Development of Dyes Removal Method From Textile Waste Water

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Dedication

To my husband and children for their patience and prayers.

Declaration

Experimental work described in this thesis was carried out by the author of this thesis in the Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh. This work has not been presented, and will not be presented, for any other degree.

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Abstract

Discharge of colored effluents without discoloration originated from textile industries may cause serious problems in the receiving environments. In this study, natural materials that are saw dust, coconut coir and jute stick powder were used as adsorbents to remove various dyestuffs used in the textile industry. These materials are cheap and available in large quantities in Bangladesh. The objective of the present study is to investigate the adsorption of reactive, direct and disperse dyes on these adsorbents. But my main concern is the reactive dyes, which I have studied details.

During preliminary experiments it was seen that adsorption equilibrium was reached in about 24 hours. In adsorption experiments, in order to obtain adsorption isotherms, a fixed amount of adsorbent and 50 mL dye solutions of different concentrations were placed in glass bottles which were shaken at 120 rpm at 25±2^{o}C for 24 hours. Then, samples were filtered and the equilibrium concentrations of dyestuffs in the solutions were determined by using spectrophotometer at appropriate wavelength corresponding to the maximum absorbence. After equilibrium concentrations of the solutions were obtained, Langmuir and Freundlich adsorption isotherm constants, kinetic constants were calculated for the adsorbents used in this study. The removal efficiencies for anionic dyes (reactive, direct) are higher than those for disperse dyes with the natural materials. Removal efficiencies of natural materials were very poor (40-50%). Therefore, modification of surface properties of natural materials with H_2SO_4 and $ZnCl_2$ or NaCl was considered to increase the removal efficiencies of anionic dyes. After modification of the surface properties, adsorption capacities of adsorbents were higher than those of natural materials (85-96%).

Finally, the adsorption capacity of treated adsorbents for the different dyes was determined to compare removal efficiency of dyes towards modified materials. The results showed that the adsorption of dyes on adsorbents used in this study fitted nicely the Langmuir Isotherm and Freundlich Isotherm Equations. Pseudo-second order equation was found to be in good agreement with those of experimental values.

Keywords: Adsorption, Saw dust, Coir, Jute stick, Freundlich Isotherm, Langmuir Isotherm

Chapter - 1

General Introduction

1.1. General Background

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[1]. 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 introduce textile industry. Man had been using various means to decorate the clothes such as fabrication, printing, dyeing, pasting etc. About a century ago, colouring matter had been nature in general and vegetation in particular[2, 3]. At present new developments of synthetic dyeing greatly welcome by all textile industry. A simple dye is a water soluble chromogen (coloured compound) that can be firmly fixed to the fabrics by physical and chemical bonding. Colour playing a dominant role in the life of a man from time immemorial, but natural colour does not exists for long time, for this man try to retain the preferable colour for long period. Today colouring mater is industrially producing synthetic dyes and pigments. Dyes exhibit considerable structural diversity and are classified in several ways[4]. These can be classified both by their chemical structure and their application to the fiber type[5] such as Reactive dyes, Direct dyes, Azo dyes, Mordent dyes, Vat dyes, Hasne yellow, etc.[6, 7].

Textile industries are the major consumers of water and they release a fair amount of dyes and other impurities. Waste water is the flow of used water from a community. The characteristics of the waste water discharges vary from location to location depending upon the population density and industrial sector working in the area, land use pattern, ground water level[8]. Textile industry is one of the most important industries in Bangladesh. The water consumption in textile industry, especially in dyeing and washing processes, is too high. Therefore, large amount of wastewater is produced and discharged to the receiving environment during textile production process[9]. We know that much of 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[10]. Approximately, 10,000 different dyes and pigments are used industrially, and over $7x10^5$ 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%[11]. During dying process, a substantial amount of azo dye is lost in wastewater. Sen et al.[12] 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[13] and discharge of these dyes in the environment poses serious ecological concern[13, 14]. A common example of an azo dye is Reactive Red 22 also known as Remazol Red (RR) that has been taken in this study.

Major classes of synthetic dyes include azo, anthraquinon and triaryl-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, pollution by dye's wastewater is becoming increasingly alarming. Human eyes can clearly detect a concentration of 0.005mg/L of reactive dyes in water[15]. 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[16, 17]. 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[18]. 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[19, 20]. 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. 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[21].

Waste water containing dyes represents massive water pollution which is harmful for mankind and also for fish, aquatic plants[17, 22]. 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 wastewater generated from textile industries[22].

