# Adsorption Properties of Mahogani (*Swietenia Mahogani*) Leaf Powder: Removal of Acid Dyes
# from Aqueous Solution.

By

**(Meghla Akther)**

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



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*Dedicated to*

*To*

*My beloved parents*

**Md.Arshad Ali Joarder**

**&**

**Mrs.Wafia Begum**

## Declaration

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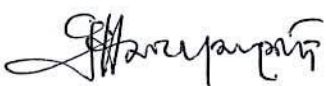

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# ABSTRACT

The Mahogani (*Switenia Mahogani*) leaf treated with sulphuric acid and formaldehyde were used as an adsorbent for the removal of Reactive yellow C8G and Reactive red M5B dye from aqueous solution. The adsorption characteristics of reactive dyes on activated Mahogani leaf powder (MLP) were evaluated as a function of pH, adsorbent dose and initial concentration of adsorbate. The amount of dye adsorbed per unit weight of the adsorbent increased with the increase of concentration and contact time. The adsorption was favored by an acidic pH range for Reactive red but not significant change for reactive yellow dyes. The adsorption processes were best described by a second-order rate equation. Reactive Yellow and Reactive Red dyes adsorption on MLP agreed with both Langmuir and Freundlich isotherms. The isotherm plots showed that the Freundlich equation gave slightly better linearity than the Langmuir equation ($R \sim 0.94$ for Langmuir plots; $R \sim 0.99$ for Freundlich plots) indicating the MLP surface to be heterogeneous in the long range, but having some amount of uniformity locally. Langmuir monolayer adsorption capacity ($q_m$) decreased from 67.11 to 11.93 mg/g for reactive yellow and from 12.39 to 2.09 mg/g for reactive red, MLP amount varying from 0.5 to 1.0 g/L. The adsorption equilibrium parameter, for reactive yellow, $b$, varied from 0.028 to 0.034 L/mg with the increase in MLP amount and similar trend observed for reactive red. The adsorption capacity, $K_f$, showed a decrease from 143.52 to 19.76 L/g with increase in MLP amount from 0.5 to 1.0 g/L. Similar results found for reactive red dye. The adsorption affinity, $n$, lies between 0.21 and 0.27 satisfying the condition $n < 1$ for favorable adsorption.

# Contents

# CHAPTER I

# Introduction

## 1.1    General

Innumerable physical, chemical and biological processes take place at the boundary between two phases, while others are initiated at that interface. The change in concentration of a given substance at the interface as compared with the neighboring phases is referred to as adsorption. Depending on the type of phases in contact, we can consider this process in the following systems: liquid gas, liquid liquid, solid liquid and solid gas.

The major development of adsorption processes on a large, industrial scale deals mainly with the solid gas[1]and solid liquid [2] interfaces, but in various laboratory separation techniques all types of interfaces are applied [3,4] . The term 'fluid' is commonly used to denote gas or liquid in contact with the boundary surface of solids.

A basic concept in adsorption occurring at every interface is the real adsorption system. Let us consider this concept in terms of the solid gas interface. The real adsorption system can be defined as an equilibrium one including the adsorbent being in contact with the bulk phase and the so-called interfacial layer. This layer consists of two regions: the part of gas residing in the force field of the solid surface and the surface layer of the solid. The term 'adsorption' deals with the process in which molecules accumulate in the interfacial layer, but desorption denotes the converse process. Adsorption hysteresis is said to occur when the adsorption and desorption curves deviate from one another. In such a case the isotherm possesses a hysteresis loop, the shape of which varies from one adsorption system to another. Hysteresis loops are mostly with mesoporous solids, where the so-called capillary condensation occurs. The material in the adsorbed state is defined as the 'adsorbate', but that in the bulk gas or vapour phase prior to being adsorbed is called the 'adsorptive'. The penetration by the adsorbate molecules into the bulk solid phase is determined as 'absorption'. The term 'sorption' together

with the terms 'sorbent', 'sorbate' and 'sorptive' is also used to denote both adsorption and absorption, when both occur simultaneously and cannot be distinguished. The fundamental concept in adsorption science is that named as the adsorption isotherm. It is the equilibrium relation between the quantity of the adsorbed material and the pressure or concentration in the bulk fluid phase at constant temperature.

The equilibrium between a bulk phase and the surface layer may be established with regard to neutral or ionic particles. If the adsorption process of one or several ionic species is accompanied by the simultaneous desorption of an equivalent amount of ionic species, this process is considered as an ion exchange.

Adsorption can result either from the universal van der Waals interactions (physical adsorption, physisorption) or it can have the character of a chemical (process chemical adsorption or chemisorption) . Contrary to physisorption, chemisorption occurs only as a monolayer[3]. Physical adsorption can be compared to the condensation process of the adsorptive. As a rule, it is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance.

Physical adsorption is very effective particularly at a temperature close to the critical temperature of a given gas. Chemisorption occurs usually at temperatures much higher than the critical temperature and by contrast to physisorption is a specific process which can only take place on some solid surfaces for a given gas. Under favourable conditions, both processes can occur simultaneously or alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic.

Experimental studies concerning the development in the measurements of gas adsorption isotherms on solid adsorbents and the various experimental techniques have been reviewed and summarized in detail see reviews[5,6] and references there in.

Most of the solid adsorbents of great industrial applications possess a complex porous structure that consists of pores of different sizes and shapes. If the pores are slit shaped we can speak of their 'width' but for the pores with a cylindrical shape the term 'diameter' is frequently used.

In terms of the experience of adsorption science, total porosity is usually classified into three groups. According to the IUPAC recommendation [7], the micropores are defined as pores of a width not exceeding 2 nm, mesopores are pores of a width between 2 and 50 nm, but

macropores represent pores of a width greater than 50 nm. The above classification is widely accepted in the adsorption literature. Nowadays, the expression 'nanopore' is used to encompass both micro- pores and mesopores.

The significance of pores in the adsorption processes largely depends on their sizes. Because sizes of micropores are comparable to those of adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. That is the fundamental difference between adsorption in micropores and larger pores like meso- and macropores. Consequently, the adsorption in micropores is essentially a pore-filling process in which their volume is the main controlling factor. Thus, as the essential parameter characterising micropores is their volume usually referred to a unit mass of the solid and characteristics of their sizes. This characteristic is expressed by the so-called micropore-distribution function evaluated mainly from the low-concentration adsorption data. Determination of microporous adsorbent specific surface area from generally accepted adsorption equations is only of a formal character, and it can often be misleading.

In the case of mesopores whose walls are formed by a great number of adsorbent atoms or molecules, the boundary of interphases has a distinct physical meaning. That means that the adsorbent surface area has also a physical meaning. In macropores the action of adsorption forces does not occur throughout their void volume but at a close distance from their walls. Therefore, the mono- and multilayer adsorption takes place successively on the surface of mesopores, and their final fill proceeds according to the mechanism of capillary adsorbate condensation. Therefore, the basic parameters characterising mesopores are: specific surface area, pore volume and pore-size or pore-volume distribution. Mesopores, like macropores, play also an essential role in the transport of adsorbate molecules inside the micropore volume.

The mechanism of adsorption on the surface of macropores does not differ from that on flat surfaces. The specific surface area of macroporous solids is very small, that is why adsorption on this surface is usually neglected. The capillary adsorbate condensation does not occur in macropores.

As mentioned earlier, a main source of information about adsorption and its mechanism is, besides the calorimetric measurements of adsorption heats, the adsorption isotherm. The fact that the adsorption isotherm is an integral characteristic of a concrete adsorption system is

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rather rarely highlighted in the literature. It means that all information derived from an adsorption isotherm deals only with a concrete adsorbent and adsorbate. By means of various adsorbates and the same adsorbent, we can obtain quite different information. It is inappropriate to consider that some of them are correct, but others are incorrect on condition . that the adsorption isotherm is reliably determined . Both kinds of information are truly valid and suitable characteristics that should be chosen according to what is required to be measured. The foregoing remarks are true regarding all real adsorption systems, but they are especially important in the case of porous adsorbents which are mostly industrial ones and contain a great variety of pores of different sizes belonging to those of a mixed structure.

## 1.2    Colorant

Colorants are characterized by their ability to absorb visible light from 400 to 700 nm, due to this reason that they appear to be coloured. There are two large groups of colorant, which are natural organic and inorganic. Man has used colorants since prehistoric times. However, it was the discovery of mauve by Perkin in 1865, which marked the start of the synthetic dye industry[8].

The most important differentiation of colorant is that colorant is either dyes or pigment. These terms are often used indiscriminately, in particular, pigments are quite often considered to be a group of dyes. Ideal pigments are characterized by being practically insoluble in the media in which they are applied. Pigment particles have to be attached to substrates by additional compounds, for example by a polymer in paint, in a plastic or in a melt. Dyes, on the other hand, are applied to various substrates (textile materials, leather, paper and hair) from a liquid in which they are completely, or at least partly, soluble. In contrast to pigments, dyes must possess a specific affinity to the substrate for which they are used.

## 1.3    Dye

Dye has been used since the prehistoric times. The prehistoric man used to dye furs, textile and other objects with natural substances, mainly vegetable, but also of animal origin. Now a

days, dyes are not only made from the natural sources but also there are synthetic dyes. They are widely used in many industries such as textile, paper, leather and mineral processing industries to colour their product. Dye is a natural or synthetic colouring material, whether soluble or insoluble, which impart its colour to a material by staining or being imbibed by it, and which employed from a solution of fine dispersion, sometimes with aid of mordant.

The scale and growth of the dyes industry has been inextricably linked to that of the textile industry. World textile production has grown steadily to an estimated 35 x 106 tons in 1990 (Hunger, 2003a)[9]. The two most important textile fibers are cotton, the largest, and polyester. Consequently, dye manufactures tend to concentrate their efforts on producing dyes for these two fibers. The estimated world production of dyes in 1990 was 1 x 106 tons. The figure is significantly smaller than that for textile fibers because a little dye goes a long way. For example, 1 ton of dye is sufficient to colour 42,000 suits (Hunger, 2003a)[9].

## 1.4    Classification Systems for Dyes

Dyes can be grouped in accordance with two different principles:

Chemical structure (chemical classification)

Dyeing methods areas of application (colouristic classification)

A review of the whole field of technical dyes shows that the two classifications overlap that there is hardly a chemical class of dye, which occurs solely in one colouristic group, and vice versa.

When classified according to the dyeing method, they may be anionic, direct or disperse dyes, depending on whether they are intended for use on protein, cellulose or polyamide fibers. Moreover, certain reactive dyes with a particular type of chemical structure can be used for several substrates, whilst others with the same type of structure are suitable for only a single substrate.

