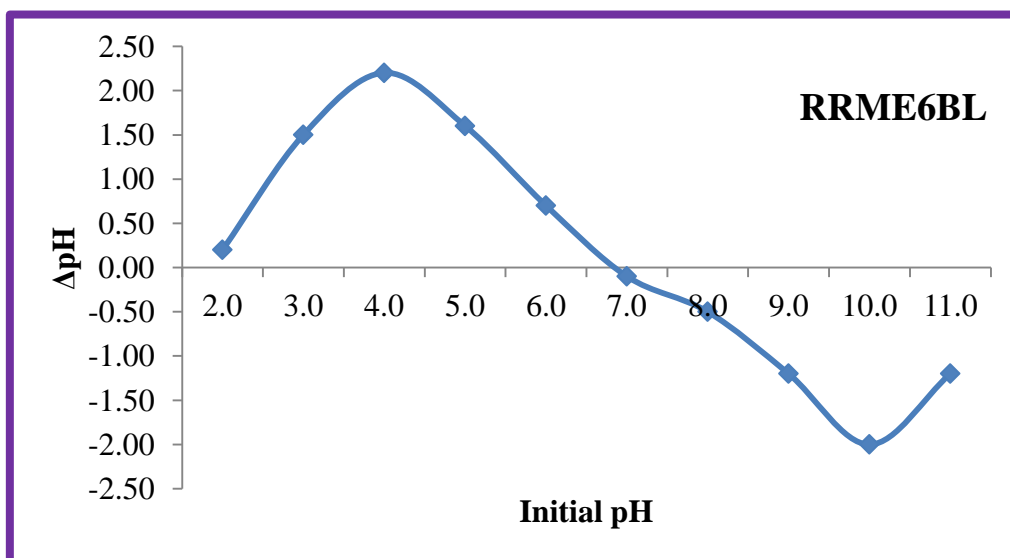
**Figure 4.3.1-3: Initial pH vs.  $\Delta$ pH curve for adsorption of aqueous AOP2R on LBS.**



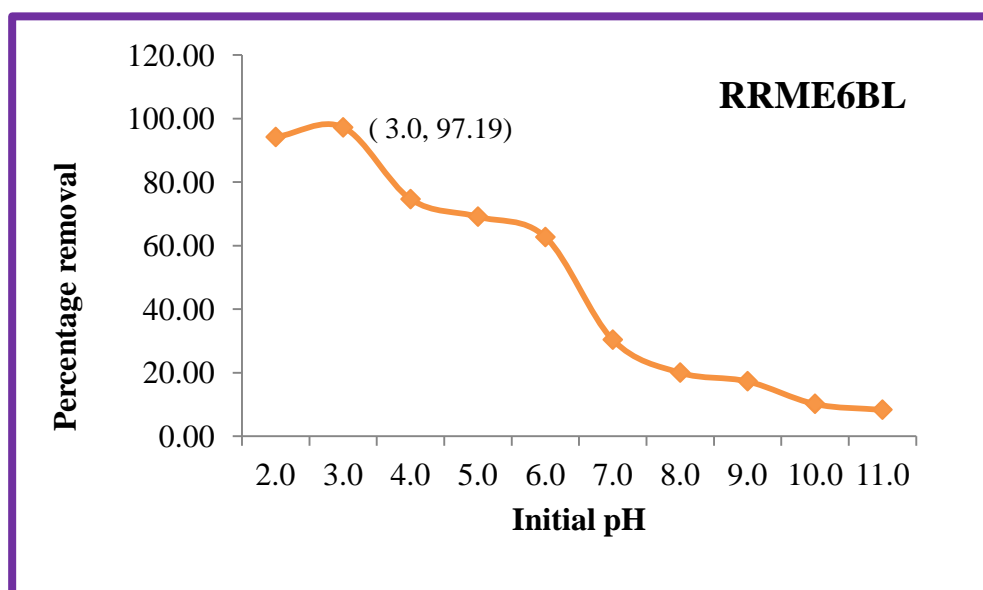
**Figure 4.3.1-4: Initial pH vs. % removal curve for adsorption of aqueous AOP2R on LBS.**

Initial pH	$\lambda_{\max}$ (nm)	Initial Absorbance ( $A_0$ )	Equilibrium pH	Equilibrium Absorbance ( $A_e$ )	$\Delta$ pH	% of Absorbance $[A_0 - A_e]/A_0 \times 100$	% removal
2.0	555.0	0.857	2.20	0.050	0.20	94.17	94.17
<b>3.0</b>		<b>0.890</b>	<b>4.50</b>	<b>0.025</b>	<b>1.50</b>	<b>97.19</b>	<b>97.19</b>
4.0		0.965	6.20	0.245	2.20	74.61	74.61
5.0		1.003	6.60	0.310	1.60	69.09	69.09
6.0		1.125	6.70	0.420	0.70	62.67	62.67
7.0		1.235	6.90	0.860	-0.10	30.36	30.36
8.0		1.275	7.50	1.020	-0.50	20.00	20.00
9.0		1.348	7.80	1.115	-1.20	17.28	17.28
10.0		1.346	8.00	1.209	-2.00	10.18	10.18
11.0		1.358	9.80	1.245	-1.20	8.32	8.32

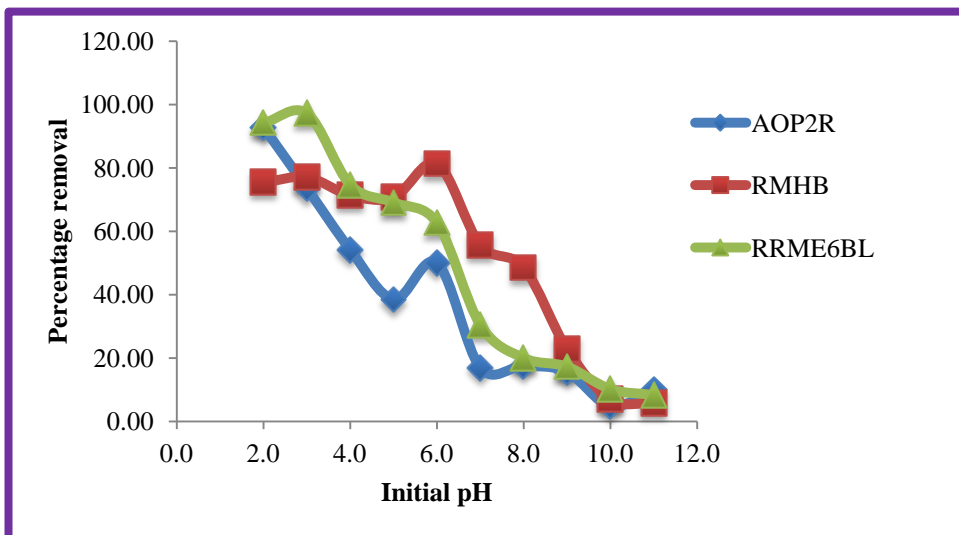




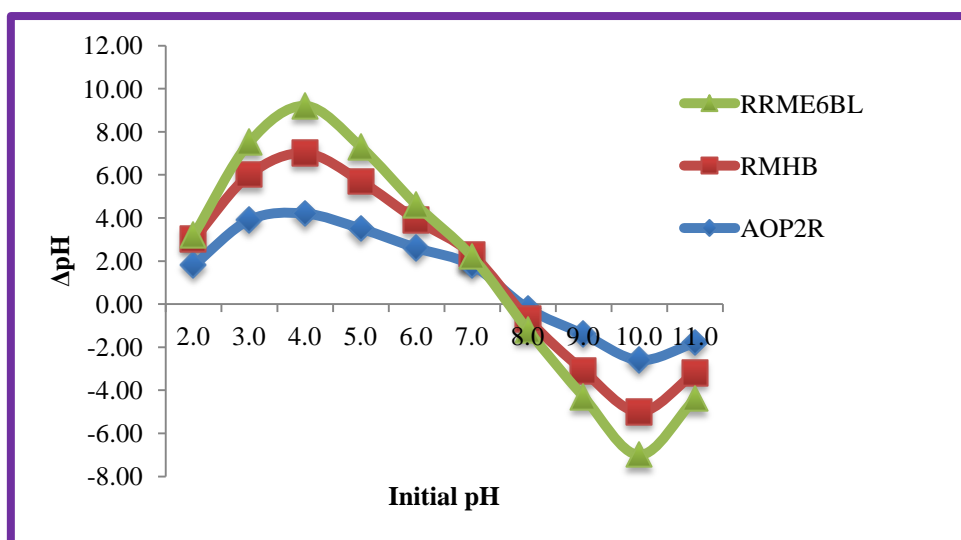
**Figure 4.3.1-5: Initial pH vs.  $\Delta\text{pH}$  curve for adsorption of aqueous RRME6BL on LBS**



**Figure 4.3.1-6: Initial pH vs. % removal curve for adsorption of aqueous RRME6BL on LBS.**



**Figure 4.3.1-7: Initial pH vs. percentage removal for adsorption of aqueous RMHB, AOP2R and RRME6BL on LBS.**



**Figure 4.3.1-8: Initial pH vs. ΔpH curve for adsorption of aqueous RMHB, AOP2R and RRME6BL on LBS.**

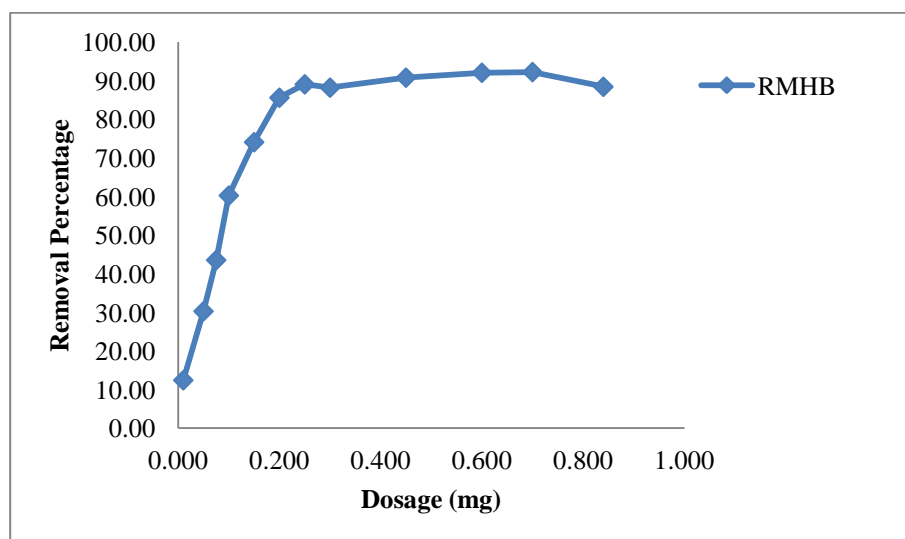
### **4.3.2 Effect of adsorbent dose on adsorption**

The effect of dosage of LBS on the dye removal from the aqueous solutions was studied. The determination of LBS dosage is important because it determines the efficiency of dye removal and may also be used to predict the cost of LBS per unit of solution to be treated. As expected, the efficiency of dye removal increases significantly as adsorbent dosage increases. The results are represented in Table 4.3.2-1, Table 4.3.2-2 and Table 4.3.2-3. The effect of dose of adsorbent on the percentage removal of dye is shown in (Figure 4.3.2-1, Figure 4.3.2-2 and Figure 4.3.2-3). The graph indicates that the percentage removal is above 90% with the increase in adsorbent amount 0.200g to 0.400g. At higher adsorbent amount, the amount of percentage removal of dyes was not change significantly. This is due to the binding of almost all dye molecules to adsorbent surface and it was also noted that the time required reaching equilibrium decreased at higher doses of adsorbent.

#### **Experimental Conditions for RMHB**

- Temperature: 30±1° C
- Concentration of RMHB: 510.6 mg/L
- Volume of the solution taken: 50 mL
- Amount of Adsorbent (LBS): 160 mg
- Agitation rate : 190 rpm ; Shaking Time: 3 hours
- Reference: Deionized water of pH 6.0
- pH of aqueous RMHB: 6.0

<b>Table 4.3.2-1: Observed data of percentage removal of aqueous RMHB at various amount of adsorbent dosage by adsorption.</b>					
Amount of LBS (g)	Equilibrium absorbance ( $A_e$ )	Equilibrium concentration, $C_e$ ( $\text{mg L}^{-1}$ )	Initial Concentration, $C_0$ ( $\text{mg L}^{-1}$ )	$q_e$ ( $\text{mg L}^{-1}$ )	% removal
0.010	1.520	447.06	510.6	63.54	12.44
0.050	1.210	355.88		154.72	30.30
0.075	0.980	288.24		222.36	43.55
0.100	0.690	202.94		307.66	60.25
0.150	0.450	132.35		378.25	74.08
0.200	0.250	73.53		437.07	85.60
0.250	0.190	55.88		454.72	89.06
0.300	0.205	60.29		450.31	88.19
0.450	0.160	47.06		463.54	90.78
0.600	0.138	40.59		470.01	92.05
0.700	0.135	39.71		470.89	92.22
0.840	0.201	59.12		451.48	88.42



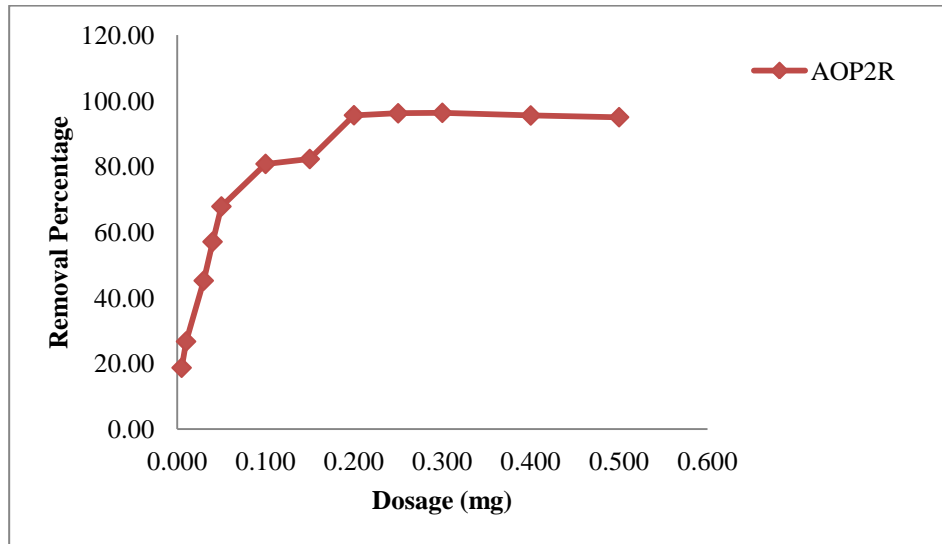
**Figure 4.3.2-1: Plot of percentage removal as a function of adsorbent dosage for adsorption of aqueous RMHB solution of pH 2.0 on LBS**