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 waste water[23, 24]. Adsorption by activated charcoal is the effective and cheap method for removing dyes from waste water[21, 25]. The present communication deals with the preparation of modified saw dust, jute stick powder and coconut coir dust and then applying them for the removal of various dyes.

1.2. Environment and Pollution

The term environment means surroundings. It is considered as a composite term for the conditions in which living beings live. It consists of air, water, soil, food and sunlight, which are the basic needs of all living organism. In other words, environment consists of both biotic and abiotic substances. 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. Based on the medium where the pollution occurs, environmental pollution can be classified as follows:

(a) Air pollution: pollution in the atmosphere

(b) Water pollution: pollution occurs in aquatic medium and

(c) Soil pollution: pollution occurs in lithosphere.

1.3. Pollution in Aquatic Environment

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[26 - 28].

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 break down 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.

1.4. A Growing Textile Economy of Bangladesh

The textile industry has played an important role in Bangladesh's economy for a long time. Currently, the textile industry in Bangladesh accounts for 45 percent of all industrial employment and contributes 5 percent to the total national income. The industry employs nearly 4 million people, mostly women. A huge 78 percent of the country's export earnings come from textiles and apparel, according to the latest figures available. Bangladesh exports its apparel products worth nearly $5 billion per year to the United States, European Union (EU), Canada and other countries of the world. It is the sixth largest apparel supplier to the United States and EU countries.

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. Bangladesh's textile industry can be divided into three main categories: public sector; handloom sector; and the organized private sector. The private sector is the fastest growing sector in the country. The handloom industry provides employment for a large segment of the population of Bangladesh and supplies a large portion of the fabric required by the local market. About 20 percent of existing mills in Bangladesh are large-scale mills, roughly 30 percent are medium-scale mills, and the remaining 50 percent are small-scale mills. The number of spinning mills in the country is increasing day-by-day.

Combined, the textile and apparel sectors consist of 3,600 firms. There is a concentration of manufacturing activity in and around the capital city of Dhaka and a growing garment manufacturing presence in the country's export processing zones. When Bangladesh gained its independence from Pakistan in 1971, the new government nationalized the textile industry. All of the country's textile factories were then organized under the Bangladesh Textile Mills Corp. (BTMC).

At present, there are 21 textile companies under BTMC. They operate 24 spinning facilities with an installed capacity of 490,892 spindles and 1,036 looms. Out of that total, 13 of the companies - which operate 16 plants - utilize 320,228 spindles under the service charge system producing different counts of yarn in the range of 32/1 to 80/1. Another five companies have 128,088 spindles in operation. Other leading textile associations in the country include the BGMEA, Bangladesh Jute Mills Association, and Bangladesh Knitwear Manufacturers and Exporters Association[29, 30].

1.5. Present Scenario of water pollution of Dhaka

Industrial development plays a vital role for development of economic growth in the developing country, like Bangladesh. In Bangladesh most of the industries are located at the bank of river because of suitability of transportation. Dhaka the capital city of Bangladesh, is bounded by five rivers which are polluted for unplanned industrial development. So it is essential to control the industrial river water pollution in the Dhaka and around Dhaka city, which include Narayangonj, Gazipur, and Savar etc. The water resource of Bangladesh becomes a major health hazard due to inadequate solid waste and industrial effluent management. The present environmental condition of Bangladesh is not at all equilibrium. Severe water pollutions are threatening human health, ecosystems and economic growth of Bangladesh. Necessary steps are to be taken to protect the environment for our own existence.

Bangladesh observed industrialization since last one hundred years. The process was in small level but with the change of time, the appearance of industrialization has changed. Garments industries have taken the place of handlooms. Now our country is facing great challenges to protect the environment because of this kind of industrialization. The Industrial belts are being more and more polluted by numerous populations. The main industrial belts of Dhaka and around the Dhaka City are Dhaka, Narayangonj, Gazipur, Savar, and Tongi. Narayangonj is the largest industrial belt of DMDP area. Most of the dyeing industries of Bangladesh are situated here, which causes water pollution[31, 32].