It is possible to devise a logical method of chemical classification. With some classes of dyes, however, we have abandoned the conventional nomenclature, since it is either wrong (for instance, 'basic' instead of 'cationic' dyes) or insufficiently comprehensive (for example phthalocyanine as a sub group of aza annulene structure). Both classifications are used by the

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Colour Index (1971) which lists all dyes and pigments used commercially for large-scale colouration purposes, that is dyeing of textile fibers, for pigment colouration of plastics, paints, printing inks and for the colouration of liquids (solvent and so on). According to Fu and Viraraghavan (2001)[10] dyes are classified as anionic, cationic and nonionic. Anionic dyes are the direct, acid and reactive dyes. A cationic dye is basic dyes; while a nonionic dye is disperse dyes. Nonionic dyes refer to disperse dyes because they do not ionize in an aqueous medium. The chromophores in anionic and nonionic dyes are mostly azo groups or anthraquinone types. Where, chromophore is the group producing the colour. Table 2.1 summarized the application classes of dyes and their chemical types (Hunger, 2003a)[9].

## 1. 5 Disadvantages of Dyes

Dyes are sometimes being viewed as something other than ordinary chemical. But, actually it is an individual chemical itself like all other chemical such as sodium chloride, acetic acid and benzidine. They are similar in their reactions to some other chemicals, and distinctly different from other. Therefore, there is a possibility that they are toxic. This is because many dyes are made from known carcinogens, such as benzidine and other aromatic compounds (Fu and Viraraghavan, 2001)[10].

It is estimated that over 10,000 different dyes and pigments are used industrially and over 7 x $10^5$ tons of synthetic dyes are annually produced worldwide[11,12,13]. Textile materials can be dyed using batch, continuous or semi-continuous processes. The kind of process used depends on many characteristics including type of material as such fiber, yarn, fabric, fabric construction and garment, as also the generic type of fiber, size of dye lots and quality requirements in the dyed fabric. Among these processes, the batch process is the most common method used to dye textile materials[14].

In the textile industry, up to 200,000 tons of these dyes are lost to effluents every year during the dyeing and finishing operations, due to the inefficiency of the dyeing process[13]. Unfortunately, most of these dyes escape conventional wastewater treatment processes and persist in the environment as a result of their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and perspiration[15]. In

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addition, anti-microbial agents resistant to biological degradation are frequently used in the manufacture of textiles, particularly for natural fibers such as cotton [15,16]. The synthetic origin and complex aromatic structure of these agents make them more recalcitrant to biodegradation [17,18]. However, environmental legislation obliges industries to eliminate color from their dye-containing effluents, before disposal into water bodies[13,16].

The textile industry consumes a substantial amount of water in its manufacturing processes used mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition [19-21]. In addition, the increased demand for textile products and the proportional increase in their production, and the use of synthetic dyes have together contributed to dye wastewater becoming one of the substantial sources of severe pollution problems in current times [14,22].

Textile wastewater is characterized by extreme fluctuations in many parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, color and salinity. The composition of the wastewater will depend on the different organic-based compounds, chemicals and dyes used in the dry and wet-processing steps[22,23]. Recalcitrant organic, colored, toxicant, surfactant and chlorinated compounds and salts are the main pollutants in textile effluents[14]. These days, environmental pollution can undoubtedly be regarded as one of the main problems in developed and developing countries. This is due, not just to one, but to a number of factors, such as the misuse of natural resources, inefficient legislation and a lack of environmental awareness. Fortunately, in recent years there has been a trend for change and a series of scientific studies are being used as an important tool in the development of new treatment technologies and even in the implementation of processes and environmentally friendly actions[24-28].

Every industrial process is characterized by the use of inputs (raw materials, water, energy, etc.) that undergo transformation giving rise to products, byproducts and waste. The wastes produced at all stages of the various types of human activity, both in terms of composition and volume, vary according to the consumption practices and production methods. The main concerns are focused on the impact these can have on human health and the environment.

Hazardous waste, produced mainly by industry, is particularly worrying, because when incorrectly managed, it becomes a serious threat to the environment and therefore to human health. Thus the study of new alternatives for the treatment of different types of industrial effluent continues to be a challenge to combat anthropogenic contamination.

In addition, the effects caused by other pollutants in textile wastewater, and the presence of very small amounts of dyes (<1 mg/L for some dyes) in the water, which are nevertheless highly visible, seriously affects the aesthetic quality and transparency of water bodies such as lakes, rivers and others, leading to damage to the aquatic environment [29,30].

During the dyeing process it has been estimated that the losses of colorants to the environment can reach 10–50% [17,18,21,31,32]. It is noteworthy that some dyes are highly toxic and mutagenic, and also decrease light penetration and photosynthetic activity, causing oxygen deficiency and limiting downstream beneficial uses such as recreation, drinking water and irrigation [17,18,33]. Due to their chemical structure, dyes possess a high potential to resist fading on exposure to light and water. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity, which are not adequately treated in conventional wastewater treatment Plant. Numerous studies have been conducted to assess the harm impacts of colorants on the ecosystem. It was found that colorants may cause problems in water in several ways: (i) dyes can have acute and/or chronic effects on exposed organisms with this depending on the dye concentration and on the exposure time; (ii) dyes are inherently highly visible, minor release of effluent may cause abnormal coloration of surface waters which captures the attention of both the public and the authorities; (iii) the ability of dyes to absorb/reflect sunlight entering the water, this has drastic effects on the growth of bacteria and upsets their biological activity; (iv) dyes have many different and complicated molecular structures and therefore, are difficult to treat and interfere with municipal waste treatment operations; (v) dyes in wastewater undergo chemical and biological changes, consume dissolved oxygen from the stream and destroy aquatic life; (vi) dyes have a tendency to sequester metal ions producing micro toxicity to fish and other organisms.

There are various conventional methods of removing dyes including coagulation and flocculation, oxidation or ozonation and membrane separation. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and electrochemical oxidations, coagulation are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used. The most common adsorbent materials are: alumina silica, metal hydroxides and activated carbon. As proved by many researchers, removal of dyes by activated carbon is economically favorable and technically easier. However, the technology for manufacturing good quality activated carbon is still very cost-prohibitive and the regeneration or disposal of the spent carbon is often problematic. This has prompted the use of various materials as adsorbents in order to develop cheaper alternatives by utilizing agricultural and other wastes. The leaf of Mahogani trees which were activated with sulfuric acid and used as low cost easily available and renewable adsorbent for the removal of dyes from aqueous solution. The variable parameters such as pH, adsorbent dose, and initial concentration of adsorbate have been checked.

# CHAPTER II

## Literature Review

### 2.1    General

Adsorption is not necessarily a physical phenomenon always. It may as well be a chemical process involving chemical interaction between the surface atoms of the adsorbent & the atoms of the adsorbate. This type of adsorption is known as chemisorption. For example, oxygen is chemisorbed by carbon & hydrogen is chemisorbed by nickel under suitable conditions. In conventional waste water treatment methods, it is not possible to remove all the soluble compounds from the raw wastewater. Use of granular activated carbon for the adsorption of organic materials from water & wastewater has been introduced as a reliable & economical non-biological or physio-chemical process. Adsorbents are available as irregular granules, extruded pellets and formed pellets. The size reflect the need to pack as much surface area as possible into a given volume of bed and at the same time minimize pressure drop for flow through the bed.

The adsorbent must have following features;

•It should have large surface area.

•The area should be accessible through pore enough to admit the molecule to be adsorbed. It is a bonus if the pores are also small enough to exclude molecules which it is not desired to adsorb.

•It should be easily regenerated

•The adsorbent should not age rapidly, that it loses its adsorptive capacity through continuous recycling.

The adsorption process is one of the effective methods for removal dyes from the waste effluent.

The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. Adsorption is effectively in removing trace components

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from a liquid phase and may be used either to recover the components or simply to remove noxious substance from industrial waste. Any potential application of adsorption has to be considered along with alternatives such as distillation, absorption and liquid extraction. Each separation process exploits a difference between properties of substance to separate. In distillation the property applied is volatility, in absorption it is solubility, in extraction it is distribution coefficient. Separation by adsorption depends on one component being more readily adsorbed than other. The selection of a suitable process depends upon the ease with which the separated components are removed.

## 2.2 Natural adsorbents used for color removal

### 2.1.1 Clay

Clay are natural adsorbent classified based on their difference in layered structure. The available classes of clay materials include smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite[34]. The process by which adsorption takes place is as a result of net negative charge on the structure of minerals, and it's this negative charge that gives the clay mineral the capability to adsorb positively charged species. Most of Their sorption properties depends their high surface area and high porosity[35]

### 2.1.2 Siliceous materials

Natural Siliceous materials are one of the most availability and low price adsorbent. It includes silica beads, perlite and dolomite, alunite and glasses. The use of these minerals was based on chemical reactivity of their hydrophilic surface and mechanically stable, which results from the presence of silanol groups. But among all this, silica beads is given particular attention in the use of the material as adsorbent [36-38]. However, Ahmed [39] reports that, a major problem with this kind of application is their low resistance toward alkaline solutions their usage is limited to media of pH less than 8.

### 2.1.3 Zeolites

Zeolites occur naturally as porous alumino silicates consisting of different cavity structures and are linked together by shared oxygen atoms[40]. Zeolite has a wide variety of species. More

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than 40 natural species are available which includes clinoptilolite and chabazite. But, clinoptilolite, a mineral of the heulandite group is the most and frequently studied material, due to its have high selectivity for certain pollut ants. Intensive research has been done on the use and application of zeolite as adsorbent in removing trace quantities of pollutants such as heavy metal ions and phenols with regards to their cage-like structures suitable for ion exchange [41-43]

## 2.3    Color removal using activated carbons from solid waste

Activated carbons are derived from natural material s such as wood, lignite or coal, which are commercially available. But almost any carbonaceous material may be used as pre cursor for the preparation of carbon adsorbents [44-46]. Coal is the most commonly used precursor for AC production Because of its availability and cost effective [47,48]. Coal comprises of different mixtures of carbonaceous materials and mineral matter, which results from the degradation of plants. The nature,origin and the extent of the physical–chemical changes occurring after deposition of vegetation, determines the sorption properties of each individual coal. In a research conducted by Karaka et al [49] attention has been drawn on the use of coal as a successful sorbents for dye removal. Additionally, coal is not a pure material, and thus will have different sorption properties due to its large variety of surface properties. Recently there has been report on the use of activated carbon in the treatment of dye and heavy effluents. Material such as peanut shell[50], bael shell carbon[51], raw pine and acid-treated pine cone powder[52], Calotrop is procera [53], Neem Leaf [54], Coconut Shell [55], Super paramagnetic PVA-Alginate Microspheres [57] were able to reduce the concentration of pollutants in wastewater successfully. Their sorption capacity increases with increasing in adsorbent dosage.