### **Experimental Conditions for AOP2R**

- Temperature: 30±1° C
- Concentration of AOP2R: 264.8 mg/L
- Volume of the solution taken: 50 mL
- Amount of Adsorbent (LBS): 160 mg
- Agitation rate : 190 rpm ; Shaking Time: 3 hours
- Reference: Deionized water of pH 2.0
- pH of aqueous AOP2R: 2.0

**Table 4.3.2-2: Observed data of percentage removal of aqueous AOP2R at various amount of adsorbent dosage by adsorption**

Amount of LBS (g)	Equilibrium absorbance (A <sub>e</sub> )	Equilibrium concentration, C <sub>e</sub> (mg L <sup>-1</sup> )	Initial Concentration, C <sub>0</sub> (mg L <sup>-1</sup> )	q <sub>e</sub> (mgL <sup>-1</sup> )	% removal
0.005	1.098	215.29	264.8	49.51	18.70
0.010	0.990	194.12		70.68	26.69
0.030	0.740	145.10		119.70	45.20
0.040	0.580	113.73		151.07	57.05
0.050	0.435	85.29		179.51	67.79
0.100	0.260	50.98		213.82	80.75
0.150	0.240	47.06		217.74	82.23
0.200	0.060	11.76		253.04	95.56
0.250	0.052	10.20		254.60	96.15
0.300	0.050	9.80		255.00	96.30
0.400	0.061	11.96		252.84	95.48
0.500	0.068	13.33		251.47	94.96

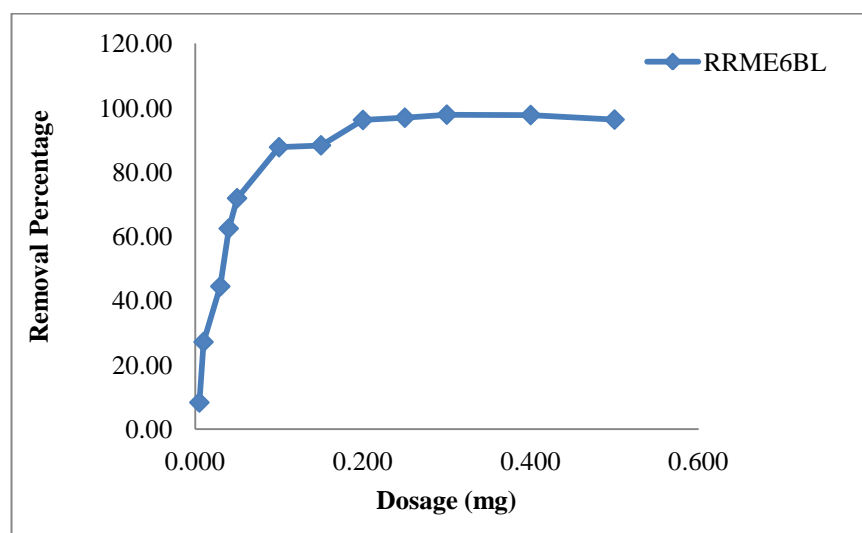


**Figure 4.3.2-2: Plot of percentage removal as a function of adsorbent dosage for adsorption of aqueous AOP2R solution of pH 2.0 on LBS.**

**Experimental Conditions for RRME6BL**

- Temperature: 30±1° C
- Concentration of RRME6BL: 250.0 mg/L
- Volume of the solution taken: 50 mL
- Amount of Adsorbent (LBS): 160 mg
- Agitation rate : 190 rpm ; Shaking Time: 3 hours
- Reference: Deionized water of pH 3.0
- pH of aqueous RRME6BL: 3.0

<b>Table 4.3.2-3: Observed data of percentage removal of aqueous RRME6BL at various amount of adsorbent dosage by adsorption</b>					
Amount of LBS (g)	Equilibrium absorbance ( $A_e$ )	Equilibrium concentration, $C_e$ ( $\text{mg L}^{-1}$ )	Initial Concentration, $C_0$ ( $\text{mg L}^{-1}$ )	$q_e$ ( $\text{mg L}^{-1}$ )	% removal
0.005	0.780	229.41	250.0	20.59	8.24
0.010	0.620	182.35		67.65	27.06
0.030	0.473	139.12		110.88	44.35
0.040	0.320	94.12		155.88	62.35
0.050	0.240	70.59		179.41	71.76
0.100	0.105	30.88		219.12	87.65
0.150	0.100	29.41		220.59	88.24
0.200	0.033	9.71		240.29	96.12
0.250	0.027	7.94		242.06	96.82
0.300	0.019	5.59		244.41	97.76
0.400	0.020	5.88		244.12	97.65
0.500	0.032	9.41		240.59	96.24



**Figure 4.3.2-3: Plot of percentage removal as a function of adsorbent dosage for adsorption of aqueous RRME6BL solution of pH 2.0 on LBS.**

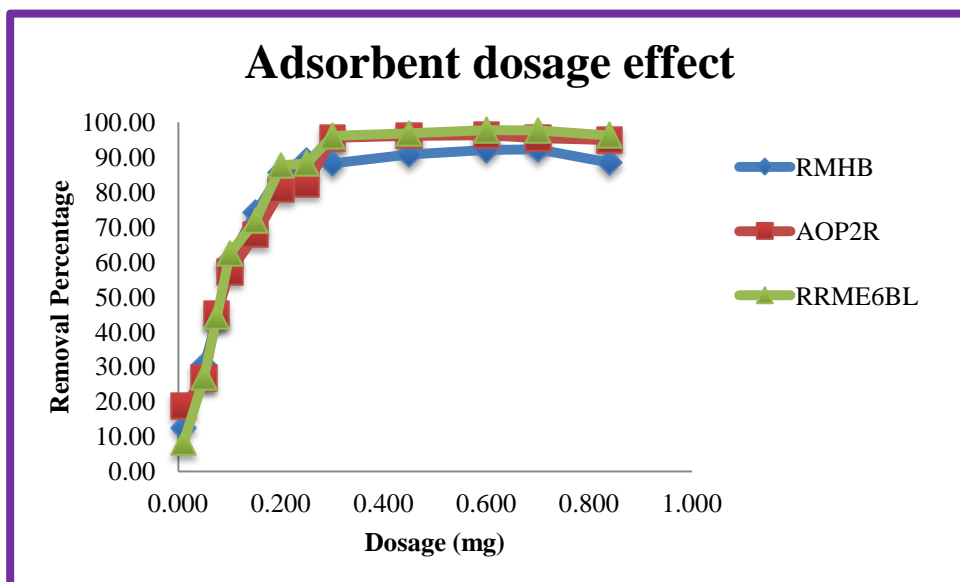


Figure 4.3.2-4: Plot of percentage removal as a function of adsorbent dosage for adsorption of aqueous RMHB, AOP2R RRME6BL solution of pH 6.0, 2.0 and 3.0 respectively on LBS.

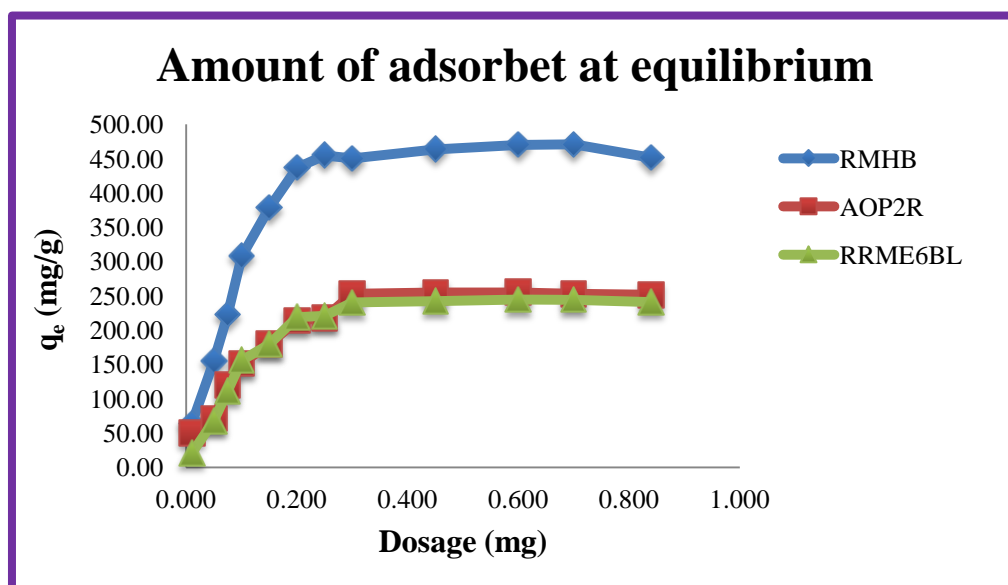


Figure 4.3.2-5: Plot of  $q_e$  as a function of adsorbent dosage for adsorption of aqueous RMHB, AOP2R and RRME6BL solution of pH 6.0, 2.0, and 3.0 respectively on LBS.



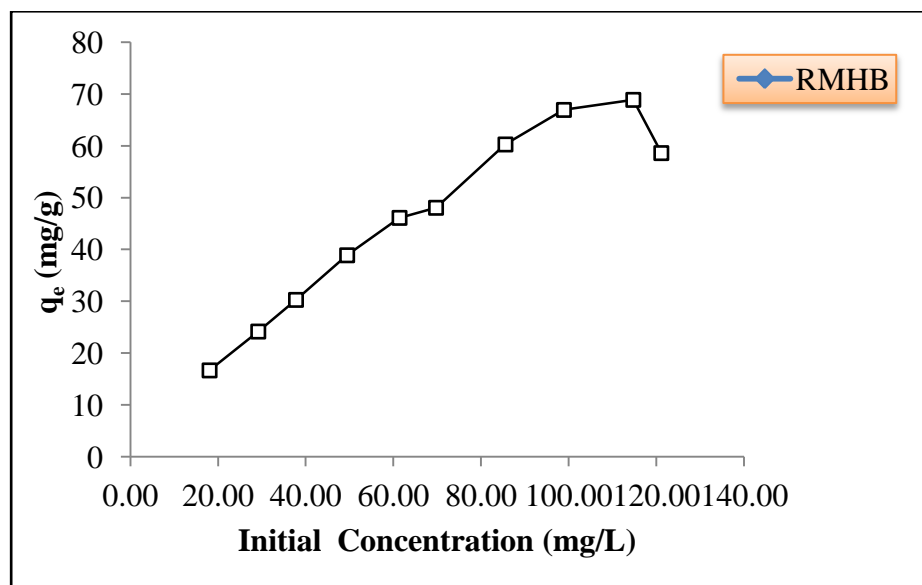
### **4.3.3 Effect of initial concentration of dyes**

The adsorption of RMHB, AOP2R and RRME6BL onto LBS was studied for different concentrations of dye solution. The data obtained are provided in the Table 4.3.3-1, Table 4.3.3-2 and Table 4.3.3-3. The experiment was conducted at optimum condition 164 mg adsorbent dosage, 30 °C and pH 6.0, pH 2.0 and pH 3.0 for contact time of 1 hour with the agitation rate 180 rpm. Maximum dye removal occurred for low initial concentration that showed gradual reduction when initial concentration of were raised. It could be ascribed to fixed concentration of adsorbent dosage. With increase in initial dye concentration the adsorption sites were fixed and achieved saturation at low dye concentration. Hence with increase in dye concentration no further adsorption could be achieved and resulted in reduced removal of dye with increase in dye concentration.

#### **Experimental Conditions:**

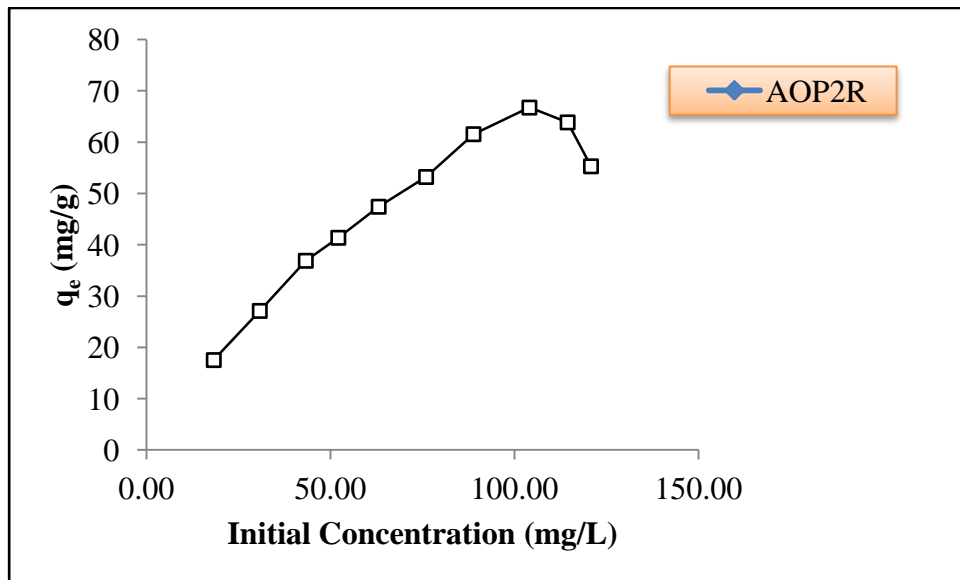
- Temperature: 30±1° C
- Concentration of RMHB, AOP2R and RRME6BL solution: 120.0 mg/L
- pH of RMHB, AOP2R and RRME6BL solutions: 6.0 , 2.0 and 3.0 respectively
- Amount of Adsorbent (LBS): 164 mg
- Agitation rate: 180 rpm
- Shaking Time: 1 hours
- Reference: Deionized water of pH 6.0, 2.0 and 3.0 .