The DMDP area is surrounded by five rivers- Buriganga, Shitalakkhya, Turag, Balu and Dhalesshori. These five rivers are surrounded by several types of industries, which are responsible for polluting water of these rivers. Such water pollution has severe impacts on the usefulness and value of water resources with negative impacts on ecosystem, fisheries, food production, health, social development and economic activities. Polluted water also hampers the aesthetic views of river. The water of Buriganga and Shitalakkhya river is one of the main source of water supply of DWASA[33]. So it is harmful for human health and also other organism, other purpose. Some causes of industrial river pollutions are given below:

- Haphazard growth of industries in Dhaka and around Dhaka city without proper zoning.
- Presence of many unregistered small industries which do not have any treatment plant.
- Lack of effluent treatment system (ETP).
- Lack of economically viable treatment process.
- Lack of personal awareness.

Textile industries are located in large clusters in Dhaka and around Dhaka city. So water pollution from textile sector is a great threat for Bangladesh. Due to lack of resources, low cost technology and awareness, not much is being done to control harmful pollutants or recycle them. Water of these five rivers of Bangladesh is highly polluted and known to contain strong colour, a large amount of suspended solid, a highly fluctuated pH and a high temperature[34]. The effluent runs off the river through the canal and pollutes all surface water. Finally it is the right time for the concerned authority to take necessary action to protect public health as well as the urban environment.

1.6. Present Effluent Treatment Status of Bangladesh

The treatment of textile effluents is now well-established technology and as part of a study on effluent treatment. It’s a method of saving water to reduce the amount of effluent to be treated and the re-cycling of suitably treated effluent should be considered together. For more than 90% of the earth’s population, water is a limited resource with many regions having less than 10 L/day/person available. In contrast, the textile processing industry requires 50-150 L/kg of textile material processed[35, 36].

The Bangladesh Ministry of Environment and Forest (MOEF) enacted an environment protection law in 1995 that demanded that all new textile wet-processing plants must install an effluent treatment plant (ETP). Unsurprisingly, at present ETP in place, in some cases enlarging them, using modern treatment technology but not always anxious to discuss treatment details.

The MOEF in conjunction with stakeholders and regulatory bodies have been implementing the above legal requirements. Across all industries, there are 806 industrial facilities that require an ETP of which 489 (61%) had complied by December 2010. There are 311 textile wet processing plants and although no precise data are available, about 90 of these (29%) have complied. These are mainly large to medium sized enterprises. Many of the small to medium sized enterprises state that they cannot afford the capital expenditure to install ETP while the companies that have installed such plants state that the running cost is the difference between profit and loss, so that such plants may be run spasmodically, if at all. Many companies are more concerned with high running costs than the capital cost. Large international retailers, with 'social and environmental' agendas, insist that treatment should be carried out but are not prepared to give an increase in price. The government stance is that wet-processing suppliers must include the capital and running costs of ETP in the sales price of the product. Pressure is being exerted on the wet-processing units who have not yet complied to install ETP and are currently being fined for non-compliance[37, 38]. With the country infrastructure in Bangladesh, 'in-house' ETP are a logical request for continuing discharge to river courses. Both capital expenditure and operational costs of an ETP adds to the cost of dyeing and it is not unrealistic to anticipate a sales price increase to cover this[39]. Considering the mentioned situation, a low cost effluent treatment method is essential for Bangladesh.

Fig.1.1. Water pollution due to hazardous discharge of industrial effluents.

Every day 25-30kg of dead fish is found floating in the Meghna at Kadamtali of Gajaria upzila in Munshigunj. Farmers blame this to toxic wastes dumped into the river by the textile factories near the farms.

Fig.1.2. Adverse effect of water pollution

1.7. Dyes

Dyes or dyestuffs may be defined as a coloured substance capable of imparting their characteristic colours. A good dye is one which when applied to the fabrics show good fastness to washing, light and heat. Synthetic dye manufacturing started in 1856, when the English chemist W.H. Perkin, in an attempt to synthesize quinine, obtained a bluish substance instead of quinine, with excellent dyeing properties that later became known as aniline purple, Tyrian purple or mauveine. Perkin 18 years old, patented his invention and set up a production line. This concept of research and development was soon to be followed by others and new dyes began to appear on the market, a process that was strongly stimulated by Kékulé.s discovery of the molecular structure of benzene in 1865. In the beginning of the 20th century, synthetic dyestuffs had almost completely supplanted natural dyes 344.