## 2.4    Agricultural waste materials used as low cost adsorbent

The use of biomass (dead or living), fungi, algae and other microbial cultures in the removal of methylene blue was the subject of many recent researches. Biological materials used to accumulate and concentrate dyes from aqueous solution are termed as bioadsorbents. Major disadvantage in these biomaterials is its non-selective (i.e. it cannot isolate each pollutant and get it removed independently of one another) all the target and non-target contaminants if

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present are concentrated on the surface of the adsorbent. Unlike the conventional ion exchange the process are selective to the ions it needs to adsorb by selecting the ion in such a way that it is having affinity only that ion. Bioadsorption is a novel approach, and considered to be relatively superior to other techniques because of its low cost, simplicity of design high efficiency, availability and ability to separate wide. Recent literature on the methods of removal of dye from wastewater focuses on MB adsorption. Adsorption capacities of different biosorbent for the removal of MB from wastewater; the excellent ability and economic promise of adsorbents prepared from biomass exhibited high sorption properties from selected literatures in the last one decade are summarized in the tables below. With the recent development on the use of low cost adsorbent, this review has made tremendous effort to cover a wide range of current researches on nonconventional adsorbents in order to enlighten researchers on the adsorption capacities of different biological material used in recent times as shown from the tables above. In all the studies compiled, it was observed that Equilibrium isotherms and kinetic studies were all determined as observed. Different adsorption isotherm models ranging from Lagmuir, Freundlich, BET, Temkin and Redlich- Peterson were used during to analyzed the fitness. Furthermore, based on the knowledge acquired so far, the process of studies on biosorption should further be widen in the light of regeneration of bioadsorbents and recovery. Directional modeling, and disposal of the waste material in order to achieve high efficiency. Moreover, it is also observed that most of the studies were reported in batch process, and as such this will provide a room for continuous flow systems design with viable industrial applications, which can be more economical and efficient at commercial level.

## 2.5    Low cost alternative adsorbents

Activated carbon has been found to be a versatile adsorbent, which can remove diverse types of pollutants such as metal ions, dyes, phenols and a number of other organic and inorganic compounds and bio-organisms. However, its use is sometimes restricted due to higher cost. Due to the higher cost of activated carbon, attempts are being made to regenerate the spent activated carbon. Chemical as well as thermal regeneration methods are used for this purpose. However, these procedures are not very cheap and also produce additional effluents and result

in considerable loss of the adsorbent. Therefore, in situations where cost factors play a major role, scientists are looking for low cost adsorbents for control of water pollution. As such, for quite sometime, efforts have been directed towards developing low cost alternative adsorbents. A wide variety of materials have been investigated for this purpose and they can be classified into three categories: (i) natural materials (ii) agricultural wastes and (iii) industrial wastes. These materials are generally available free of cost or cost little as compared to activated carbons. Various naturally occurring materials having characteristics of an adsorbent are available in large quantities. The abundance of these materials in most Agricultural wastes as adsorbents The disposal of waste materials is increasingly becoming a cause for concern because these wastes represent unused resources. A large amount of solid wastes are produced in the agricultural sector in most countries of the world. A major part of this waste is normally used as a domestic fuel. However, for better utilization of this cheap and abundant agricultural waste, it can be explored as a low cost alternative adsorbent owing to relatively high fixed carbon content and presence of porous structure. Rengaraj et al.[57] developed activated carbon from rubber seed coat for removal of phenols using batch and column operations. Chamarthy et al [58] prepared an adsorbent from peanut shell by heat treatment in presence of phosphoric acid or citric acid and used it for the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II). Their investigations showed that phosphoric acid modified shells adsorbed metal ions in larger amounts Bagasse pith is a waste product produced from sugar refining industry. It is the name given to the residual cane pulp remaining after sugar has been extracted. Bagasse pith is composed largely of cellulose, pentosan and lignin [59].The research was carried out on adsorption of dyes, Astrazone blue, Maxillon red and Telon blue using bagasse pith [60]. Based on cost analysis, they showedthat the bagasse pith is economically attractive than commercially available activated carbon.

The sewage treatment plant biosolids (sludge) was used as adsorbent in removing basic dyes, Basic blue 3, Basic red 22 and Basic black 9 from aqueous solutions[61]. The magnetically modified *Saccharomyces cerevisiae* subsp. *uvarum* cells was studied as adsorbent in removing water soluble dyes, Aniline blue, Congo red, Crystal violet, Naphthol blue black and Safranine – O from aqueous solutions [62]. The results revealed that the maximum adsorption capacity of the magnetic cells differed substantially for individual dyes; the highest value was found for aniline blue, 220 mg/g. The dyes removal by activated carbon prepared from cassava (*Manihot*

*esculenta*) peel was studied[63]. Cassava peel is an agricultural waste from the food processing industry. Activated carbons prepared from waste cassava peel employing physical and chemical methods were tested for their efficiency in the removal of dyes and metal ions from aqueous solution. They have reported that the material impregnated with $H_3PO_4$ showed higher efficiency than the heat treated materials while both of these were efficient as adsorbents for dyes and metal ions. The removal of a basic dye, Rhodamine – B, by using tapioca peel activated carbon as an adsorbent was also studied . The soil was used as adsorbent for removal of dyes, Methylene blue, Malachite green and Rhodamine – B from aqueous solutions.

The jack fruit peel activated carbon was used as adsorbent in removing a basic dye, Rhodamine – B from aqueous solution [64]. The jack fruit peel activated carbon was also used as adsorbent in removing a dye, Malachite green, from aqueous solution [65]. The removal of acid dyes by using groundnut shell powder activated by zinc chloride solution was studied as an adsorbent [66]. The results revealed that the maximum adsorption capacity was found to be 55.5 mg/g of the adsorbent for 100 ppm initial concentration of dye solution.

The neem leaf powder was used to remove three water soluble dyes, viz., brilliant green, congo red and methylene blue from aqueous medium [67]. The removal of acid red 183 from aqueous solution was studied by activated carbon, raw kaolinite and montmorillonite using an agitated batch adsorber [68]. Rice bran based activated carbon and guava seeds activated carbon, followed by pyrolysis were also used as adsorbents to remove dyes from aqueous solutions [69,70].

As proved by many researchers, it has prompted the use of various materials as adsorbents in order to develop cheaper alternatives by utilizing agricultural and other wastes. The Mahogani tree of family of *Swietenia Mahogani* is found all over of Bangladesh and its woods have been used for varieties of furniture. The Mahogani tree defoliates its leaf naturally during January - February each year. In the present work, Mahogani leaf powder (MLP) used as an adsorbent for removal of acid dyes from aqueous solution as a model system.

# CHAPTER III

## Experimental Section

### 3.1 Preparation of Adsorbent

The mature mahogani (*Switenia Mahogani*) leaves used in the present investigation were collected from the trees in the area of Khulna University of Engineering and Technology. The leaves were washed twice with water to remove dust and water soluble impurities and were dried until the leaves become crisp. The dried leaves were grinded into powder and were boiled in distilled water to remove lignin and colouring components about one hour and filtered. The residue left was treated with formaldehyde and finally with very dilute solution of sulphuric acid, stirred for 30 minutes vigorously using magnetic stirrer at room temperature, it was filtered and washed with distilled water repeatedly to remove free acid. After chemical treatment residue were dried first in air and finally in oven at 105°C for 24 hours.



**Figure 3.1** Electric oven.

**Figure 3.2** MLP Powder used as absorbent.

The homogeneous powder was then passed through mesh for desired particle size. The adsorbent once prepared were used throughout the experimental work.

## 3.2 Preparation of Adsorbate Solution

The Reactive Yellow C8G and Reactive Red M5B dyes were used without further purification. A stock solution of strength 602 mg/L for Reactive Yellow C8G and 606 mg/L for Reactive Red M5B were made by dissolving the appropriate quantity of the substrates in 1 L double distilled water. The pH of the dye solutions for Reactive Yellow C8G and Reactive Red M5B were 4.8 and 4.9 respectively. All other solutions of various concentrations were made from this solution.

## 3.3 Batch Adsorption Experiments

The adsorption experiments were done in a batch process. The batch experiments were carried out in 250 mL stopper plastic bottle by mixing a pre-weighed amount of activated powder and 50 mL of aqueous dye solution of fixed concentration. The bottles were then kept in shaker (Gemmy orbit shaker, VRN-480) at constant oscillation of 180 osc/min. The samples were agitated for a predetermined time interval. The parameters such as pH, time of contact, adsorbent amount and dye concentration were varied during different sets of batch

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experiments. The pH was maintained at different values either by addition of a few drops of dilute hydrochloric acid or sodium hydroxide.



**Figure 3.3** Helios Gamma Spectrophotometer, UVG-152411.

After adsorption, the mixtures were allowed to settle, and portions of supernatant liquids were centrifuged. The supernatant solutions were analyzed using a UV-Visible spectrometry (Helios Gamma Spectrophotometer, UVG-152411) by monitoring the absorbance changes at a wavelength of maximum absorbance 420 nm for Reactive Yellow C8G and 548 nm for Reactive Red M5B



**Figure 3.4** Gemmy orbit shaker, VRN-480.

### 3.4 Adsorption Isotherm Studies

The adsorption data for a wide range of adsorbate concentration and adsorbent doses were analyzed using Langmuir and Freundlich isotherm in order to find the adsorption capacity of dye adsorbate.

### 3.5 Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, and (in environmental SEM) in wet conditions.

The most common mode of detection is by secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons is a function of the angle between the surface and the beam. On a flat surface, the plume of secondary electrons is mostly contained by the sample, but on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the tilt of the surface is created.

The types of signals produced by a SEM include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence) (CL), specimen current and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown above. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a

powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays, because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen. BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.



**Figure 3.5** Scanning Electron Microscopy (SEM) analyzer.

## 3.5 Glassware and Apparatus

All glass wares (Conical flasks, Measuring cylinders, Beakers, Petri plates and Test tubes etc.) used are of Borosil/Rankem. The instruments and apparatus used throughout the experiment are
listed below:

    i)    Electronic weight balance

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ii) pH meter

iii) Helios Gamma Spectrophotometer, UVG-152411

iv) Gemmy orbit shaker, VRN-480

v) Electric oven

vi) Others glassware



**Figure 3.6** Before adsorption of Reactive Red M5B.



**Figure 3.7** After adsorption of Reactive Red M5B.

# CHAPTER IV

## Results and Discussion

### 4.1 Effect ofpH

It was observed that $\lambda_{max}$ for bothdyes changed very little in the studied pH range 2.0-10.0.In the present study the effect of pH on the amount of dye removal was analyzed over thesaid pH range.