<b>Table 4.3.3-1: Observed data of percentage removal of aqueous RMHB by adsorption on LBS at various initial concentrations.</b>						
Stock solution and water taken in 50 mL volumetric Flask (mL)	Initial Concentration $C_0$ (mg L <sup>-1</sup> )	Initial Absorbance $A_0$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ (mg L <sup>-1</sup> )	Amount adsorbate at equilibrium $q_e$	% removal
(5.00 + 45.00)	18.06	0.0650	0.005	1.39	16.67	92.31
(10.00 + 40.00)	29.17	0.1050	0.018	5.00	24.17	82.86
(15.00 + 35.00)	37.78	0.1360	0.027	7.50	30.28	80.15
(20.00 + 30.00)	49.44	0.1780	0.038	10.56	38.89	78.65
(25.00 + 25.00)	61.39	0.2210	0.055	15.28	46.11	75.11
(30.00 + 20.00)	69.72	0.2510	0.078	21.67	48.06	68.92
(35.00 + 15.00)	85.56	0.3080	0.091	25.28	60.28	70.45
(40.00 + 10.00)	98.89	0.3560	0.115	31.94	66.94	67.70
(45.00 + 5.00)	114.72	0.4130	0.165	45.83	68.89	60.05
(50.00 + 0.00)	121.11	0.4360	0.225	62.50	58.61	48.39



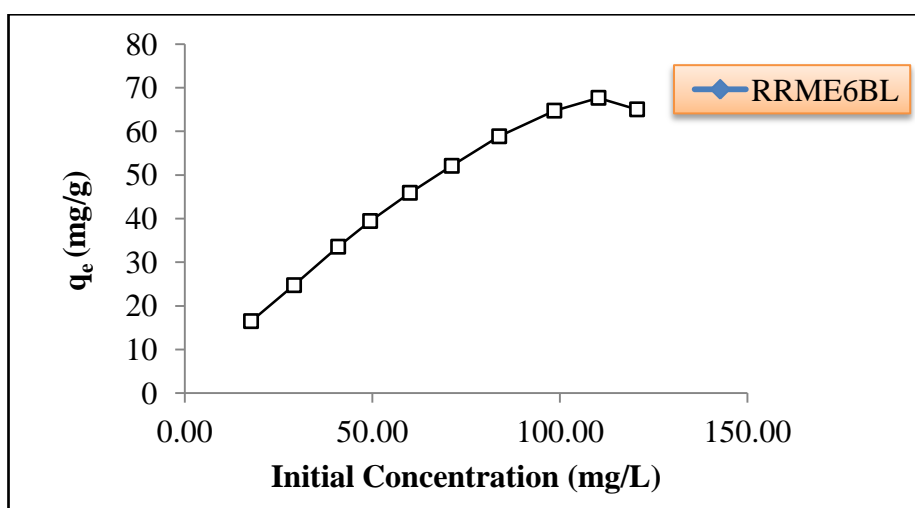
**Figure 4.3.3-1:  $C_0$  vs.  $q_e$  plot of RMHB on LBS at various  $C_0$  taking 120.00 mg/L solution of pH 6.0.**

<b>Table 4.3.3-2: Observed data of percentage removal of aqueous AOP2R solution of pH 2.0 by adsorption on LBS at various initial concentrations.</b>						
Stock solution and water taken in 50 mL flask (mL)	Initial Concentration $C_0$ (mg L <sup>-1</sup> )	Initial Absorbance $A_0$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ (mg L <sup>-1</sup> )	Amount adsorbate at equilibrium $q_e$	% removal
(5.00 + 45.00)	18.27	0.0950	0.004	0.73	17.54	96.02
(10.00 + 40.00)	30.77	0.1600	0.020	3.64	27.13	88.18
(15.00 + 35.00)	43.27	0.2250	0.035	6.36	36.91	85.29
(20.00 + 30.00)	52.12	0.2710	0.059	10.73	41.39	79.42
(25.00 + 25.00)	63.08	0.3280	0.086	15.64	47.44	75.21
(30.00 + 20.00)	75.96	0.3950	0.125	22.73	53.23	70.08
(35.00 + 15.00)	88.85	0.4620	0.150	27.27	61.57	69.30
(40.00 + 10.00)	104.04	0.5410	0.205	37.27	66.77	64.17
(45.00 + 5.00)	114.42	0.5950	0.278	50.55	63.88	55.83
(50.00 + 0.00)	120.77	0.6280	0.360	65.45	55.31	45.80



**Figure 4.3.3-2:  $C_0$  vs.  $q_e$  plot of AOP2R on LBS at various  $C_0$  taking 120.00 mg/L solution of pH 2.0.**

<b>Table 4.3.3-3: Observed data of percentage removal of aqueous RRME6BL solution of pH 3.0 by adsorption on LBS at various initial concentration</b>						
Stock solution and water taken in 50 mL flask (mL)	Initial Concentration $C_0$ (mg L <sup>-1</sup> )	Initial Absorbance $A_0$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ (mg L <sup>-1</sup> )	Amount adsorbate at equilibrium $q_e$	% removal
(5.00 + 45.00)	17.65	0.060	0.004	1.18	16.47	93.33
(10.00 + 40.00)	29.12	0.099	0.015	4.41	24.71	84.85
(15.00 + 35.00)	40.88	0.139	0.025	7.35	33.53	82.01
(20.00 + 30.00)	49.41	0.168	0.034	10.00	39.41	79.76
(25.00 + 25.00)	60.00	0.204	0.048	14.12	45.88	76.47
(30.00 + 20.00)	71.18	0.242	0.065	19.12	52.06	73.14
(35.00 + 15.00)	83.82	0.285	0.085	25.00	58.82	70.18
(40.00 + 10.00)	98.53	0.335	0.115	33.82	64.71	65.67
(45.00 + 5.00)	110.29	0.375	0.145	42.65	67.65	61.33
(50.00 + 0.00)	120.59	0.410	0.189	55.59	65.00	53.90



**Figure 4.3.3-3:  $C_0$  vs.  $q_e$  plot of RRME6BL on LBS at various  $C_0$  taking 120.59 mg/L solution of pH 3.0.**

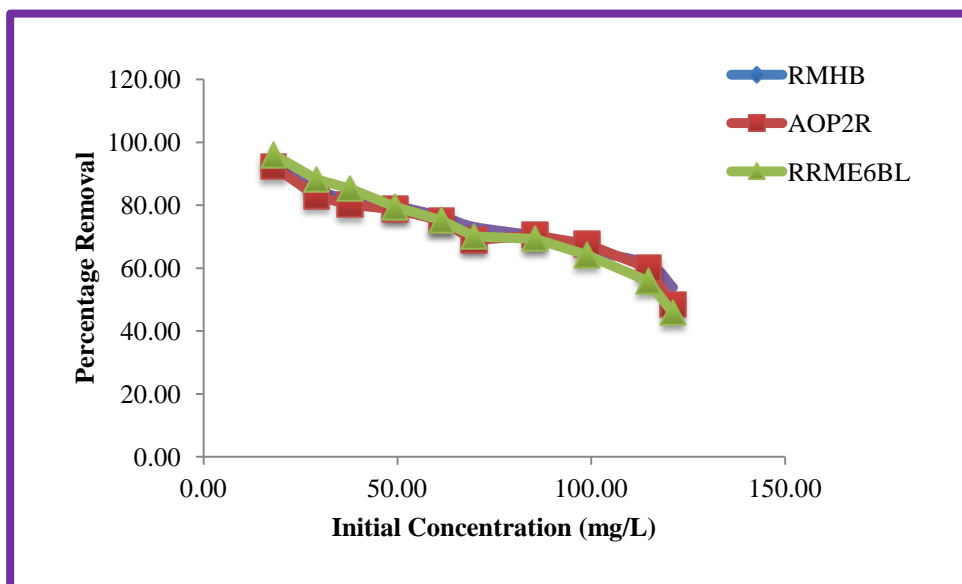


Figure 4.3.3-4:  $C_0$  vs. Percentage removal plot of RMHB, AOP2R and RRME6BL on LBS at various  $C_0$  and pH 6.0, pH 2.0 and pH 3.0 respectively

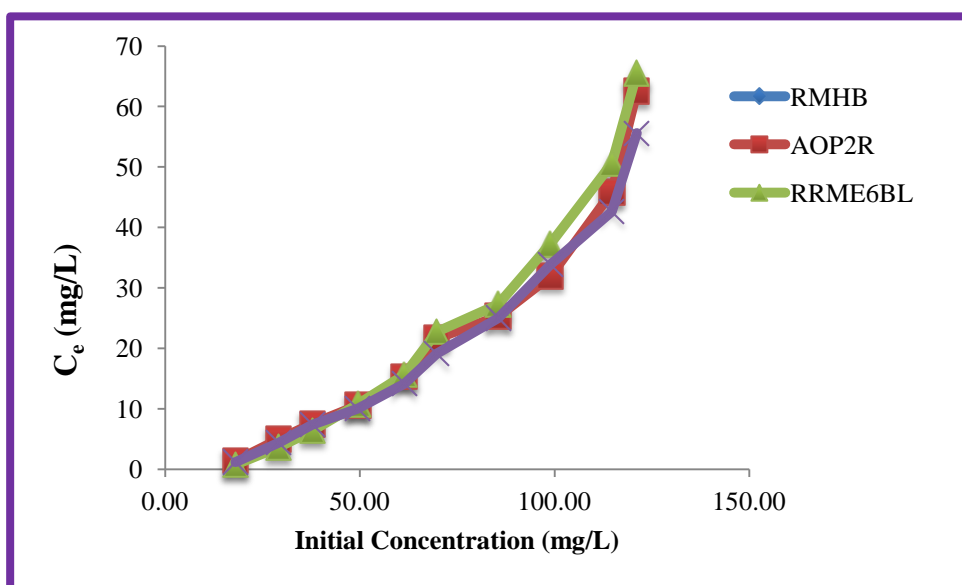
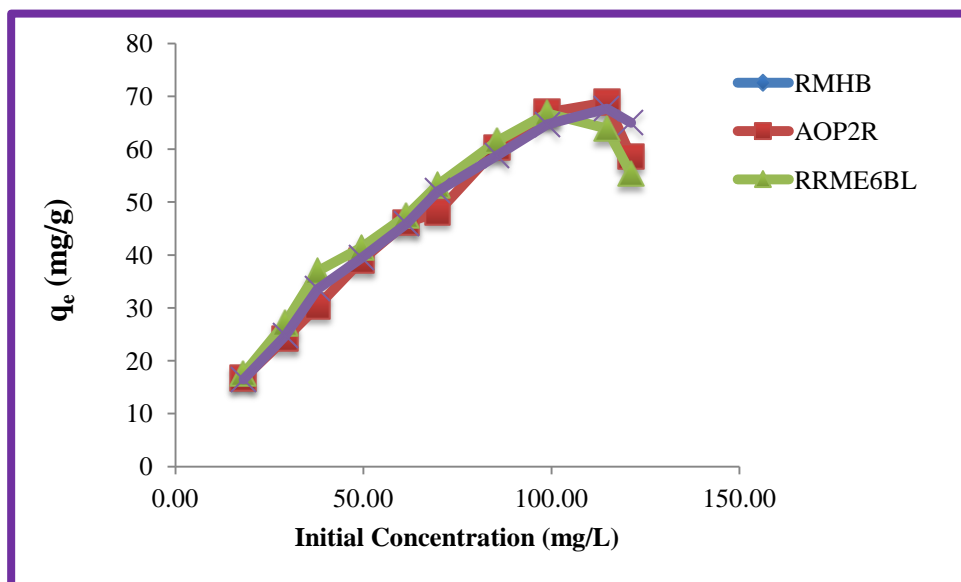


Figure 4.3.3-5:  $C_0$  vs.  $C_e$  plot of RMHB, AOP2R and RRME6BL on LBS at various  $C_0$  and pH 6.0, pH 2.0 and pH 3.0 respectively



**Figure 4.3.3-6:  $C_0$  vs.  $q_e$  plot of RMHB, AOP2R and RRME6BL on LBS at various  $C_0$  and pH 6.0, pH 3.0 and pH 2.0 respectively.**

#### **4.3.4 Effect of contact time on adsorption and Estimation of equilibrium time**

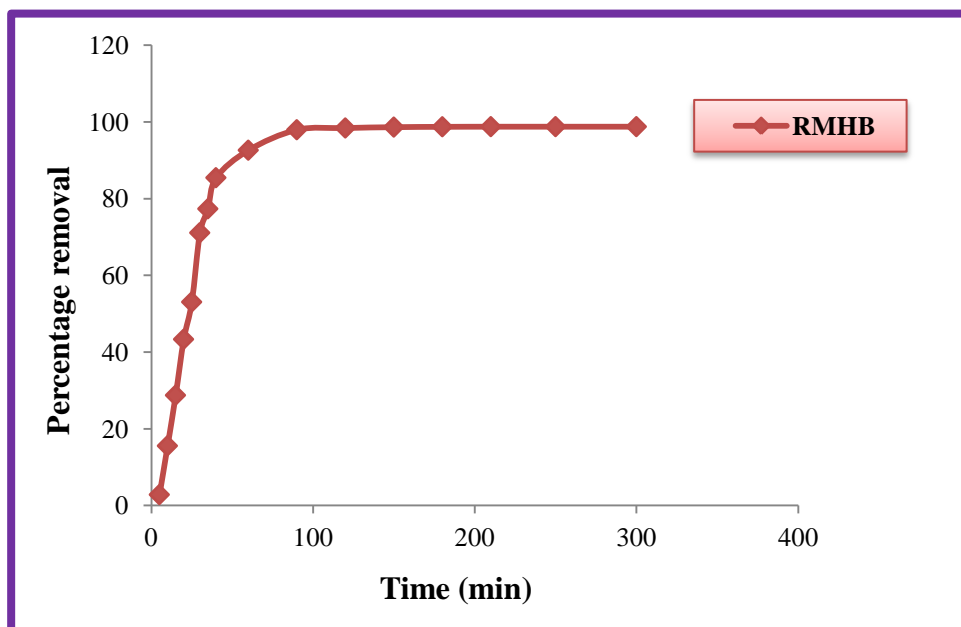
The data of the effect of contact time presented in Table 4.3.4-1, Table 4.3.4-2 and Table 4.3.4-5. The effect of contact time on adsorption process can be seen from Figure 4.3.4-1 to Figure 4.3.4-8 for the dyes. It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 2 hours from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 2 hours (120 min). From the figure it is obviously shown that adsorption reaction nearly attained equilibrium within 180 minutes and after which no substantial amount of dyes were adsorbed with increasing contact time after equilibrium was achieved. It is basically due to saturation of the active site which does not allow further adsorption to take place. The dependence of adsorption on contact time was studied using fixed amount 100 mg of adsorbent (LBS) and 120 mg/L dye solution in a fixed volume (50 mL).