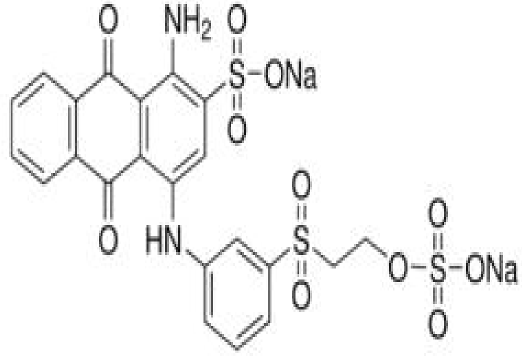
The worldwide high level of production and use of dye generates colored waste water which gives rise of environmental concern. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments appear to be colored because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments.

Fig.1.3. Dyes powder of different colour

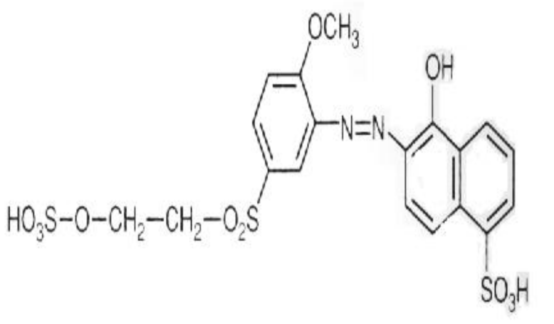
1.7.1. Classification of dyes

Dyes can be classified[5] both by their chemical structure and their application to the fiber type[4]. In many cases, a particular chemical class includes dyes of several application classes and particular application class may include dyes of varied chemical types[40]. However, the classification based on application is advantageous before considering chemical structures in detail.

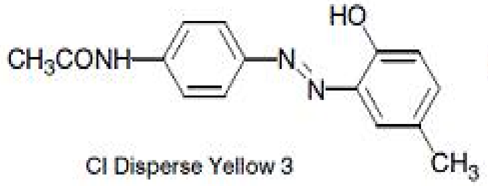
All aromatic compounds absorb electromagnetic energy but only those that absorb light with wavelengths in the visible range (~350-700 nm) are coloured. Dyes contain chromophores, delocalized electron systems with conjugated double bonds, and auxochromes, electron-withdrawing or electron donating substituents that cause or intensify the colour of the chromophore by altering the overall energy of the electron system. Usual chromophores are -C=C-, -C=N-, -C=O, -N=N-, $-NO_2$ and quinoid rings, usual auxochromes are $-NH_3$, -COOH, $-SO_3H$ and -OH. Based on chemical structure or chromophore, 20-30 different groups of dyes can be discerned. Azo (monoazo, disazo, triazo, polyazo), anthraquinone, phthalocyanine and triarylmethane dyes are quantitatively the most important groups. Other groups are diarylmethane, indigoid, azine, oxazine, thiazine, xanthene, nitro, nitroso, methine, thiazole, indamine, indophenol, lactone, aminoketone and hydroxyketone dyes and dyes of undetermined structure (stilbene and sulphur dyes). Figure 1.4 shows the structural formulas of several different dyes.



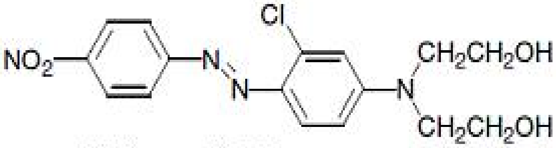
Reactive Blue



Reactive Red



CI Disperse Yellow 3



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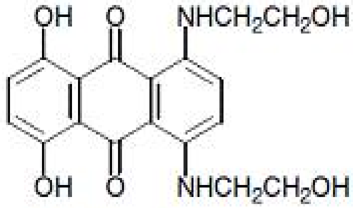

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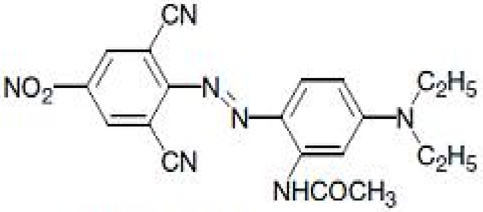
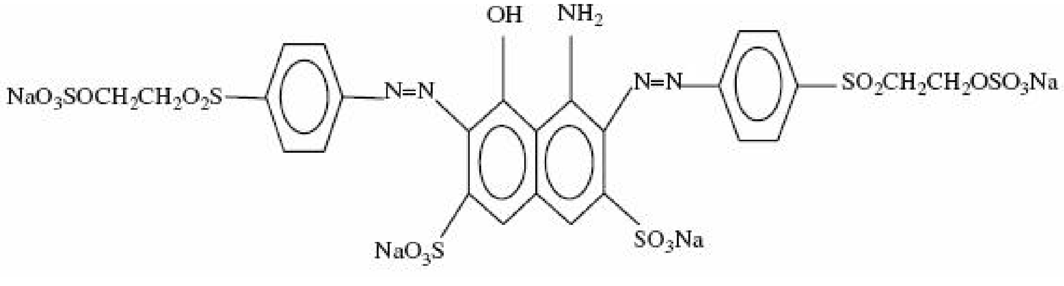