### 4.1.1 Effect of pH on Reactive RedM5B

The initial pH value of the solution can significantly influence the adsorption of dyes. In thepresent study the effect of pH on the amount of dye removal was analyzed over the pH range from 2.0 to10.0 and is presented in graphical form as given inFigure 4-1. The adsorption at lower pH may be attributed to the increase in the concentration of hydrogen ion in dye solution which neutralizes hydroxyl group in the vicinity of adsorbent surface and facilitates the diffusion of dye molecule towards the surface of adsorbent. Similar diminishing adsorption was also reported by Bahadur et.al[71], at higher pH which may be due to the availability of large number of OH- (hydroxyl ions) and consequently the diffusion barrier is increased which results in poor adsorption. Our findings are in good agreement with Prasad et.al[72-73].

### 4.1.2 Effect of pH on Reactive Yellow C8G

It showed that there is no significant change in the percent of removal of dye over the entire pH range (Figure 4-1). This indicates the strong force of interaction between the dye and MLP that either $H^+$ and OH-ions could not influence the adsorption capacity. In other words, the adsorption of reactive yellow dye on MLP does not involve ion exchange mechanism. If the adsorption would have occurred through ion exchange mechanism there would have been an influence on the dye adsorption while varying with pH.
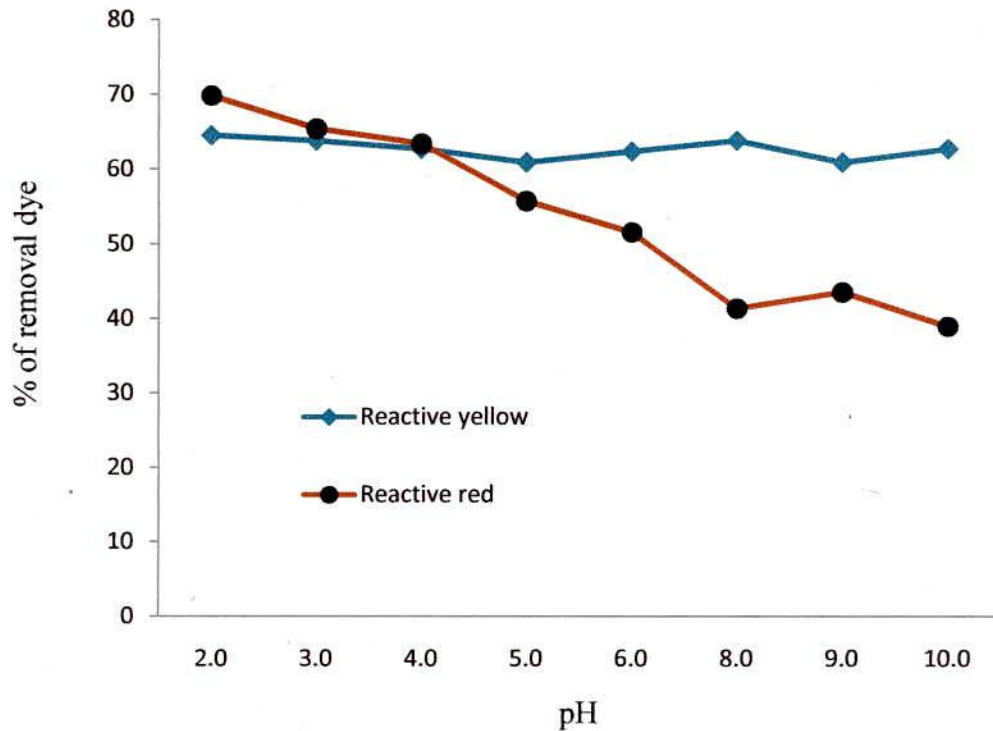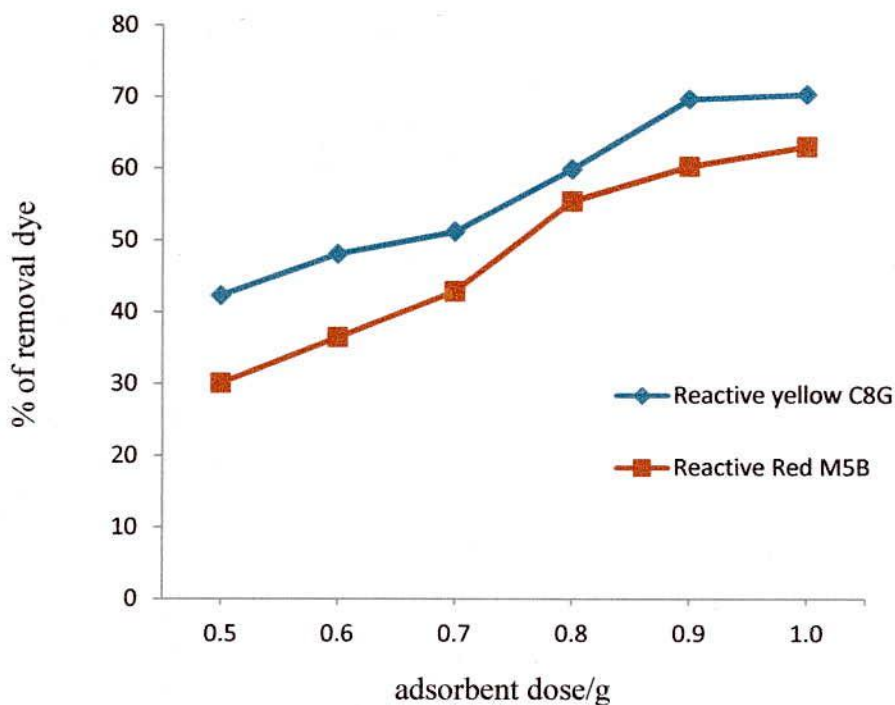
**Figure 4-1**Effect of pH on removal of Reactive yellow and Reactive red dyes.

## 4.2    Effect of Adsorbent Dose

Adsorbent dose is representing of important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of adsorbate. Effects of adsorbent dose on removal of both reactive dyes were monitored by varying adsorbent dose from 0.5g to 1.0 g. The adsorption of dye increased with the adsorbent dosage and reached on equilibrium value after 1.0 g of adsorbent (Figure 4-2). The percentage of dye removal increased with increasing amount of MLP, however the ratio of dye adsorbed to MLP (mg/g) decreased with increasing amount of adsorbent MLP. Similar results were reported by Patilet al.[74]. Many factors can attribute to this adsorbent concentration effects. The most important factor is that adsorption site remains unsaturated during the adsorption reaction. This decrease in adsorption capacity with increase in adsorbent dose is mainly attributed non saturation of the adsorption sites

during the adsorption process[75,76]. Theratio of dye adsorbed to MLP was started to reach equilibrium at 1.0 g adsorbent. When the MLP further increases after 1.0 g there is no significant change in adsorption.



**Figure 4-2** Effect of adsorbent dose on removal of reactive yellow and reactive red dyes.

## 4.3    Effect of Initial Concentration and Contact Time

### 4.3.1    Reactive Yellow C8G:

To determine proper dye adsorption and equilibrium time, initial concentrations of dye solutions were changed and time intervals were evaluateduntil no adsorption of adsorbate onto MLP took place. The adsorption data for the removal of dyeversus contact time at different concentrations were shown in Figure 4-3. This indicates that the capacity of removal of dye increased with increase in dye concentration. This is due to increase in the driving force of the

concentration gradient, as an increase in the initial dye concentration. The surface of MLP may contain a large number of active sites and the dye uptake can be related to the active sites on equilibrium time.
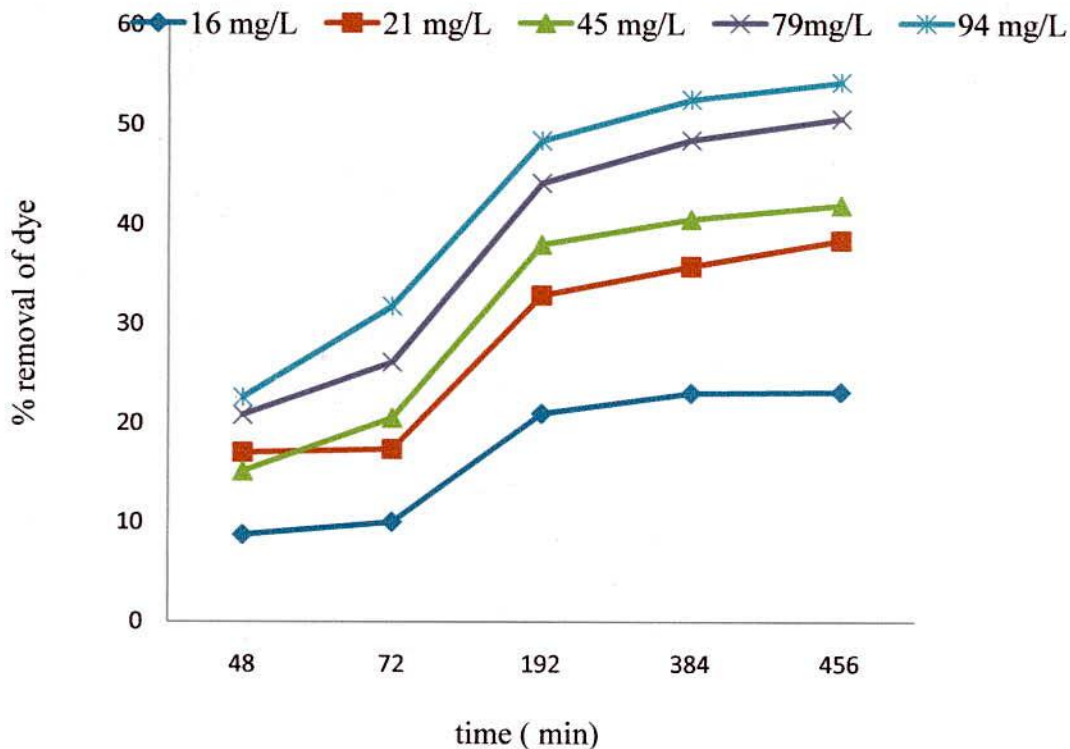


**Figure 4-3** Effectof contact time and initial concentrations on the adsorption of reactive yellow C8G dyeonto MLP.

The higher sorption rate at the initial period may be due to an increased number of vacant sites available at the initial stage, as a result thereare increased concentration gradients between adsorbate in solution and adsorbatein adsorbent surface. Theseincreased concentration gradients tend to increase in dye sorption at the initial stages. As time precedes this concentration is reduced due to the accumulation of dye particles in the vacant sites leading to a decrease in the sorption rate.