**Experimental Conditions:**

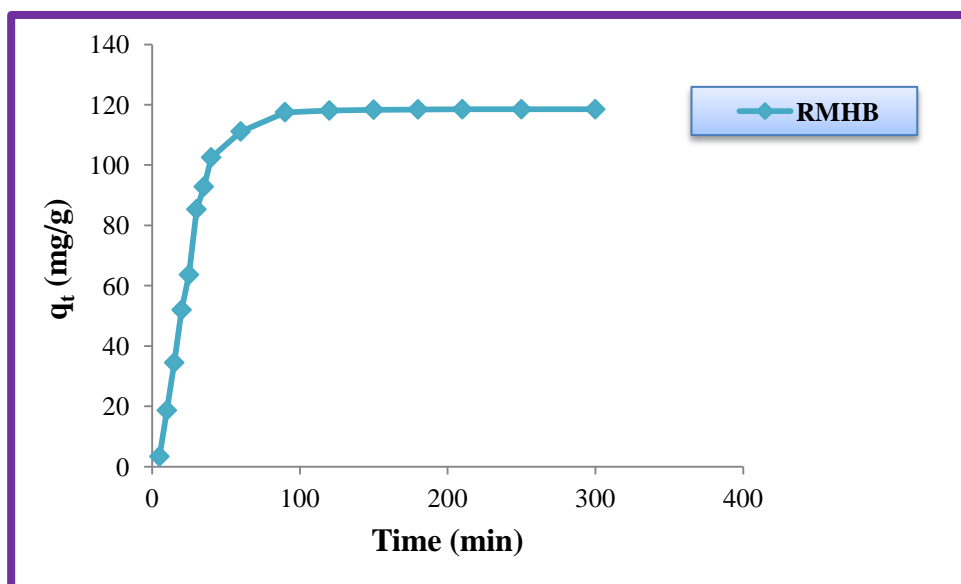
- Temperature: 30±1°C
- Concentration of RMHB: 120 mg/L
- Volume of the solution taken: 50 mL
- Amount of Adsorbent (LBS): 100 mg
- Agitation rate: 190 rpm
- Shaking Time: 3 hours
- Reference: Deionized water of pH 6.0
- pH of aqueous RMHB: 6.0

**Table 4.3.4-1: Observed data of percentage removal of aqueous RMHB by adsorption on LBS at various time and estimate the equilibrium time**

<b>Time (min)</b>	<b>Absorbance at different time <math>A_t</math></b>	<b>Concentration at different time <math>C_t</math> (mg/L)</b>	<b>Initial Concentration <math>C_0</math> (mg/L)</b>	<b>Amount adsorbed at different time <math>q_t</math> (mg/g)</b>	<b>% removal</b>
5.0	0.420	116.67	120.00	3.33	2.78
10.0	0.365	101.39		18.61	15.51
15.0	0.308	85.56		34.44	28.70
20.0	0.245	68.06		51.94	43.29
25.0	0.203	56.39		63.61	53.01
30.0	0.125	34.72		85.28	71.06
35.0	0.098	27.22		92.78	77.31
40.0	0.063	17.50		102.50	85.42
60.0	0.032	8.89		111.11	92.59
90.0	0.009	2.50		117.50	97.92
120.0	0.007	1.94		118.06	98.38
150.0	0.006	1.67		118.33	98.61
180.0	0.0056	1.56		118.44	98.70
210.0	0.0055	1.53		118.47	98.73
250.0	0.0055	1.53		118.47	98.73
300.0	0.0055	1.53		118.47	98.73



**Figure 4.3.4-1: Plot of percentage removal as a function of time for adsorption of aqueous RMHB solution of pH 6.0 on LBS.**



**Figure 4.3.4-2: Plot of amount of adsorbed as a function of time for adsorption of aqueous RMHB solution of pH 6.0 on LBS.**

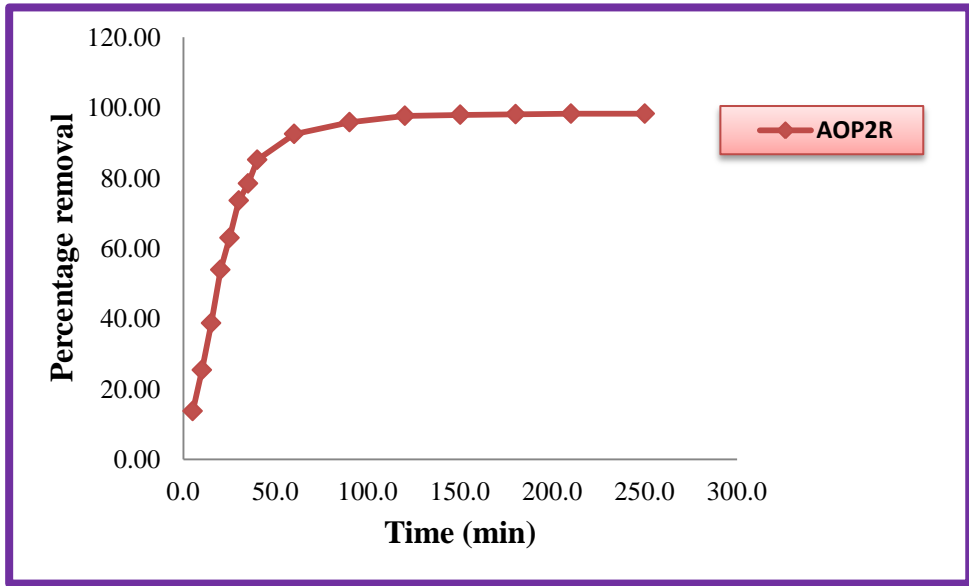


**Experimental Conditions:**

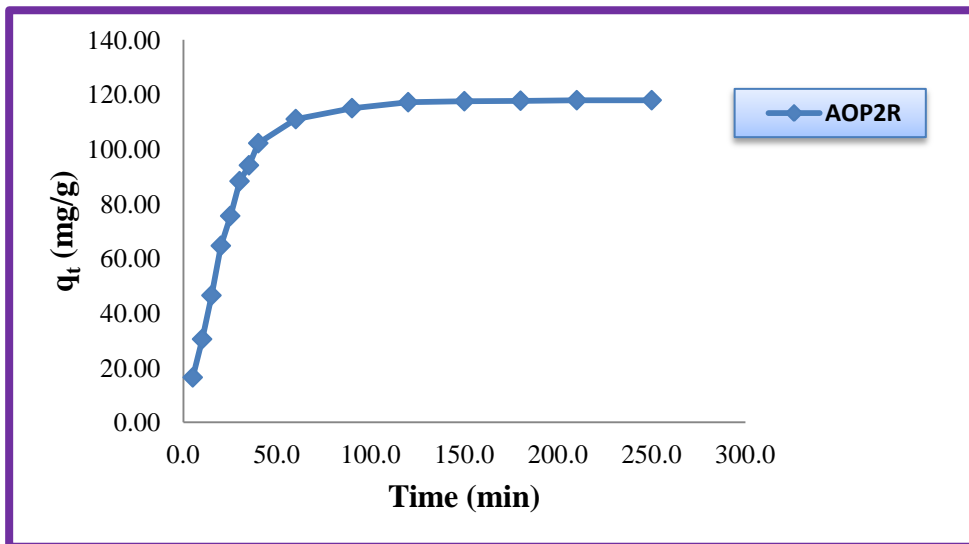
- Temperature: 30±1°C
- Concentration of AOP2R: 120 mg/L
- Volume of the solution taken: 50 mL
- Amount of Adsorbent (LBS): 100 mg
- Agitation rate: 190 rpm
- Shaking Time: 3 hours
- Reference: Deionized water of pH 2.0
- pH of aqueous AOP2R: 2.0

**Table 4.3.4-2: Observed data of percentage removal of aqueous AOP2R by adsorption on LBS at various time and estimate the equilibrium time.**

<b>Time (min)</b>	<b>Absorbance at different time <math>A_t</math></b>	<b>Concentration at different time <math>C_t</math> (mg/L)</b>	<b>Initial Concentration <math>C_0</math> (mg/L)</b>	<b>Amount adsorbed at different time <math>q_t</math> (mg/g)</b>	<b>% removal</b>
5.0	0.570	103.64	120	16.36	13.64
10.0	0.493	89.64		30.36	25.30
15.0	0.405	73.64		46.36	38.64
20.0	0.305	55.45		64.55	53.79
25.0	0.245	44.55		75.45	62.88
30.0	0.175	31.82		88.18	73.48
35.0	0.143	26.00		94.00	78.33
40.0	0.099	17.91		102.09	85.08
60.0	0.050	9.09		110.91	92.42
90.0	0.028	5.09		114.91	95.76
120.0	0.016	2.91		117.09	97.58
150.0	0.014	2.55		117.45	97.88
180.0	0.013	2.36		117.64	98.03
210.0	0.012	2.18		117.82	98.18
250.0	0.012	2.18		117.82	98.18



**Figure 4.3.4-3: Plot of percentage removal as a function of time for adsorption of aqueous AOP2R solution of pH 2.0 on LBS.**



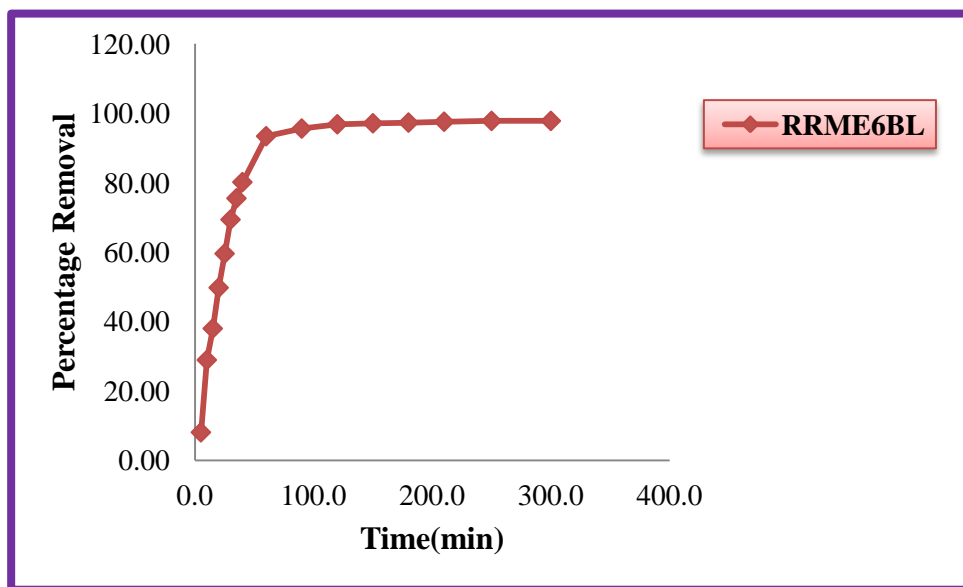
**Figure 4.3.4-4: Plot of amount of adsorbed as a function of time for adsorption of aqueous AOP2R solution of pH 2.0 on LBS.**

### Experimental Conditions:

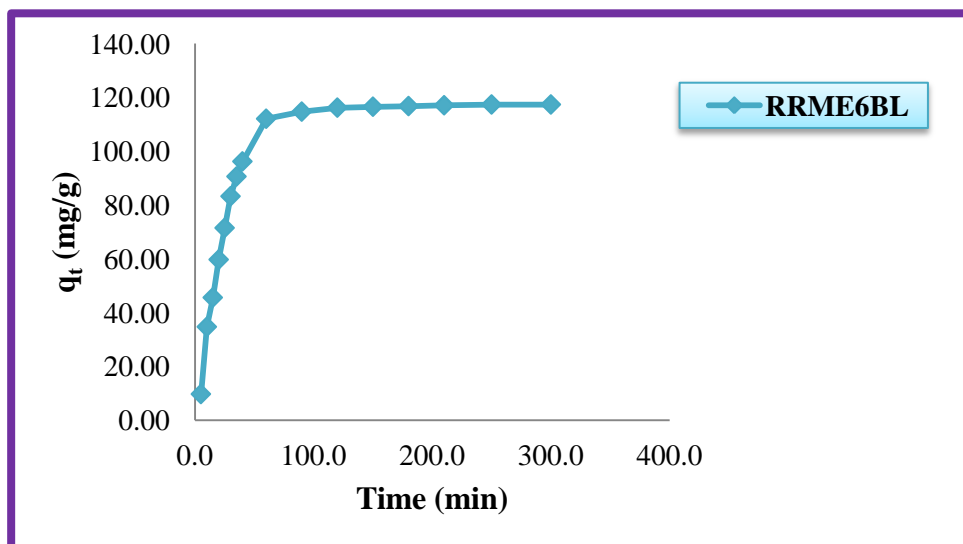
- Temperature: 30±1 °C
- Concentration of RRME6BL: 120 mg/L
- Volume of the solution taken: 50 mL
- Amount of Adsorbent (LBS): 100 mg
- Agitation rate: 190 rpm
- Shaking Time: 3 hours
- Reference: Deionized water of pH 3.0
- pH of aqueous RRME6BL: 3.0