CI Disperse Blue 165



Reactive Black 5

Fig.1.4. Structural formulas of different synthetic dyes

Reactive dyes

These dyes form a covalent bond with the fiber, usually cotton, although they are used to small extent on wool and nylon. This class of dyes first introduced commercially in 1956, made it possible to achieve extremely high wash fastness properties by relatively simple dyeing methods. The principal chemical classes of reactive dyes are azo (including metalized azo), triphendixazine, phthalocyanine, formazan, and anthraquinone, vinyl sulphone etc. High purity reactive dyes are used in the ink-jet printing of textiles, especially cotton[41].

Disperse dyes

Disperse dyes are scarcely soluble dyes that penetrate synthetic fibres (cellulose acetate, polyester, polyamide, acryl, etc.). This diffusion requires swelling of the fibre, either due to high temperatures (>120 °C) or with the help of chemical softeners. Dying takes place in dyebaths with fine disperse solutions of these dyes. Disperse dyes form the third largest group of dyes in the colour Index: about 1400 different compounds are listed, of which ~40% is currently produced. They are usually small azo or nitro compounds (yellow to red), anthraquinones (blue and green) or metal complex azo compounds (all colours).

Direct dyes

These water-soluble anionic dyes, when dyed from aqueous solution in the electrolytes, are substantive to cellulosic fibres. Direct dyes are relatively large molecules with high affinity for especially cellulose fibres[42]. Van der Waals forces make them bind to the fibre. Direct dyes are mostly azo dyes with more than one azo bond or phthalocyanine, stilbene or oxazine compounds. In the Colour Index, the direct dyes form the second largest dye class with respect to the amount of different dyes: About 1600 direct dyes are listed but only 30% of them are in current production.

Their principal use is the dyeing of cotton and regenerated cotton paper, leather, and to a lesser extent, nylon[43].

Vat dyes

Vat dyes are water-insoluble dyes that are particularly and widely used for dyeing cellulose fibres. The dyeing method is based on the solubility of vat dyes in their reduced (leuco) form. Reduced with sodium dithionite, the soluble leuco vat dyes impregnate the fabric. Next, oxidation is applied to bring back the dye in its insoluble form. Almost all vat dyes are anthraquinones or indigoids. Indigo itself is a very old example of a vat dye, with about 5000 years of application history. Vat refers to the vats that were used for the reduction of indigo plants through fermentation.

Cationic (basic) dyes

These water-soluble cationic dyes are applied to paper poly acrylonitrile, modified nylons, and modified polyesters. Their original use was for silk, wool, and tannin-mordanted cotton. Basic dyes are water-soluble and yield colored cations in solution. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine, and acridine[5]. Some basic dyes show biological activity and are used in medicine as antiseptics.

Acid dyes

These water-soluble anionic dyes are applied to nylon, wool, silk, and modified acrylics. They are also used to some extent for paper leather, ink-jet, printing, food and cosmetics[42].

Solvent dyes

These water-insoluble but solvent-soluble dyes are devoid of polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. They are used for coloring plastics, gasoline, oils and waxes. The dyes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane dyes are also used[5].

Sulfur dyes

These dyes are applied to cotton from alkaline reducing bath sodium sulfide as the reducing agent. Numerically this is a relatively small group of dyes. The low cost and good wash fastness properties of the dying make this class important from an economic stand point. However, they are under pressure from an environmental viewpoint[43].

Fluorescent brighteners

Fluorescent brighteners (or bluing agents) mask the yellowish tint of natural fibres by absorbing ultraviolet light and weakly emitting visible blue. They are not dyes in the usual sense because they lack intense colour. Based on chemical structure, several different classes of fluorescent brighteners are discerned: stilbene derivatives, coumarin derivatives, pyrazolines, 1, 2-ethene derivatives, naphthalimides and aromatic or heterocyclic ring structures. Many fluorescent brighteners contain triazinyl units and water-solubilising groups.