**4.3.2 Reactive Red M5B:**Similar result was found for reactive red M5B dyes. Dye concentration is little bit higher than the reactive yellow C8G but trend of capacity is almost same as Reactive yellow. It was shown in Figure 4-4.
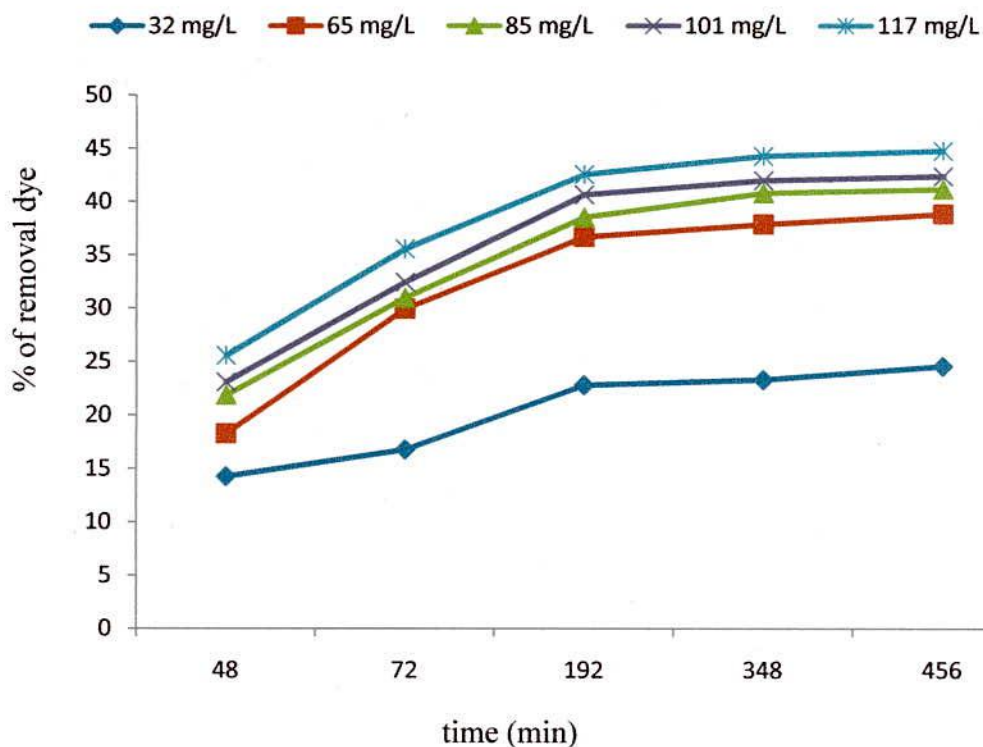


**Figure 4-4**Effect of contact time and initial concentrations on the adsorption of reactive red M5B dyeonto MLP.

## 4.4    Morphological Studies

The surface studies of adsorbent were also done before and after adsorption by taking images through scanning electron microscope (SEM) shown in Figure 4-5. It was showed the surface of adsorbent which was unsaturated before adsorption (a) and saturated after adsorption (b).
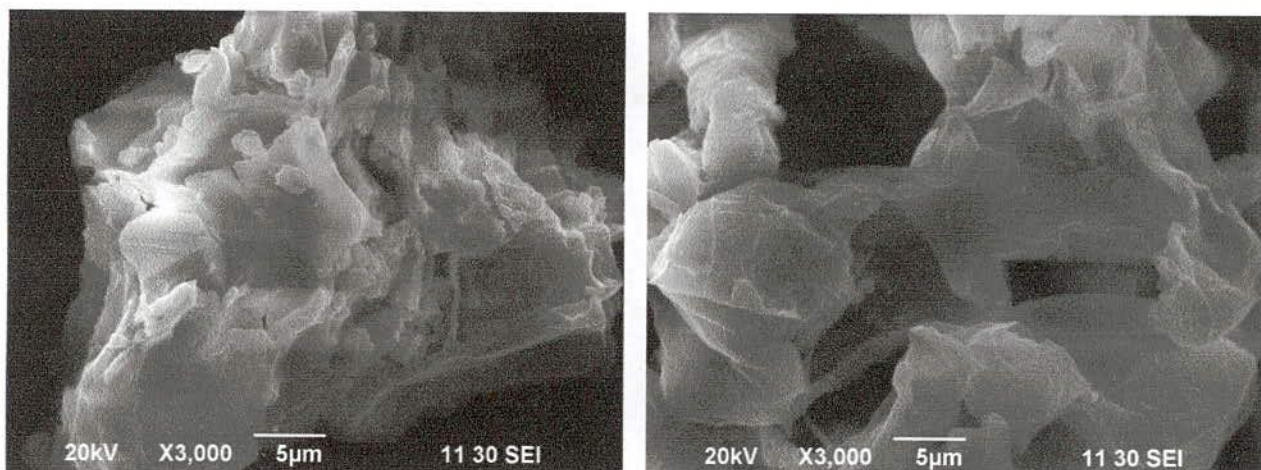
(a)                                                          (b)

**Figure 4-5  a**: SEM of adsorbent before adsorption; **b**: SEM of adsorbent after adsorption in Reactive Yellow C8G.

## 4.5    Kinetic Study

The study of adsorption kinetics is significant as it provides valuable insight into the reaction pathways and into the mechanism of the reactions. Any adsorption process isnormally controlled by three diffusion steps: (i) transport of the solute from bulk solution to the film surrounding the adsorbent,(ii) transport of the solute from the film to the adsorbent surface, and (iii) transport of the solute from the surface to the internal sites followed by binding of the adsorbate molecules to the active sites. The slowest of these steps determines the overall rate of the adsorption process and usually step (ii) leads to adsorption on the exterior surface and step (iii) leads to intraparticle diffusion resulting in adsorption on interior sites. It is generally acknowledged that the dominant rate-controlling step is not the actual physical attachment of adsorbate to adsorbent but rather intraparticle transport of the solute within the porous structure of the adsorbent. Interparticle transport from bulk fluid to the external surface of the porous adsorbent may alsohavean effect
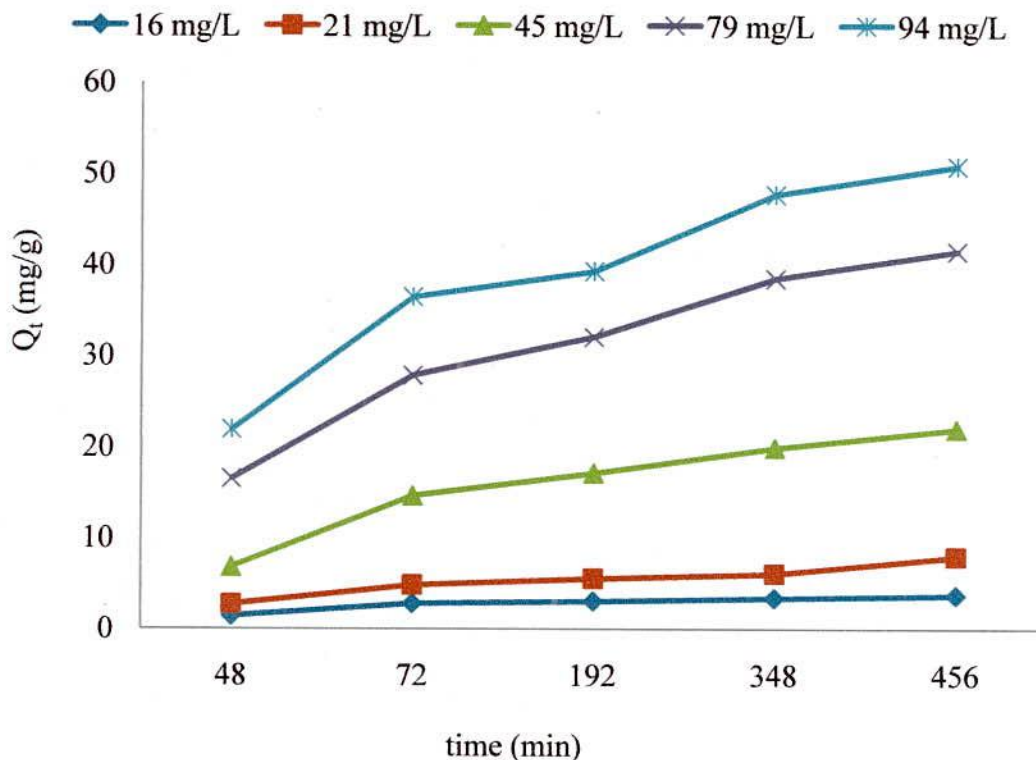
**Figure 4-6** Variation of the amount of Reactive Yellow C8G adsorbed per unit mass of MLP.

on the overall rate of adsorption under some circumstances. A series of experiments with different interaction times were carried out with a constant amount of MLP and different concentrations of bothdyes solution. Figure 4-6 and Figure 4-7 shows that the time necessary for Reactive yellow and Reactive red dyes respectively to reach saturation on the MLP surface was over 450 min. Around 10 to 60.0% of the dye was removed at the equilibrium time. The distribution of dyes in the liquid-solid interface at equilibrium is important to establish the adsorption capacity of MLP for the dyestuff[70]. Themoderate equilibrium time of 450 min and a medium percentage removal indicates that MLP possessed a normal degree of affinity fordyesReactive yellow and Reactive red.
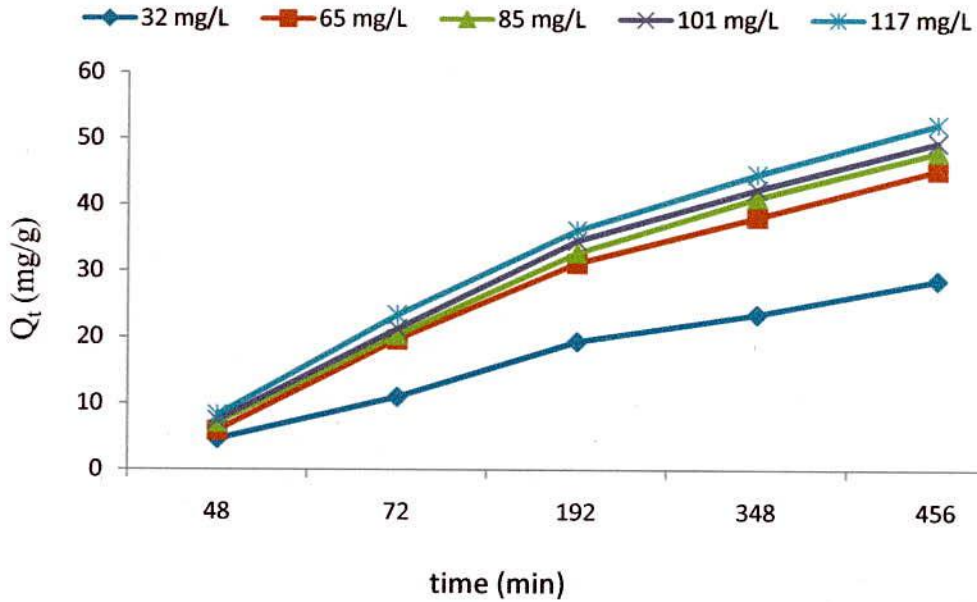
**Figure 4-7** Variation of the amount of Reactive Red M5B adsorbed per unit mass of MLP.