**Table 4.3.4-3: Observed data of percentage removal of aqueous RRME6BL by adsorption on LBS at various time and estimate the equilibrium time.**

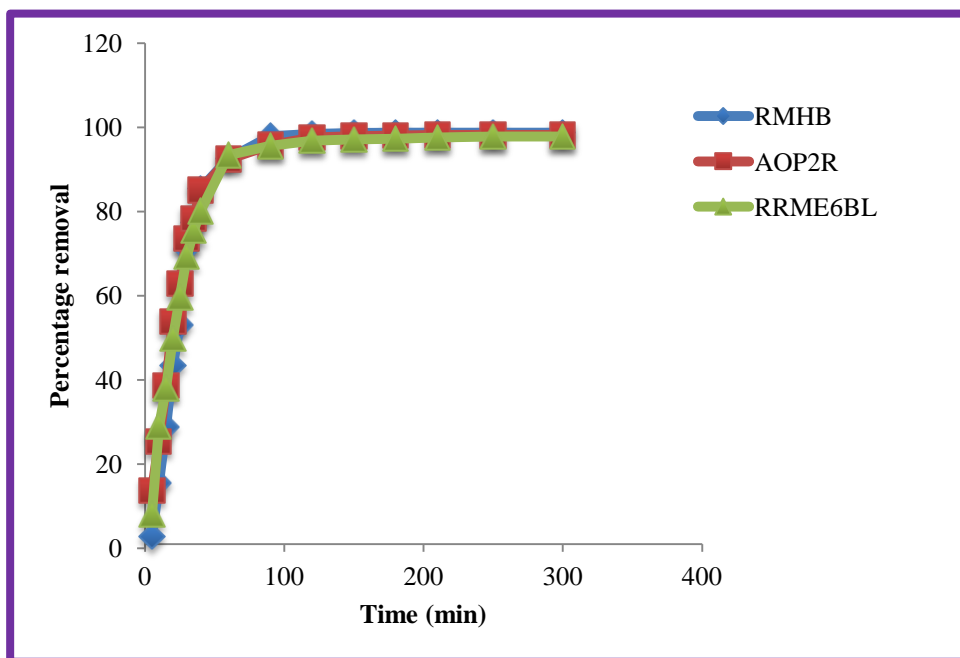
<b>Time (min)</b>	<b>Absorbance at different time <math>A_t</math></b>	<b>Concentration at different time <math>C_t</math> (mg/L)</b>	<b>Initial Concentration <math>C_0</math> (mg/L)</b>	<b>Amount adsorbed at different time <math>q_t</math> (mg/g)</b>	<b>% removal</b>
5.0	0.375	110.29	120.00	9.71	8.09
10.0	0.290	85.29	120.00	34.71	28.92
15.0	0.253	74.41	120.00	45.59	37.99
20.0	0.205	60.29	120.00	59.71	49.75
25.0	0.165	48.53	120.00	71.47	59.56
30.0	0.125	36.76	120.00	83.24	69.36
35.0	0.100	29.41	120.00	90.59	75.49
40.0	0.081	23.82	120.00	96.18	80.15
60.0	0.027	7.94	120.00	112.06	93.38
90.0	0.018	5.29	120.00	114.71	95.59
120.0	0.013	3.82	120.00	116.18	96.81
150.0	0.012	3.47	120.00	116.53	97.11
180.0	0.011	3.24	120.00	116.76	97.30
210.0	0.010	2.94	120.00	117.06	97.55
250.0	0.009	2.65	120.00	117.35	97.79
300.0	0.009	2.65	120.00	117.35	97.79



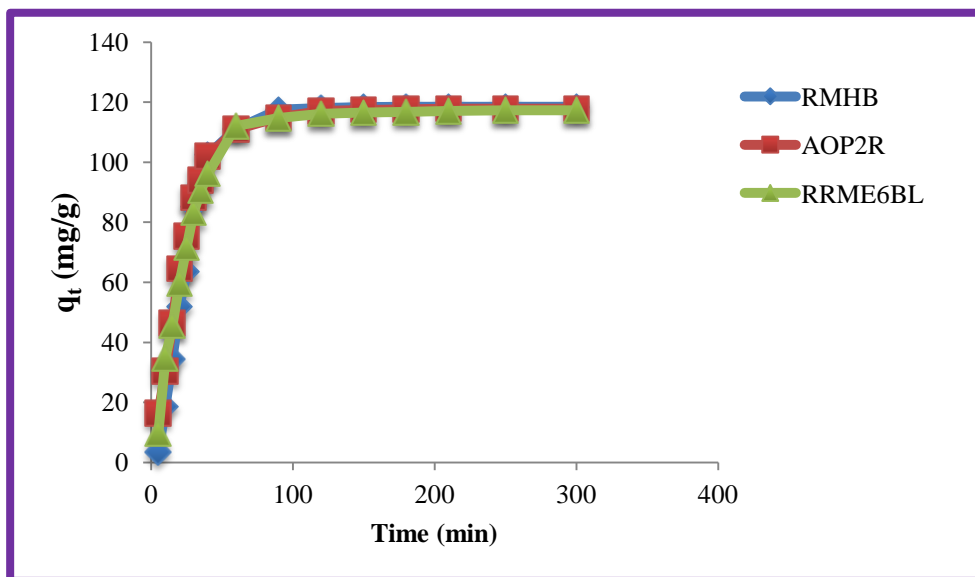
**Figure 4.3.4-5: Plot of percentage removal as a function of time for adsorption of aqueous RRME6BL solution of pH 3.0 on LBS.**



**Figure 4.3.4-6: Plot of amount of adsorbed as a function of time for adsorption of aqueous RRME6BL solution of pH 3.0 on LBS.**



**Figure 4.3.4-7: Plot of percentage removal as a function of time for adsorption of aqueous RMHB, AOP2R and RRME6BL solution of pH 6.0, pH 2.0 and pH 3.0 respectively on LBS.**



**Figure 4.3.4-8: Plot of amount of adsorbed as a function of time for adsorption of aqueous RMHB, AOP2R and RRME6BL solution of pH 6.0, pH 2.0 and pH 3.0 respectively on LBS.**

## 4.4 Adsorption Isotherm studies

### 4.4.1 The Langmuir adsorption isotherm

The linear form of Langmuir isotherm is usually written as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

Where  $C_e$  is the liquid-phase equilibrium concentration ( $\text{mg L}^{-1}$ ) of the adsorbate,  $q_e$  is the amount of adsorbate adsorbed at equilibrium ( $\text{mg g}^{-1}$ ) and  $q_m$  is the theoretical maximum monolayer adsorbent capacity ( $\text{mg g}^{-1}$ ).  $K_L$  is the Langmuir constant.  $q_m$  and  $K_L$  are related to the adsorption efficiency and the energy of adsorption.

A plot of  $C_e$  versus ( $C_e/q_e$ ) is linear showing the applicability of Langmuir adsorption isotherm for dyes adsorption using the LBS.  $K_L$  and  $q_m$  calculated from slope and intercept of the plot. (Figure 4.4.1.1, figure 4.4.1.2 and figure 4.4.1.3) shows Langmuir isotherm for the adsorption of three dyes on LBS. Values of Langmuir adsorption parameters deduced from the slopes and intercepts of the plots are recorded in (Table 4.4.1-1). Data obtained from the equilibrium study were used to fit curves for different adsorption models and it was found that the adsorption of three dyes on LBS is best described by the Langmuir adsorption isotherm.

The essential characteristics of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter ' $R_L$ ' which is defined by,

$$R_L = \frac{1}{1 + K_L C_i}$$

Where,  $C_i$  = initial concentration of the dye and  $b$ =Langmuir constant.

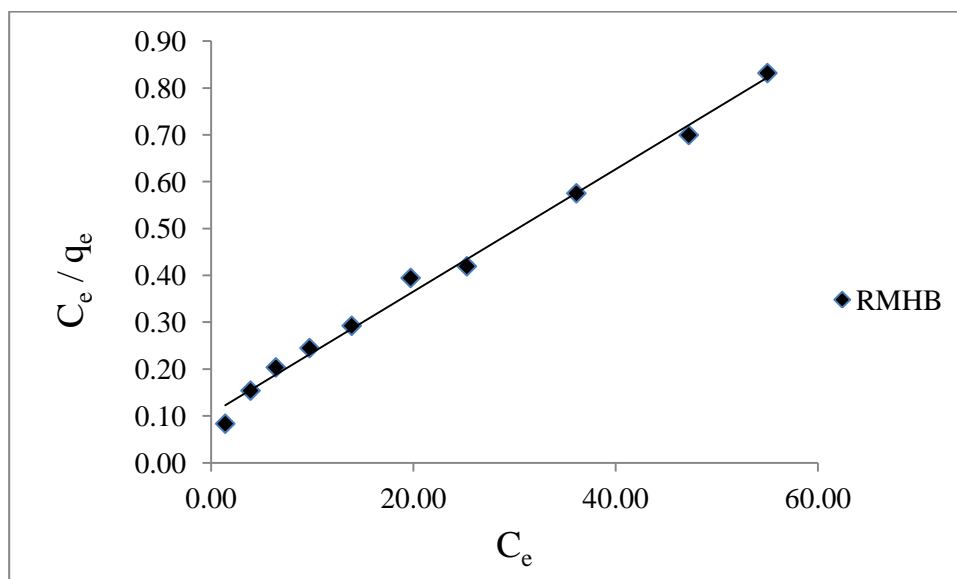
$R_L$ value	Type of adsorption
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

### Experimental Conditions:

- Temperature:  $30 \pm 1^\circ\text{C}$
- Concentration of RMHB, AOP2R and RRME6BL solution: 120.0 mg/L
- pH of RMHB, AOP2R and RRME6BL solutions: 6.0 ; 2.0 and 3.0 respectively
- Amount of Adsorbent (LBS): 164 mg
- Agitation rate: 180 rpm
- Shaking Time: 1 hours
- Reference: Deionized water of pH 6.0, 2.0 and 3.0

**Table 4.4.1-2 Data analysis for the adsorption studies of Langmuir isotherm of RMHB onto LBS**

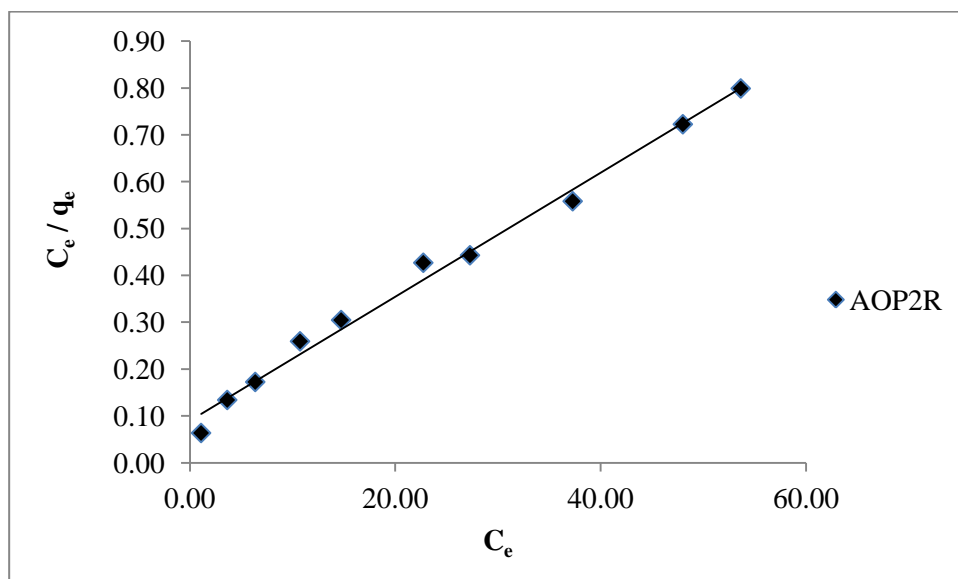
Initial Concentration $C_o$ ( $\text{mg L}^{-1}$ )	Initial Absorbance $A_o$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ ( $\text{mg L}^{-1}$ )	Amount adsorbed at equilibrium $q_e$ (mg/g)	$C_e / q_e$
18.06	0.0650	0.005	1.39	16.67	0.08
29.17	0.1050	0.014	3.89	25.28	0.15
37.78	0.1360	0.023	6.39	31.39	0.20
49.44	0.1780	0.035	9.72	39.72	0.24
61.39	0.2210	0.050	13.89	47.50	0.29
69.72	0.2510	0.071	19.72	50.00	0.39
85.56	0.3080	0.091	25.28	60.28	0.42
98.89	0.3560	0.130	36.11	62.78	0.58
114.72	0.4130	0.170	47.22	67.50	0.70
121.11	0.4360	0.198	55.00	66.11	0.83



**Figure 4.4.1-1 Langmuir adsorption isotherm for RMHB onto LBS at room temperature**

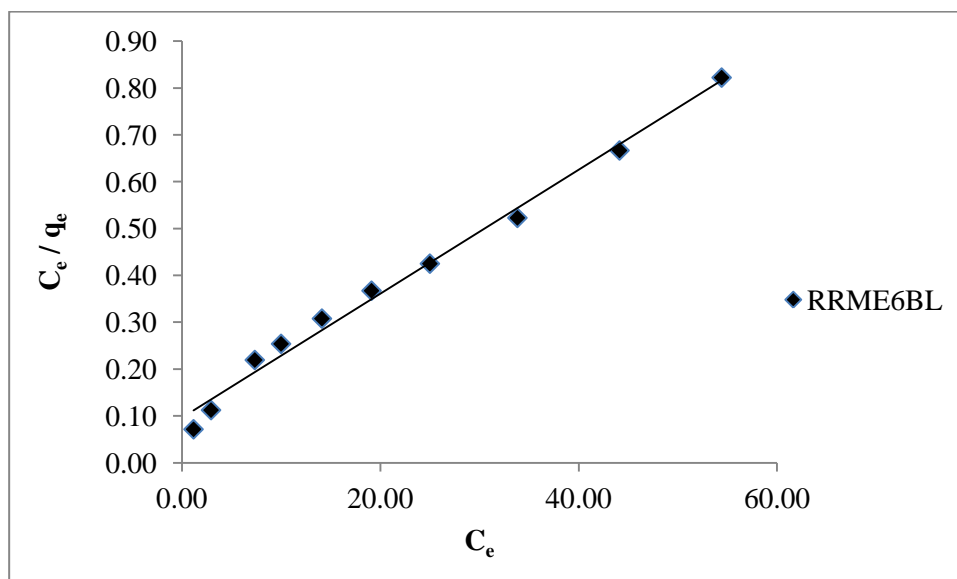
Initial Concentration $C_o$ (mg L <sup>-1</sup> )	Initial Absorbance $A_o$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ (mg L <sup>-1</sup> )	Amount adsorbed at equilibrium $q_e$ (mg/g)	$C_e / q_e$
18.27	0.0950	0.006	1.09	17.18	0.06
30.77	0.1600	0.020	3.64	27.13	0.13
43.27	0.2250	0.035	6.36	36.91	0.17
52.12	0.2710	0.059	10.73	41.39	0.26
63.08	0.3280	0.081	14.73	48.35	0.30
75.96	0.3950	0.125	22.73	53.23	0.43
88.85	0.4620	0.150	27.27	61.57	0.44
104.04	0.5410	0.205	37.27	66.77	0.56
114.42	0.5950	0.264	48.00	66.42	0.72
120.77	0.6280	0.295	53.64	67.13	0.80





**Figure 4.4.1-2 Langmuir adsorption isotherm for AOP2R onto LBS at room temperature**

<b>Table 4.4.1-4 Data analysis for the adsorption studies of Langmuir isotherm of RRME6BL onto LBS</b>					
Initial Concentration $C_o$ (mg L <sup>-1</sup> )	Initial Absorbance $A_o$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ (mg L <sup>-1</sup> )	Amount adsorbed at equilibrium $q_e$ (mg/g)	$C_e / q_e$
17.65	0.060	0.004	1.18	16.47	0.07
29.12	0.099	0.010	2.94	26.18	0.11
40.88	0.139	0.025	7.35	33.53	0.22
49.41	0.168	0.034	10.00	39.41	0.25
60.00	0.204	0.048	14.12	45.88	0.31
71.18	0.242	0.065	19.12	52.06	0.37
83.82	0.285	0.085	25.00	58.82	0.43
98.53	0.335	0.115	33.82	64.71	0.52
110.29	0.375	0.150	44.12	66.18	0.67
120.59	0.410	0.185	54.41	66.18	0.82



**Figure 4.4.1-3 Langmuir adsorption isotherm for RRME6BL on to LBS at room temperature**

Name of dye	pH of the solution	$R^2$	$q_m$	$K_L$	$R_L$
RMHB	6.0	0.9929	76.34	$12.54 \times 10^{-2}$	0.062
AOP2R	2.0	0.9913	75.76	$14.68 \times 10^{-2}$	0.054
RRME6BL	3.0	0.9902	75.76	$13.71 \times 10^{-2}$	0.057

From the above data analysis (table 4.4.1.5) it is seen that the value of  $R_L$  was calculated as (0.054 -0.068) indicating that the adsorption efficiency of the LBS is good. The correlation coefficient of Langmuir isotherm,  $R^2$  is found in range (0.9902- 0.9929). This suggests that the Langmuir isotherm provide good model of the sorption system. The  $R_L$  value, ( $0 < R_L < 1$ ) indicates that the adsorption behavior of LBS was extremely favorable for the studied dyes.

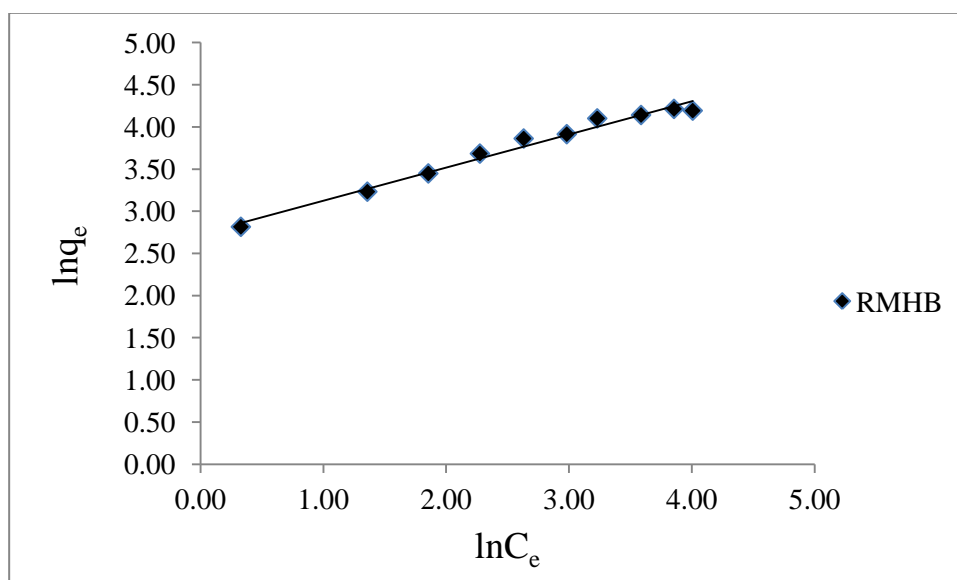
#### 4.4.2 Freundlich Adsorption studies

A plot of  $\log q_e$  versus  $\log C_e$  was linear. A value of  $1/n$  close to 1 represents a linear relationship, while  $1/n < 1$  represents a non-linear relationship.  $K_F$  is measure of adsorption capacity (mg/g) and the slope range of  $1/n$  is a measure of the adsorption intensity or surface heterogeneity. The surface heterogeneity increases as  $1/n$  approaches zero. A value for  $1/n$  below 1 indicates a Freundlich isotherm, while  $1/n$  above 1 is indicative of cooperative adsorption. Higher values denote that the system approaches a rectangular isotherm (or irreversible isotherm), especially when the value of  $n > 10$ . The  $K_F$  constant can be regarded as the maximum adsorption capacity of the adsorbent only with a very large value of  $n$ .

##### Experimental Conditions:

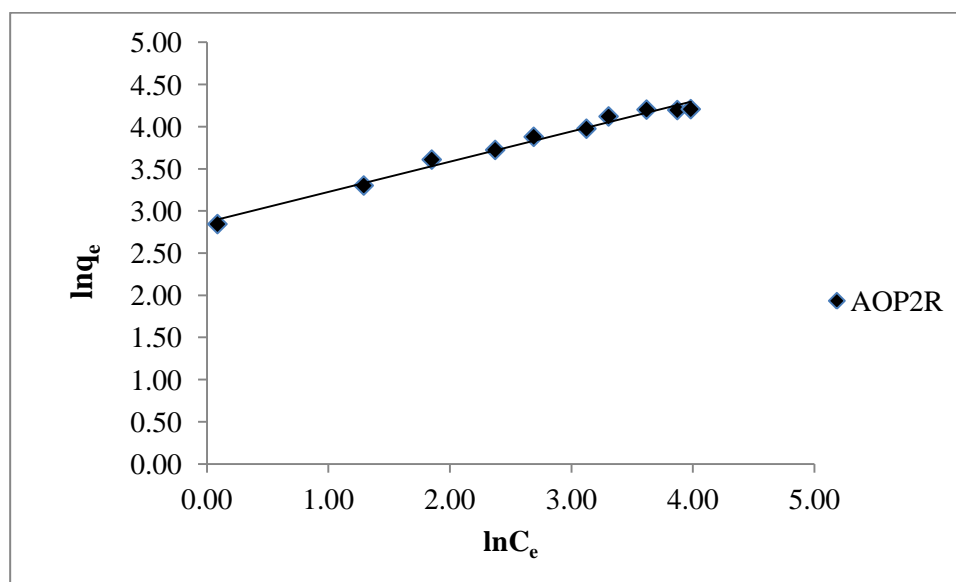
- Temperature:  $30 \pm 1^\circ \text{C}$
- Concentration of RMHB, AOP2R and RRME6BL solution: 120.0 mg/L
- pH of RMHB, AOP2R and RRME6BL solutions: 6.0 ; 2.0 and 3.0 respectively
- Amount of Adsorbent (LBS): 164 mg
- Agitation rate: 180 rpm
- Shaking Time: 1 hours
- Reference: Deionized water of pH 6.0, 2.0 and 3.0

Initial Concentration $C_o$ (mg L <sup>-1</sup> )	Initial Absorbance $A_o$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ (mg L <sup>-1</sup> )	Amount adsorbed at equilibrium $q_e$ (mg/g)	$\ln C_e$	$\ln q_e$
18.06	0.0650	0.005	1.39	16.67	0.33	2.81
29.17	0.1050	0.014	3.89	25.28	1.36	3.23
37.78	0.1360	0.023	6.39	31.39	1.85	3.45
49.44	0.1780	0.035	9.72	39.72	2.27	3.68
61.39	0.2210	0.050	13.89	47.50	2.63	3.86
69.72	0.2510	0.071	19.72	50.00	2.98	3.91
85.56	0.3080	0.091	25.28	60.28	3.23	4.10
98.89	0.3560	0.130	36.11	62.78	3.59	4.14
114.72	0.4130	0.170	47.22	67.50	3.85	4.21
121.11	0.4360	0.198	55.00	66.11	4.01	4.19



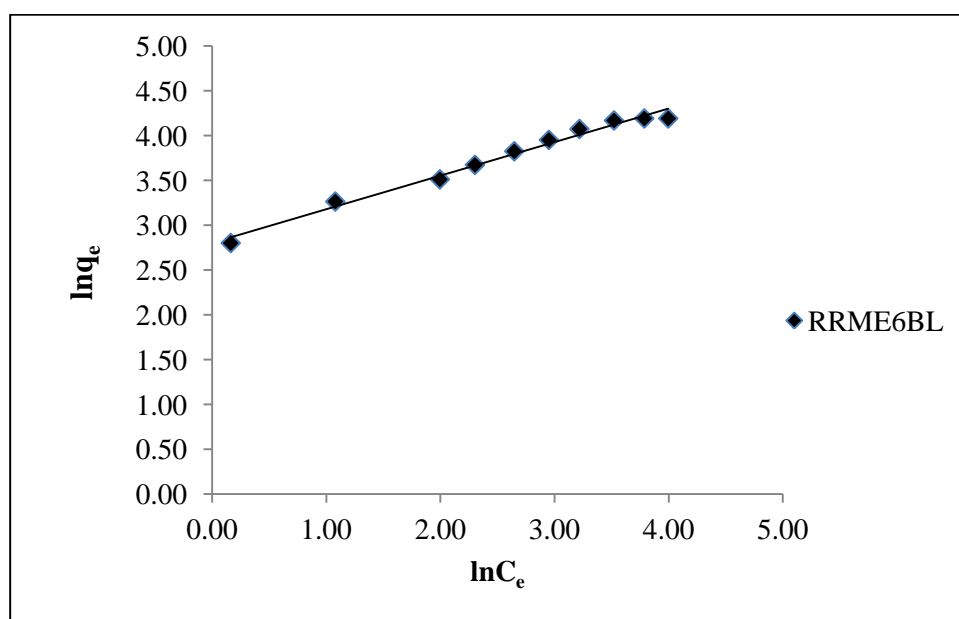
**Figure 4.4.2-1 Freundlich adsorption isotherm for RMHB on to LBS at room temperature**

<b>Table 4.4.2-2 Data analysis for the adsorption studies of Freundlich isotherm of AOP2R onto LBS</b>						
Initial Concentration $C_o$ (mg L <sup>-1</sup> )	Initial Absorbance $A_o$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ (mg L <sup>-1</sup> )	Amount adsorbed at equilibrium $q_e$ (mg/g)	$\ln C_e$	$\ln q_e$
18.27	0.0950	0.006	1.09	17.18	0.09	2.84
30.77	0.1600	0.020	3.64	27.13	1.29	3.30
43.27	0.2250	0.035	6.36	36.91	1.85	3.61
52.12	0.2710	0.059	10.73	41.39	2.37	3.72
63.08	0.3280	0.081	14.73	48.35	2.69	3.88
75.96	0.3950	0.125	22.73	53.23	3.12	3.97
88.85	0.4620	0.150	27.27	61.57	3.31	4.12
104.04	0.5410	0.205	37.27	66.77	3.62	4.20
114.42	0.5950	0.264	48.00	66.42	3.87	4.20
120.77	0.6280	0.295	53.64	67.13	3.98	4.21



**Figure 4.4.2-2 Freundlich adsorption isotherm for AOP2R on to LBS at room temperature**

<b>Table 4.4.2-3 Data analysis for the adsorption studies of Freundlich isotherm of RRME6BL onto LBS</b>						
Initial Concentration $C_o$ (mg L <sup>-1</sup> )	Initial Absorbance $A_o$	Equilibrium Absorbance $A_e$	Equilibrium Concentration $C_e$ (mg L <sup>-1</sup> )	Amount adsorbed at equilibrium $q_e$	$\ln C_e$	$\ln q_e$
17.65	0.060	0.004	1.18	16.47	0.16	2.80
29.12	0.099	0.010	2.94	26.18	1.08	3.26
40.88	0.139	0.025	7.35	33.53	2.00	3.51
49.41	0.168	0.034	10.00	39.41	2.30	3.67
60.00	0.204	0.048	14.12	45.88	2.65	3.83
71.18	0.242	0.065	19.12	52.06	2.95	3.95
83.82	0.285	0.085	25.00	58.82	3.22	4.07
98.53	0.335	0.115	33.82	64.71	3.52	4.17
110.29	0.375	0.150	44.12	66.18	3.79	4.19
120.59	0.410	0.185	54.41	66.18	4.00	4.19



**Figure 4.4.2-3 Freundlich adsorption isotherm for RRME6BL on to LBS at room temperature**

<b>Table 4.4.2-4 Freundlich parameters of adsorption isotherms for removal of studied dyes onto LBS</b>					
Name of dye	pH of the solution	$R^2$	$K_F$ (mg/g)	1/n	n
RMHB	6.0	0.9796	$5.39 \times 10^{-2}$	0.39	2.54
AOP2R	2.0	0.9839	$7.34 \times 10^{-2}$	0.36	2.79
RRME6BL	3.0	0.9840	$6.37 \times 10^{-2}$	0.38	2.67

The applicability of the linear form of Langmuir and Freundlich model to LBS was confirmed by the high correlation coefficient  $R^2 > 0.98$ . This suggests that the Langmuir isotherm and Freundlich models both provide good model of the sorption system. The value of 1/n is lower than 1, (n is greater than one) indicating that studied dyes are favorably adsorbed by LBS.