The equilibrium time also depends on other factors such as the molecular weight and the structural complexity of the dye molecules. Desai et al.[78] have shown in their study of adsorption of acid dyes by neutral alumina that complex molecular structures adsorb less and take more time to attain equilibrium.In other words, the equilibrium adsorption and desorption kinetics is dependent upon the molecular dimensions of the dyes. The kinetics of both Reactive yellowand reactive red dyes adsorption on MLP is verified with respect to the pseudo-first-order rate equation of Lagergren:

$$\log(q_e\text{-}q_t) = (k_1/2.303)t + \log q_e \qquad (1)$$

where$q_t$and $q_e$ are the amounts adsorbed per unit mass at time $t$ and equilibrium time, and $k_1$ is the first-order rate coefficient. Plot of $\log(q_e\text{-} q_t)$ vs$t$, which should ideally give a straight line is used to obtain $k_1$. The first order kinetics is considered to be valid when comparable values of $q_e$from the intercept of the Lagergren plot[79]and from experiments are obtained. The Lagergren plots for reactive yellow and reactive red are depicted in Figure 4-8 and Figure 4-9 respectively.
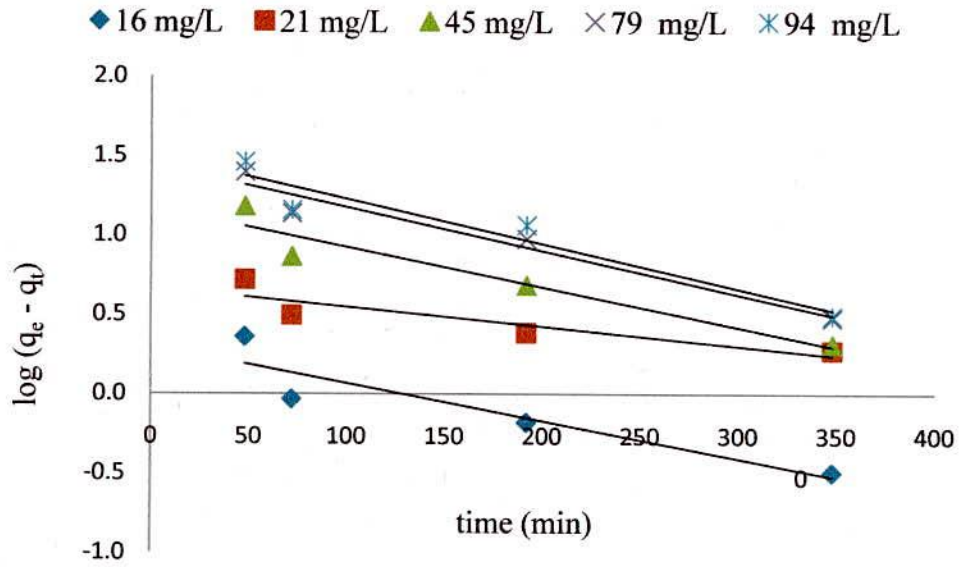
**Figure 4-8** Pseudo-first-order kinetic plots for adsorption of reactive yellow C8G on MLP at different concentration of the aqueous dye solution.
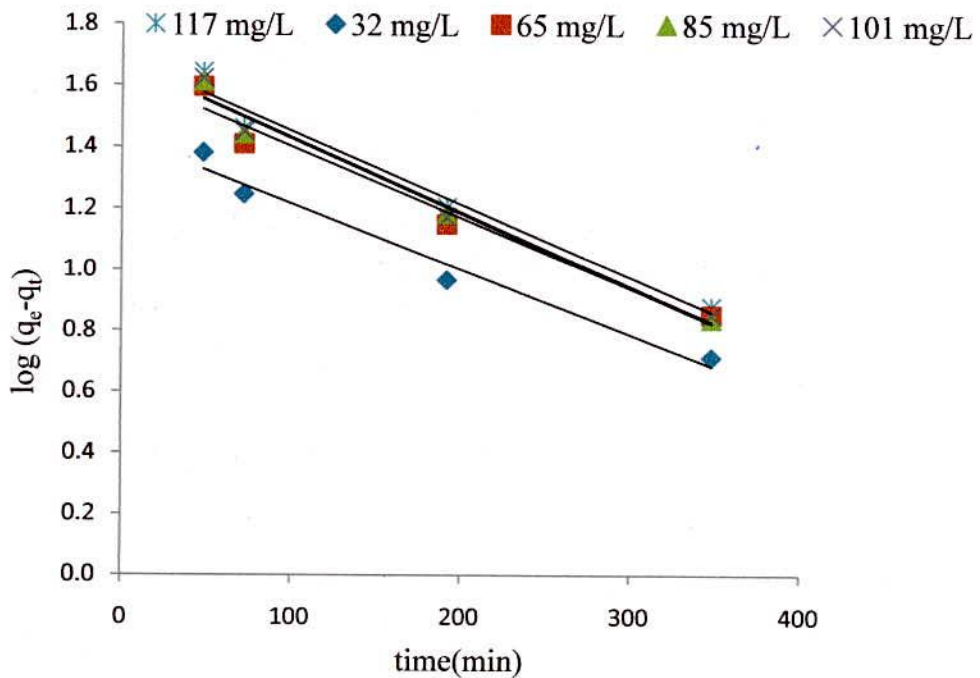


**Figure 4-9** Pseudo-first-order kinetic plots for adsorption of reactive red M5B on MLP at different concentration of the aqueous dye solution.

If the two do not match, it is necessary to test the validity of the second-order kinetics given by the equation[80]

$$t/q_t = 1/q_e t + k_2 q_e^2 (2)$$

which again should yield straight line plot for $t/q_t$vs$t$, allowing computation of $q_e$ and $k_2$. The test of validity could be administered by comparing the experimental $q_e$value with that obtained from the second-order plots. The second-order kinetic plots $t/q_t$vs$t$for a constant amount of MLP (1 g/L) and different dye concentrations of Reactive yellow and reactive red are shown in Figures 4-10 and 4-11respectively. The values are obtained from first order kinetic and second order kinetic for reactive yellow and reactive red are summarized in Table 4-1 to Table 4-4.



**Figure4-10** Second-order kinetic plots for adsorption of reactive yellow C8G on MLP at different concentration of the aqueous dye solution.
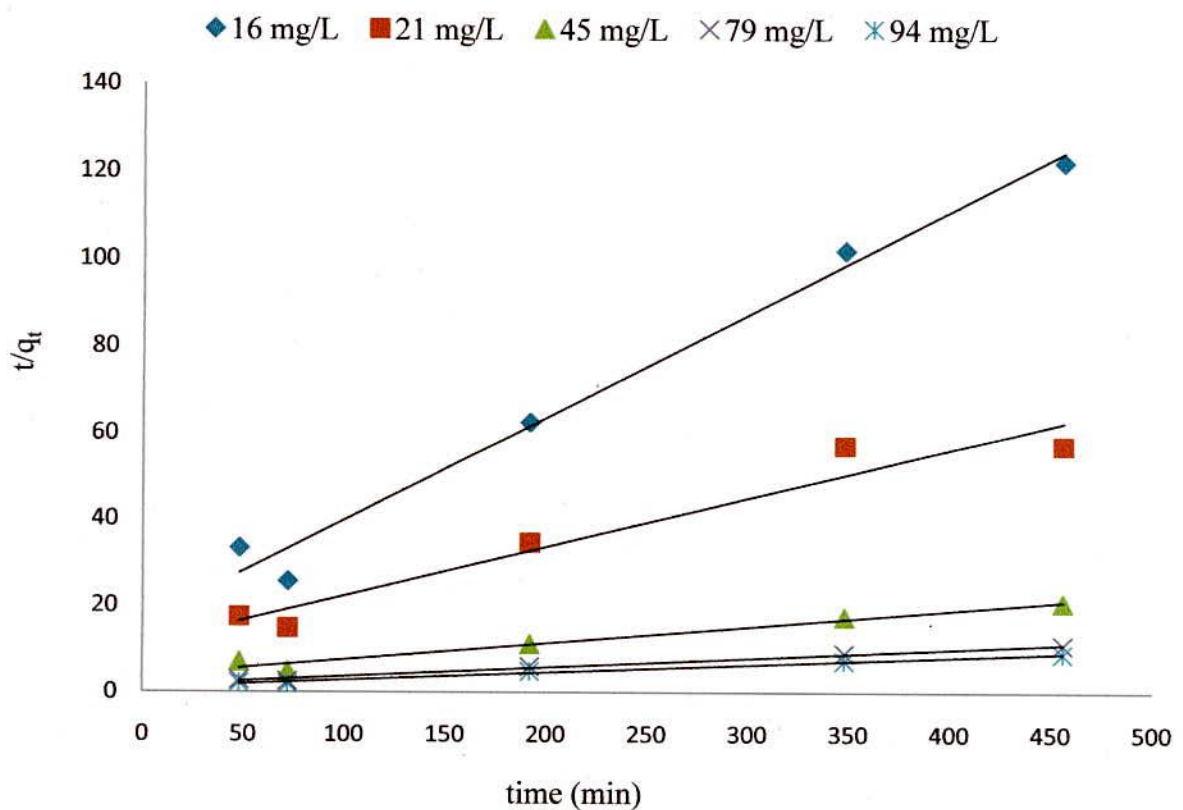
31
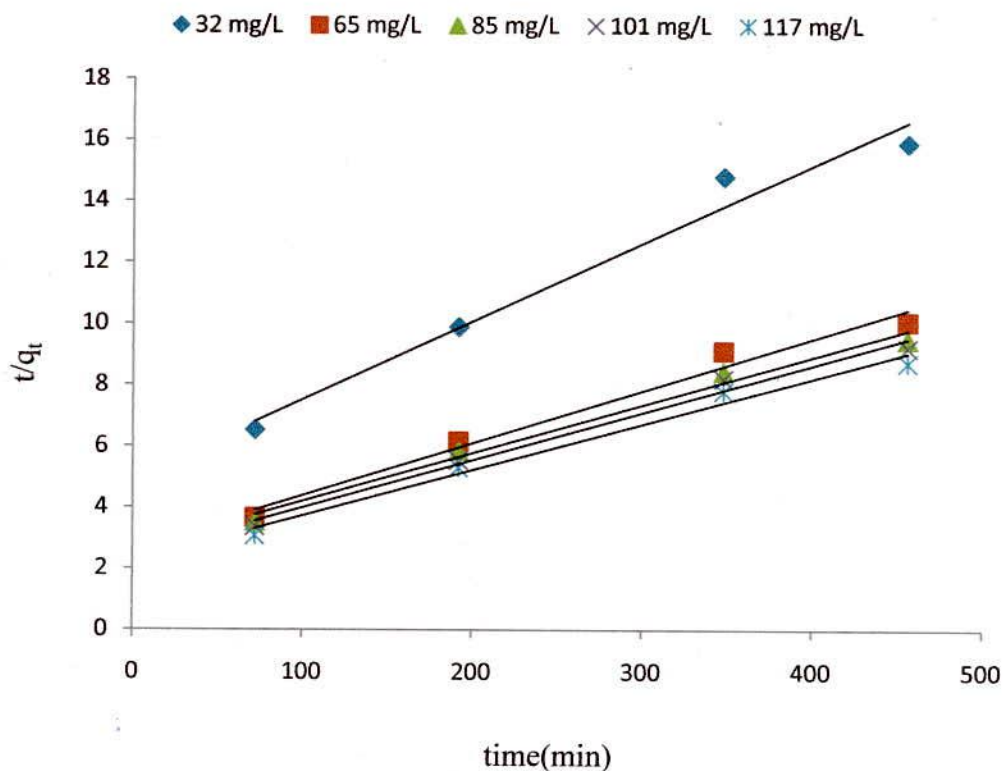
**Figure4-11** Second-order kinetic plots for adsorption of reactive red on MLP at different concentration of the aqueous dye solution.

**Table 4-1** Differences between Experimental $q_e$ and those obtained from the plots of first-order and second-order kinetics for adsorption of reactive yellow C8G on MLP

| dye mg/L | $q_e$ (exp) mg/L | first-order plots $q_e$(cal) mg/L | second-order plots $q_e$ (cal) mg/L |
|---|---|---|---|
| 16 | 3.736104 | 2.022 | 4.21763 |
| 21 | 7.983838 | 4.69 | 8.857396 |
| 45 | 21.97685 | 15.02 | 26.5252 |
| 79 | 41.49965 | 28.11 | 47.84689 |
| 94 | 50.84727 | 32.32 | 57.47126 |

**Table 4-2** Diffusion Rate Coefficients for Adsorption of Reactive yellow C8Gon MLP for Different Concentrations of the Dye Solutions

| dye mg/L | $k_1$ min$^{-1}$ | $R$ | $k_2$ g/mg/min | $R$ |
|---|---|---|---|---|
| 16 | $5.5 \times 10^{-3}$ | 0.845 | $9.1 \times 10^{-1}$ | 0.985 |
| 21 | $2.8 \times 10^{-3}$ | 0.791 | $1.4 \times 10^{-1}$ | 0.942 |
| 45 | $5.8 \times 10^{-3}$ | 0.916 | $5.4 \times 10^{-3}$ | 0.972 |
| 79 | $6.2 \times 10^{-3}$ | 0.949 | $7.1 \times 10^{-4}$ | 0.990 |
| 94 | $6.4 \times 10^{-3}$ | 0.918 | $3.6 \times 10^{-4}$ | 0.989 |

**Table 4-3** Differences between Experimental qe and those obtained from the plots of first-order and second-order kinetics for adsorption of reactive red M5B on MLP

| dye mg/L | $q_e$ (exp) mg/L | first-order plots $q_e$ (cal) mg/L | second-order plots $q_e$ (cal) mg/L |
|---|---|---|---|
| 32 | 28.66799 | 44.41 | 39.21569 |
| 65 | 45.31565 | 85.66 | 58.82353 |
| 85 | 48.04903 | 83.52 | 63.69427 |
| 101 | 49.46585 | 77.71 | 64.51613 |
| 117 | 52.24049 | 85.66 | 67.11409 |

However, it was seen that the experimentally obtained $q_e$ values did not match those determined from the pseudo first-order Lagergren plots in case of both dyes. Therefore, the validity of pseudo-first-order model of kinetics of adsorption of reactive red on MLP was not good and could not be established with certainty. The second-order rate coefficients had widely different values but the experimental and theoretical $q_e$ values now match each other

with small deviations for both dyes. It is therefore more likely that the adsorption of Reactive yellow and Reactive red dyes on MLP might take place through a second-order mechanism. Earlier also it has been shown by Allen et al.[81] that the adsorption kinetics of the acid dyes are described by a pseudo second-order chemical reaction and that this reaction is significant in the rate-controlling step.

**Table 4-4** Diffusion Rate Coefficients for Adsorption of Reactive Red M5B on MLP for Different Concentrations of the Dye Solutions

| Dye mg/L | $k_1$ min$^{-1}$ | $R$ | $k_2$ g/mg/min | $R$ |
|----------|------------------|-------|----------------|-------|
| 32 | $5.2 \times 10^{-1}$ | 0.981 | $3.2 \times 10^{-3}$ | 0.974 |
| 65 | $5.8 \times 10^{-1}$ | 0.984 | $7.7 \times 10^{-4}$ | 0.980 |
| 85 | $5.9 \times 10^{-1}$ | 0.983 | $6.5 \times 10^{-4}$ | 0.985 |
| 101 | $5.7 \times 10^{-1}$ | 0.990 | $5.8 \times 10^{-4}$ | 0.987 |
| 117 | $5.8 \times 10^{-1}$ | 0.984 | $4.9 \times 10^{-4}$ | 0.983 |

## 4.6    Adsorption Isotherms

The Langmuir isotherm equation

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad ------- (3)$$

describes the relationship between $C_e$, the liquid phase concentration of the dye, and $q_e$, the solid phase concentration of the dye (i.e., the amount adsorbed per unit mass), both at equilibrium. The Langmuir coefficient, $q_m$, is defined as the amount adsorbed to form a monolayer on unit mass of the adsorbent (monolayer capacity) and $b$ is the other Langmuir coefficient related to the adsorbate-adsorbent equilibrium. A plot of $C_e/q_e$ vs $C_e$ gives a straight line with $1/q_m$ as the slope and $1/q_m b$ as the intercept from which both the Langmuir

coefficients can be found. Another coefficient, $R_L$, known as the separation factor such that $0 < R_L < 1$ for favorable adsorption, is found from the expression, $R_L = 1/(1+bC_e)$
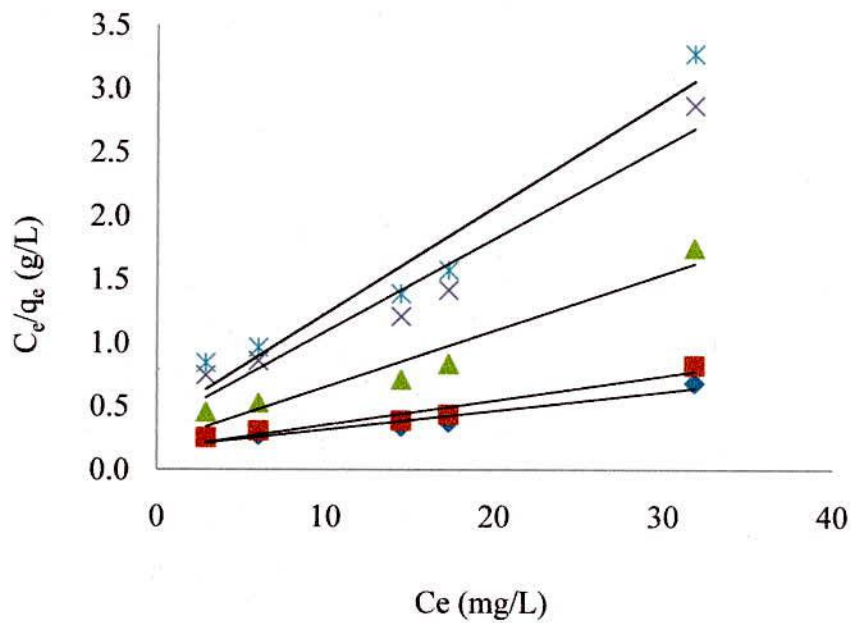


**Figure 4-12** Langmuir isotherm for reactive yellow C8G adsorption onto MLP
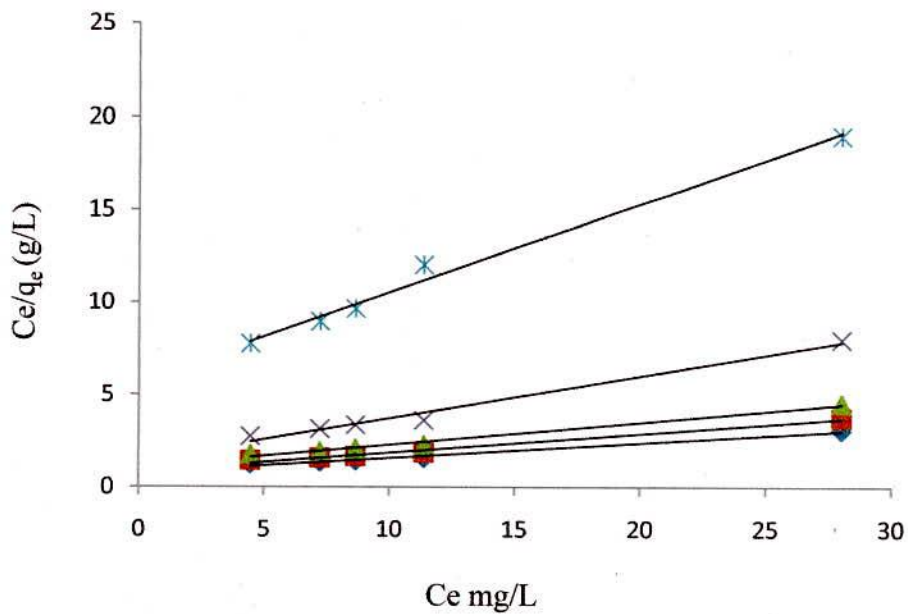


**Figure 4-13** Langmuir isotherm for reactive red adsorption onto MLP.

**Table 4-5** LangmuirIsotherm for Reactive Yellow

| $q_m$(mg/g) | 67.11 | 51.81 | 22.57 | 13.66 | 11.93 |
|---|---|---|---|---|---|
| b(L/mg) | 0.034 | 0.031 | 0.0283 | 0.028 | 0.028 |
| R | 0.943 | 0.946 | 0.934 | 0.948 | 0.934 |
| $R_L$ | 0.908 | 0.840 | 0.708 | 0.670 | 0.525 |