## 4.5 Kinetic of adsorption

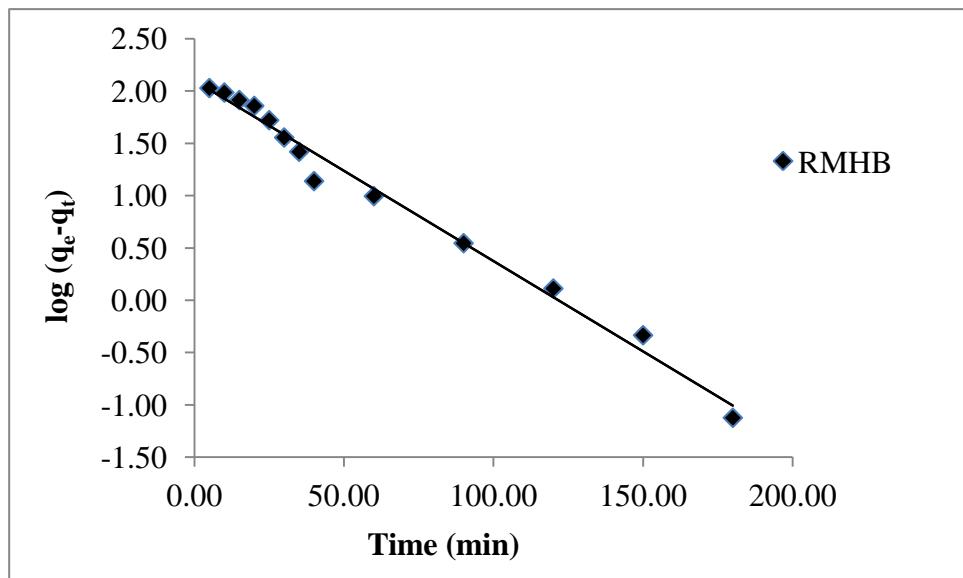
The rate constants of chemical adsorption for dyes were determined using both pseudo-first order and pseudo-second-order equations.

### 4.5.1 Lagergren pseudo-first-order equation

The kinetics of adsorption was analyzed by the Lagergren pseudo-first-order equation as depicted in (Equation-10). Based on experimental results, linear plot of  $\log(q_e - q_t)$  versus t was tested for the applicability of Lagergren first order equation (Figure 4.5.1-1, Figure 4.5.1-2 and Figure 4.5.1-3, to the adsorption of dyes.

- Experimental Conditions:
- Temperature:  $30 \pm 1^\circ \text{C}$
- Concentration of RMHB, AOP2R and RRME6BL solution: 120.0 mg/L
- pH of RMHB, AOP2R and RRME6BL solutions 6.0 ; 2.0 and 3.0 respectively
- Amount of Adsorbent (LBS): 164 mg
- Agitation rate: 180 rpm
- Reference: Deionized water of pH 6.0, 2.0 and 3.0.

<b>Table 4.5.1-1 Pseudo first order kinetic study for adsorption of 120.0 mg/L RMHB on LBS</b>						
Time (min)	Amount of adsorbed $q_t$ (mg/g)	Equilibrium amount of adsorbed $q_e$ (mg/g)	$t^{1/2}$	$\ln t$	$\log (q_e - q_t)$	$t / q_t$
5.00	11.67	118.52	2.24	1.61	2.03	0.43
10.00	21.67		3.16	2.30	1.99	0.46
15.00	36.39		3.87	2.71	1.91	0.41
20.00	46.39		4.47	3.00	1.86	0.43
25.00	65.83		5.00	3.22	1.72	0.38
30.00	82.50		5.48	3.40	1.56	0.36
35.00	92.22		5.92	3.56	1.42	0.38
40.00	104.72		6.32	3.69	1.14	0.38
60.00	108.61		7.75	4.09	1.00	0.55
90.00	115.00		9.49	4.50	0.55	0.78
120.00	117.22		10.95	4.79	0.11	1.02
150.00	118.06		12.25	5.01	-0.33	1.27
180.00	118.44		13.42	5.19	-1.12	1.52

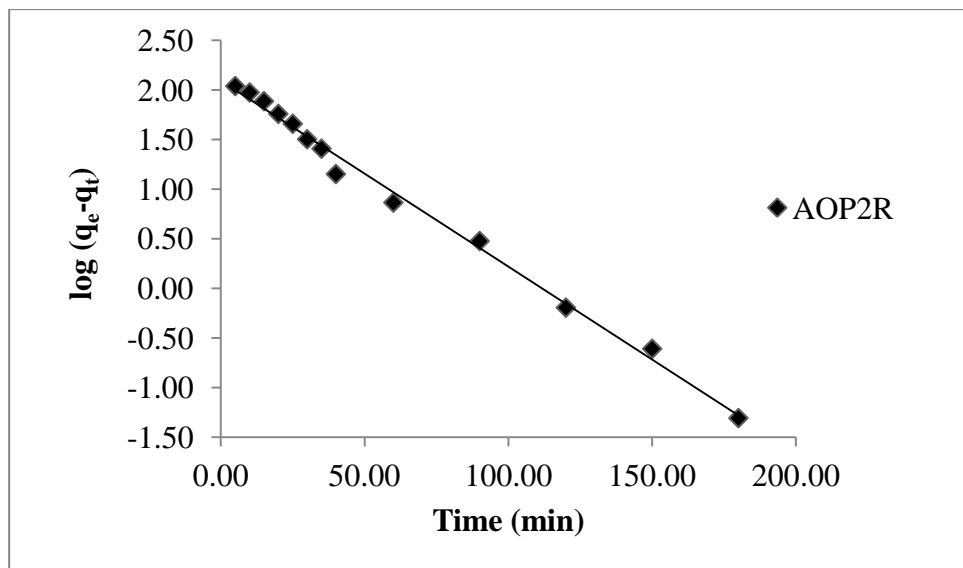


**Figure 4.5.1-1 Pseudo-first-order kinetics of RMHB adsorption onto LBS**



**Table 4.5.1-2 Pseudo first order kinetic study for adsorption of 120.0 mg/L AOP2R on LBS**

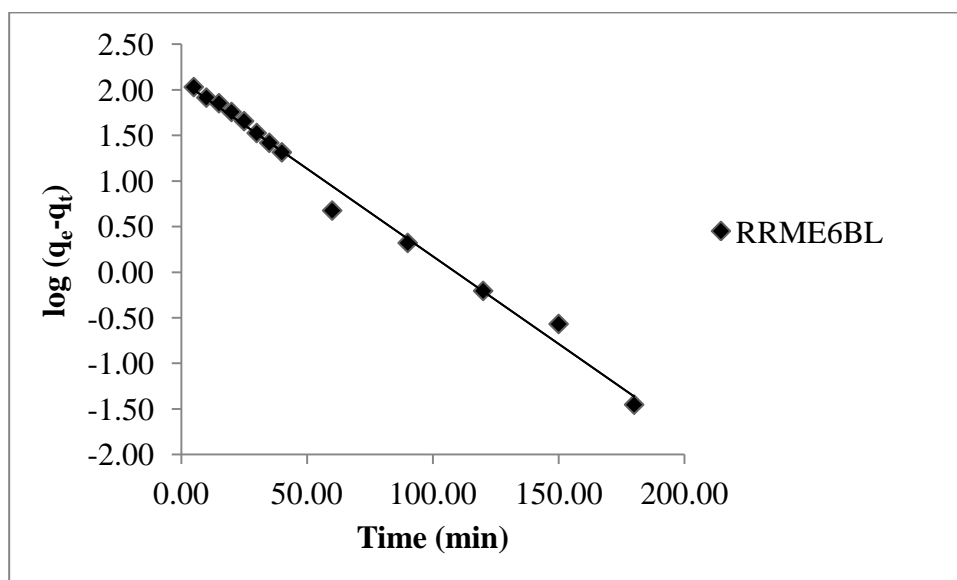
Time (min)	Amount of adsorbed $q_t$ (mg/g)	Equilibrium amount of adsorbed $q_e$ (mg/g)	$t^{1/2}$	$\ln t$	$\log (q_e - q_t)$	$t / q_t$
5.00	8.24	117.50	2.24	1.61	2.04	0.61
10.00	23.33		3.16	2.30	1.97	0.43
15.00	40.59		3.87	2.71	1.89	0.37
20.00	60.20		4.47	3.00	1.76	0.33
25.00	71.96		5.00	3.22	1.66	0.35
30.00	85.69		5.48	3.40	1.50	0.35
35.00	91.96		5.92	3.56	1.41	0.38
40.00	103.33		6.32	3.69	1.15	0.39
60.00	110.20		7.75	4.09	0.86	0.54
90.00	114.51		9.49	4.50	0.48	0.79
120.00	116.86		10.95	4.79	-0.20	1.03
150.00	117.25		12.25	5.01	-0.61	1.28
180.00	117.45		13.42	5.19	-1.31	1.53



**Figure 4.5.1-2 Pseudo-first-order kinetics of AOP2R adsorption onto LBS**

**Table 4.5.1-3 Pseudo first order kinetic study for adsorption of 120.0 mg/L RRME6BL on LBS**

Time (min)	Amount of adsorbed $q_t$ (mg/g)	Equilibrium amount of adsorbed $q_e$ (mg/g)	$t^{1/2}$	$\ln t$	$\log (q_e - q_t)$	$t / q_t$
5.00	9.71	116.80	2.24	1.61	2.03	0.52
10.00	34.71		3.16	2.30	1.91	0.29
15.00	45.59		3.87	2.71	1.85	0.33
20.00	59.71		4.47	3.00	1.76	0.33
25.00	71.47		5.00	3.22	1.66	0.35
30.00	83.24		5.48	3.40	1.53	0.36
35.00	90.59		5.92	3.56	1.42	0.39
40.00	96.18		6.32	3.69	1.31	0.42
60.00	112.06		7.75	4.09	0.68	0.54
90.00	114.71		9.49	4.50	0.32	0.78
120.00	116.18		10.95	4.79	-0.21	1.03
150.00	116.53		12.25	5.01	-0.57	1.29
180.00	116.76		13.42	5.19	-1.45	1.54

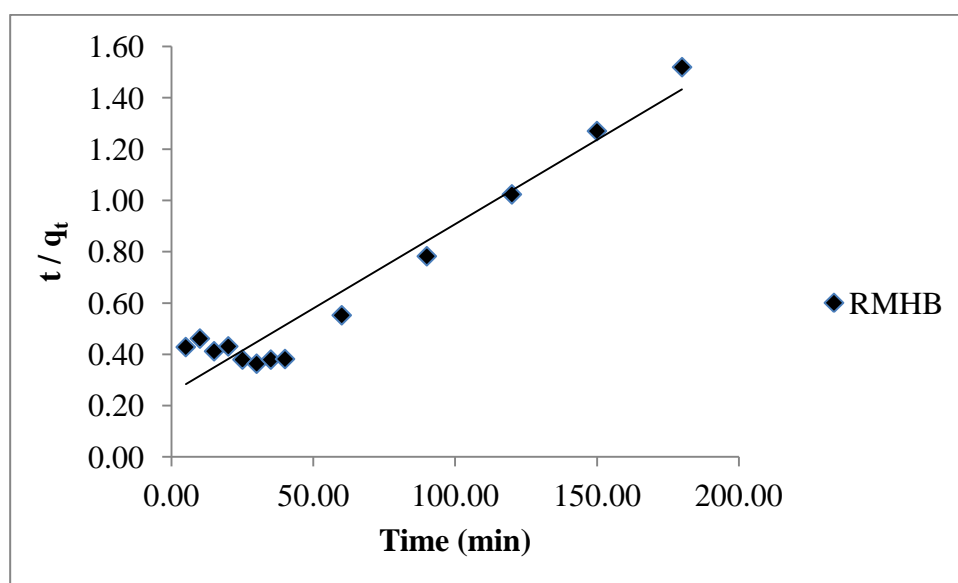


**Figure 4.5.1-3 Pseudo-first-order kinetics of RRME6BL adsorption onto LBS**

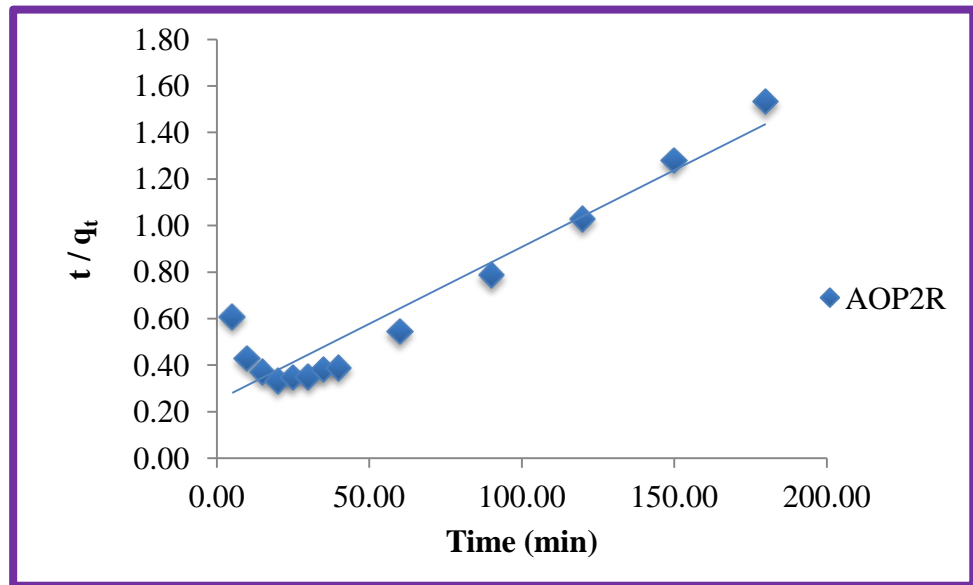
<b>Table 4.5.1-4 Results of first order kinetic parameters for the adsorption of three dyes onto LBS obtained at 120 mg/L concentrations.</b>						
Name of dyes	pH of the solution	R <sup>2</sup>	k <sub>1</sub> (min <sup>-1</sup> )	q <sub>e</sub> (exp.) (mg/g)	q <sub>e</sub> (cal.) (mg/g)	Percentage of deviation of q <sub>e</sub>
RMHB	6.0	0.9896	3.98 × 10 <sup>-2</sup>	118.52	125.52	5.91
AOP2R	2.0	0.9958	4.30 × 10 <sup>-2</sup>	117.50	124.22	5.72
RRME6BL	3.0	0.9907	4.42 × 10 <sup>-2</sup>	116.80	124.02	6.18

#### 4.5.2 The pseudo second-order equation

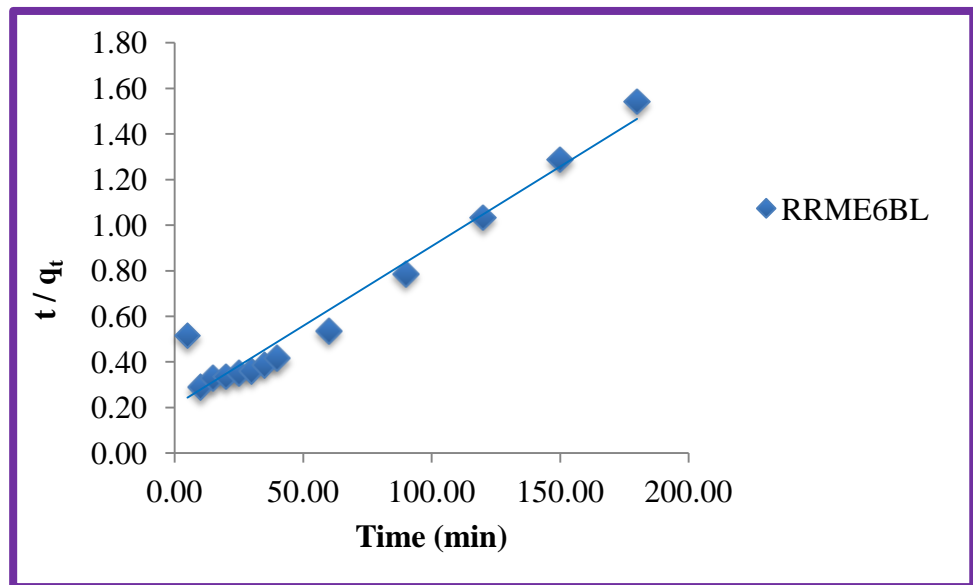
Using (Equation-11), having its linear form, the plot of (t/q<sub>t</sub>) versus t is shown in (Figure 4.5.2-1, Figure 4.5.2-2, and Figure 4.5.2-3). From the linear relationship q<sub>e</sub> and k<sub>2</sub> are determined from the slope and intercept of the plot, respectively.



**Figure 4.5.2-1 Pseudo-second order kinetics of RMHB adsorption onto LBS (adsorbent dose, 164 gm., pH, 6.0, agitation rate, 180 rpm at room temperature)**



**Figure 4.5.2-2 Pseudo-second order kinetics of AOP2R adsorption onto LBS (adsorbent dose, 164 gm., pH, 2.0, agitation rate, 180 rpm at room temperature)**



**Figure 4.5.2-3 Pseudo-second order kinetics of RRME6BL adsorption onto LBS (adsorbent dose, 164 gm., pH, 3.0, agitation rate, 180 rpm at room temperature)**

Name of dyes	pH of the solution	R <sup>2</sup>	Rate constant, k <sub>2</sub> (g / mg min <sup>-1</sup> )	q <sub>e</sub> (exp.) (mg/g)	q <sub>e</sub> (cal.) (mg/g)	Percentage of deviation of q <sub>e</sub>
RMHB	6.0	0.9414	1.75 × 10 <sup>-4</sup>	118.52	152.52	28.69
AOP2R	2.0	0.9025	1.73 × 10 <sup>-4</sup>	117.50	152.52	29.80
RRME6BL	3.0	0.9473	2.33 × 10 <sup>-4</sup>	116.80	142.85	22.30

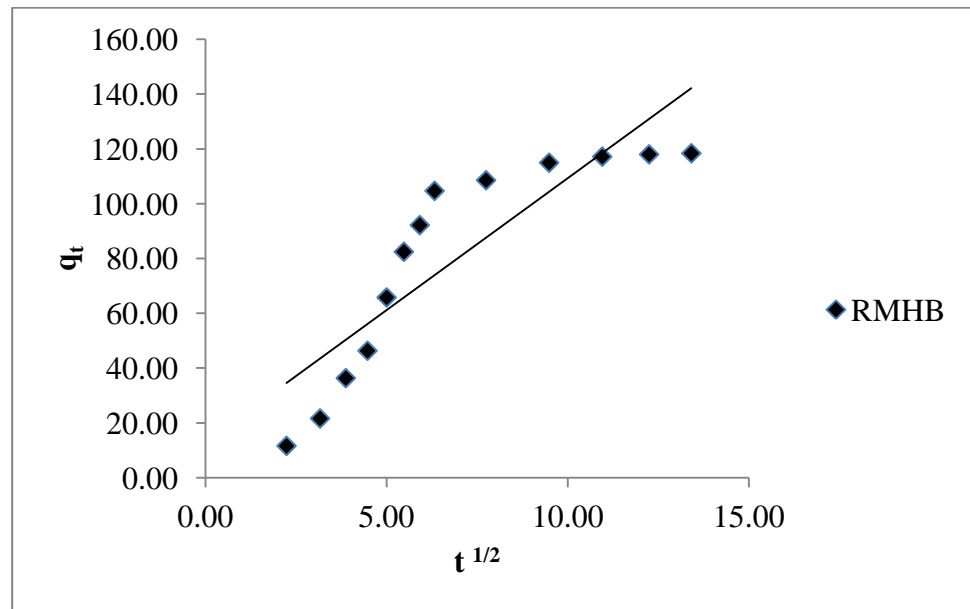
Name of dyes	pH of the solution	Pseudo first order			Pseudo second order		
		R <sup>2</sup>	k <sub>1</sub> (min <sup>-1</sup> )	q <sub>e</sub> (cal.)	R <sup>2</sup>	k <sub>2</sub>	q <sub>e</sub> (cal.)
RMHB	6.0	0.9896	3.98 × 10 <sup>-2</sup>	125.52	0.9414	1.75 × 10 <sup>-4</sup>	152.52
AOP2R	2.0	0.9958	4.30 × 10 <sup>-2</sup>	124.22	0.9025	1.73 × 10 <sup>-4</sup>	152.52
RRME6BL	3.0	0.9907	4.42 × 10 <sup>-2</sup>	124.02	0.9473	2.33 × 10 <sup>-4</sup>	142.85

From the above data analysis it is seen that the plot of pseudo-first order has a high correlation coefficient than the plot of pseudo-second order but it should mention in both cases the value of R<sup>2</sup> is close to the unity. More over the values of q<sub>e</sub> dramatically differ from the experimental values in case of pseudo-second order .It has been reported that if the calculated values of q<sub>e</sub> are not the same as the experimental values, the kinetic of adsorption will not follow this model even if it gives high correlation coefficient. So, the adsorption of tested dyes on LBS is more appropriately followed the pseudo-first order model when compared with that of the pseudo-second order model.

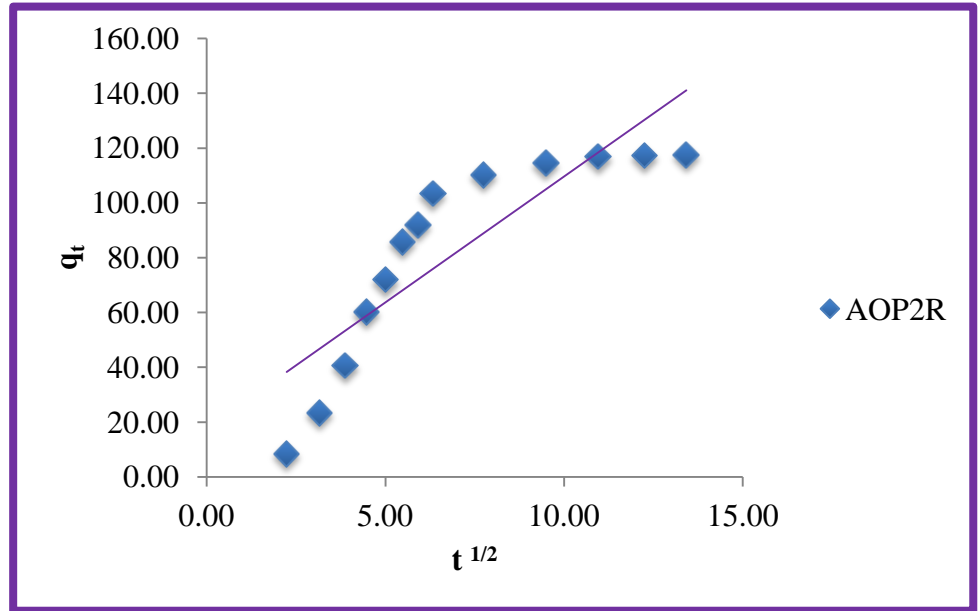
### 4.5.3 Intraparticle diffusion model

Weber and Morris (1963a) proposed the intra-particle diffusion model to explain the transient behavior of dye adsorption. Accordingly, if a plot of dye uptake versus  $t^{1/2}$  is a straight line passing through the origin, then the effect of external film resistance is negligible. On the other hand, if the intercept deviates from the origin, this shows the importance of the external film resistance. The intercept of the plot reflects the boundary layer effect. If the regression of the plot is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step. In the present study, the linear plots did not pass through the origin. This indicates that the intra-particle diffusion was not only a rate controlling step. It may be concluded that surface adsorption and intra-particle diffusion were concurrently operating during the dyes and adsorbent interactions.

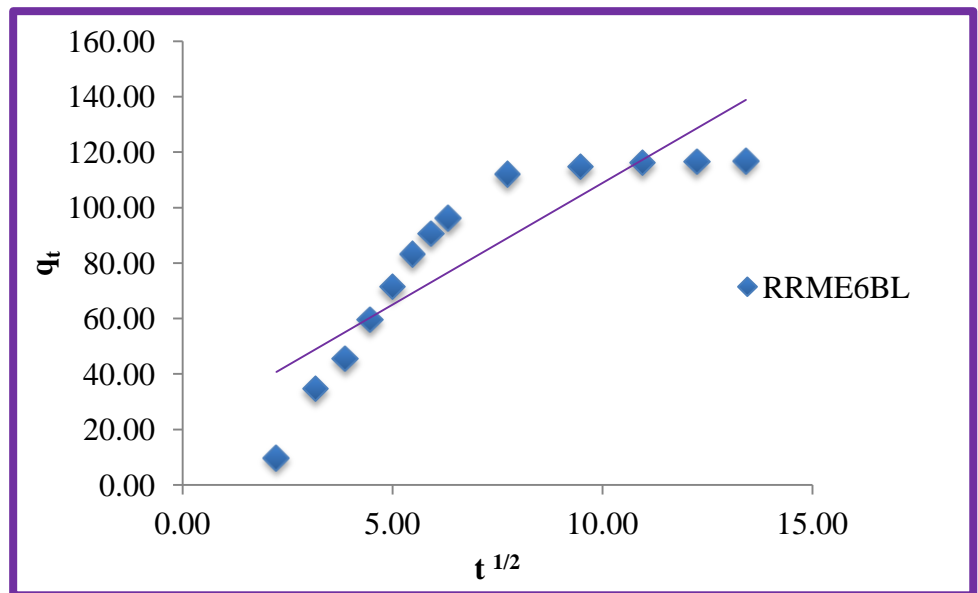
A plot of  $q_t$  versus  $t^{1/2}$  gives a linear relationship (Figure 4.5.3-1, Figure 4.5.3-2 and Figure 4.5.3-3), from which  $k_{id}$  is determined from the slope.



**Figure 4.5.3-1 Intra particle diffusion plot for RMHB adsorption onto LBS (adsorbent dose, 164 gm., pH, 6.0, agitation rate, 180 rpm at room temperature)**



**Figure 4.5.3-2 Intra particle diffusion plot for AOP2R adsorption onto LBS (adsorbent dose, 164 gm., pH, 2.0, agitation rate, 180 rpm at room temperature)**



**Figure 4.5.3-3 Intra particle diffusion plot for RRME6BL adsorption onto LBS (adsorbent dose, 164 gm., pH, 3.0, agitation rate, 180 rpm at room temperature)**

**Table 4.5.3-1 Results of intra-particle diffusion parameters for the adsorption of three dyes onto LBS obtained at 120 mg/L concentrations**

Name of dyes	pH of the solution	R <sup>2</sup>	Rate constant, k <sub>id</sub>
RMHB	6.0	0.7656	9.6153
AOP2R	2.0	0.7447	9.1907
RRME6BL	3.0	0.773	8.7795

From (table 4.5.3-1) it is seen the R<sup>2</sup> value for studied dyes adsorption is very less. At the same time it is also seen that the linear plot did not pass through the origin, indicating that the intra-particle diffusion was not only a rate controlling step.



## Conclusion

Lima bean seed's powder was found to be a good adsorbent for the removal of three reactive dyes, Reactive Magenta HB (RMHB), Active Orange P2R (AOP2R) and Reactive Red ME6BL (RRME6BL) from their aqueous solution. The adsorption process was favored at acidic medium. RMHB, AOP2R and RRME6BL showed highest removal efficiency at pH 6.0, 2.0 and pH 3.0, respectively. Adsorption efficiency is dependent on adsorbent dosage, contact time and initial dye concentration. Adsorption process followed pseudo-first order model. Both Langmuir and Freundlich models were fitted to the adsorption process. Therefore, Lima bean seed's powder can be recommended as bio-adsorbent since it is cheap, easily available and possess high removal capacity of dyes in aqueous system.

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