**Table 4-6** LangmuirIsotherm for Reactive Red

| $q_m$(mg/g) | 12.39 | 9.85 | 8.25 | 4.37 | 2.09 |
|---|---|---|---|---|---|
| b(L/mg) | 16.10 | 11.59 | 7.64 | 3.92 | 3.62 |
| R | 0.990 | 0.984 | 0.990 | 0.990 | 0.990 |
| $R_L$ | 0.089 | 0.021 | 0.014 | 0.05 | 0.013 |

The empirical isotherm equation given by Freundlich and useful in describing nonspecific adsorption is

$$log q_e = \log K_f + n\, log C_e -------- (4)$$

where$q_e$ and $C_e$ have similar meaning as earlier with $K_f$ and $n$ being the Freundlich coefficients. When eq.4 is obeyed, the plot of log $q_e$vs log $C_e$ yields a straight line and both the Freundlichcoefficients could be obtained from the slope and the intercept of the plot. Reactive yellow and reactive red adsorption on MLP followed both Langmuir isotherm (Figure 4-12 and Figure 4-13) and Freundlich isotherm (Figure 4-14 and Figure 4-15) respectively. The Langmuir plots *for* Reactive yellowhave good linearity, R 0.93 to 0.95, and the Langmuirmonolayer adsorption capacity ($q_m$) decreased from 67.11 to11.93 mg/g for MLP

amount varying from 0.5 to 1.0 g/L, whereas for Reactive red have also have good linearity, $R \sim 0.99$ , and the Langmuir
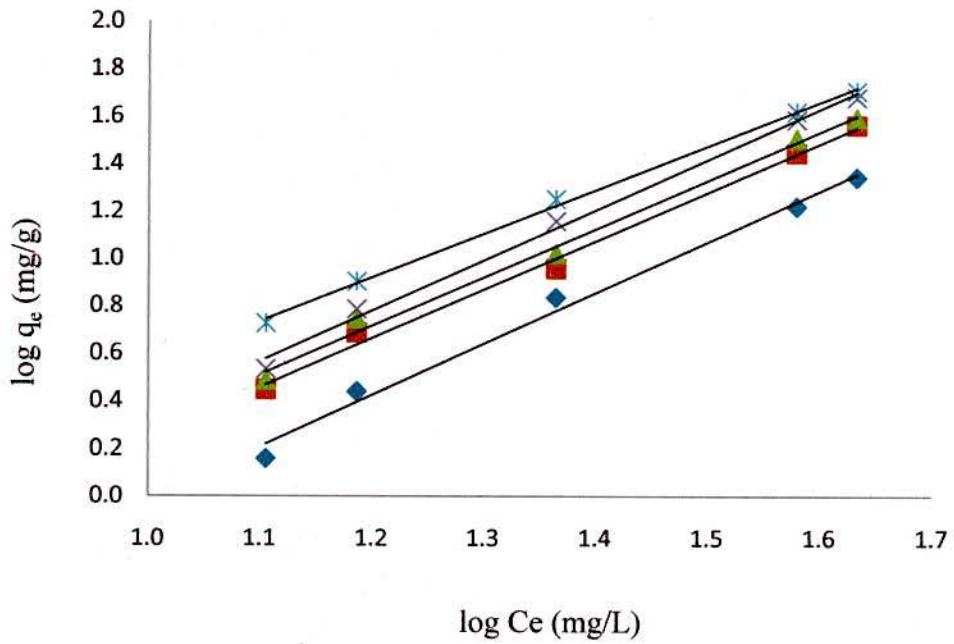


**Figure 4-14** Freundlichisotherm for reactive yellow adsorption onto MLP.
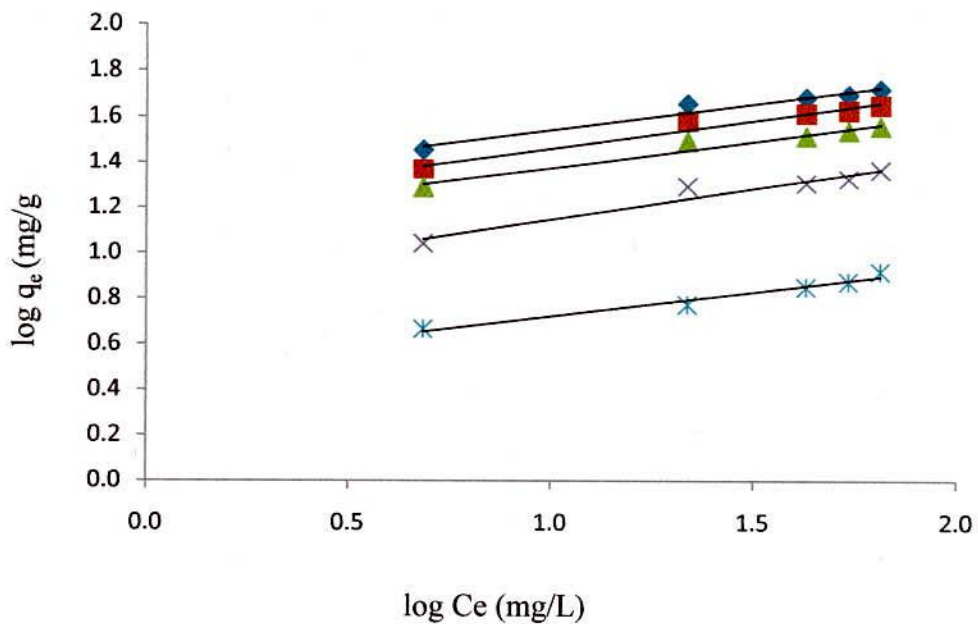


**Figure 4-15**Freundlichisotherm for reactive red adsorption onto MLP.

monolayer adsorption capacity ($q_m$) decreased from 12.39 to2.09 mg/g for MLP amount varying from 0.5 to 1.0 g/L . The adsorption equilibrium parameter, for Reactive yellow,$b$, varied from 0.028 to 0.034 L/mg with the increase in MLP amount and similar trend observed for reactive red. The results are summarized in Table 5 and Table 6. In order to predictwhether the adsorption process by MLP is favorable or unfavorable for the Langmuir type adsorption process, the isotherm shape can be classified by a term "$R_L$", a dimensionless constant separation factor.[28,41,42] The dimensionless parameter, $R_L$, had values in the range of 0.53 - 0.90 for reactive yellow and 0.08 -0.013 for reactive red, consistent with therequirement for a favorable adsorption process defined by $0 < R_L < 1$.

The Freundlich plots have slightly better linearity, $R \sim 0.99$ for Reactive yellow . The adsorption capacity, $K_f$, showed a decrease from 143.52 to 19.76 L/g with increase in MLP amount from 0.5 to 1.0 g/L. Similar results found for Reactive red dye. The adsorption affinity, $n$, lies between 0.21 and 0.27 satisfying the condition $n < 1$ for favorable adsorption. The valuesof the coefficients are shown in Table 4-7 and Table 4-8.

**Table4-7**Freundlich Isotherm for Reactive Yellow

| $n$ | 2.15 | 2.05 | 2.04 | 2.12 | 1.84 |
|---|---|---|---|---|---|
| $K_f$ (L/g) | 143.52 | 63.04 | 55.11 | 59.18 | 19.76 |
| $R$ | 0.998 | 0.995 | 0.998 | 0.994 | 0.99 |

**Table4-8**Freundlich Isotherm for Reactive Red

| $n$ | 0.21 | 0.27 | 0.23 | 0.24 | 0.22 |
|---|---|---|---|---|---|
| $K_f$ (L/g) | 3.23 | 7.48 | 13.88 | 16.6 | 20.8 |
| $R$ | 0.958 | 0.963 | 0.96 | 0.944 | 0.971 |

It is to be noted that the applicability of Langmuir equationis limited to the formation of a chemisorbed monolayer on ahomogeneous surface of identical sites that are equally availableand energetically equivalent such that each site carries equal number of molecules, which do not interact with one another[82] (no adsorbate-adsorbate interactions). On the other hand, the Freundlich equation describes adsorption (possibly multilayer in nature) on a highly heterogeneous surface consisting of non-identical and energetically nonuniform sites. In the present work, although both the equations are obeyed, the Freundlich isotherms have a slightly better correlation coefficient indicating that the MLP surface is heterogeneous in the long-range, but may have short-range uniformity.

# CHAPTER V

## Conclusion

It is found from this study that the powder made from mature, dried leaves of the tree Mahogani *(SwiteniaMahogani)* could be a usefulbiosorbent for removal of dyes from aqueous medium. The results indicate the following:

(i) Biosorption of the dye was favored in acidic pH range. Still, removal of up to 60 % of the dye could be achieved of the aqueous dye solution.

(ii) Adsorption of the dye reached equilibrium at 450 min. Second-order kinetics was found to be most suitable in describing the biosorption. Intraparticle diffusion and liquid film diffusion might have some influence in controlling the biosorption process.

iii) The second-order rate coefficients had widely different values but the experimental and theoretical $q_e$ values now match each other with small deviations for both dyes. It is therefore more likely that the adsorption of Reactive yellow and Reactive red dyes on MLP might take place through a second-order mechanism.

(iv) Reactive Yellow and Reactive Red dyes adsorption on MLP agreed with both Langmuir and Freundlich isotherms. The isotherm plots showed that the Freundlich equation gave slightly better linearity than the Langmuir equation ($R$ ) ~0.94 for Langmuir plots; 0.99 for Freundlich plots) indicating the MLP surface to be heterogeneous in the long range, but having some amount of uniformity locally. Langmuir monolayer adsorption capacity ($q_m$) decreased from 67.11 to11.93 mg/g for reactive yellow and from 12.39 to2.09 mg/g for reactive red, MLP amount varying from 0.5 to 1.0 g/L.The adsorption equilibrium parameter, for reactive yellow, $b$, varied from 0.028 to 0.034 L/mg with the increase in MLP amount and similar trend observed for reactive red.The adsorption capacity, $K_f$, showed a decrease from 143.52 to 19.76 L/g with increase in MLP amount from 0.5 to 1.0 g/L.  Similar results found

for reactive red dye. The adsorption affinity, $n$, lies between 0.21 and 0.27 satisfying the condition $n < 1$ for favorable adsorption.

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