Other dye classes

Apart from the dye classes mentioned above, the Colour Index also lists food dyes and Natural dyes. Food dyes are not used as textile dyes and the use of natural dyes (mainly anthraquinone, indigoid, flavenol, flavone or chroman compounds that can be used as mordant, vat, direct, acid or solvent dyes) in textile-processing operations is very limited.

1.7.2. Discharge statistics of dyes

The principal route by which dyes enter the environment is via wastewater[44]. To judge the relative share of the different dye classes in the wastewater of textile-processing industries, dye consumption data should be considered together with the degree of fixation of the different dye classes. These are listed in Table 1.1.

Table1.1. Estimated degree of fixation for different dye/fibre combinations[44].

Dye class	Fibre	Degree of fixation (%)	Loss to effluent (%)
Acid	polyamide	80 - 95	05 - 20
Basic	acrylic	95 - 100	00 - 05
Direct	cellulose	70 - 95	05 - 30
Disperse	polyester	90 -100	00 -10
Metal-complex	wool	90 - 98	02 - 10
Reactive	cellulose	50 -90	10 - 50
Sulphur	cellulose	60 -90	10 - 40
Vat	cellulose	80 - 95	05 - 20

1.7.3. Dyes, Environmental Concern

Wastewater from the textile industry is a complex mixture of many polluting substances ranging from organochlorine-based pesticides to heavy metals associated with dyes or the dyeing process[45]. Many dyes are visible in water at concentrations as low as 1 mg L^{-1}. Textile-processing wastewaters, typically with dye content in the range 10-200 mg L^{-1}[46] 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 dermatoses, eczema (Su and Horton, 1998), and may affect the liver, the lungs, the vasco-circulatory system, the immune system and the reproductive system [47]of experimental animals as well as human systems. Dyes with azo bonds nitro-or amino-groups are carcinogenic, causing tumors of liver and urinary bladder in experimental animals[48]. 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[49].

The toxicity of aromatic amines depends on the nature and location of other substituents. As an example the substitution with nitro, methyl or methoxy groups or halogen atoms may increase the toxicity; whereas substitution with carboxyl or sulphonate groups generally lower the toxicity[50]. As most soluble commercial azo dyestuffs contain one or more sulphonate groups, insight in the potentials danger of sulphonated aromatic amines is particularly important. Sulphonated aromatic amines, in contrast to some of their unsulphonated analogues, have generally no or very low genotoxic and tumorigenic potential[51].

1.8. Experimental Methods for Removal of Dyes

To remove dyes and other contaminants from waste water, several physical, chemical and biological methods have been developed, such as membrane separation, flocculation coagulation, adsorption, ozonization and acrobic/ anacrobic treatments. However, these developed methods are varying in their effectiveness, cost and environmental impact[52, 53]. Therefore, a suitable cheapest removal technology is needed. Adsorption by activated charcoal has been found to be promising techniques for dye wastewater treatment |because of its low cost, simplicity, high efficiency and wide-ranging availability for removing dyes.

Several factors determine the technical and economic feasibility of each single dye removal technique:

- Dye type
- Wastewater composition
- Dose and costs of required chemicals
- Operation costs (energy and material)
- Environmental fate and handling costs of generated waste products

In general, each technique has its limitations. The use of one individual process may often not be sufficient to achieve complete decolourisation. Dye removal strategies consist therefore mostly of a combination of different techniques.

There are three categories methods for dye removal: a) Physical b) Chemical c) Biological. The advantages and disadvantages of these methods are given in table 1.2.

1.8.1. Physical methods

Different physical methods are widely used such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption technique. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. Membrane separation techniques were reported to be suitable for removing AOX, COD, and color from pulp and paper mills. Merrill et al.[54] stated that membrane filtration and granular-membrane filtrations (GMF) were suitable for removing heavy metals from the pulp and paper mill wastewater.

In accordance with the literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the adsorbent is inexpensive. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications[55].

1.8.2. Chemical methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe(ll)/$Ca(OH)_2$, electroflotation, eiectrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes [40]. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems[56].

The most important dye removal techniques are briefly discussed below-

1.8.3. Membrane filtration

Nanofiltration and reverse osmosis, using membranes with a molecular weight cut-off (MWCO) below ~10,000 Dalton, can be applied as main or post treatment processes for separation of salts and larger molecules including dyes from dyebath effluents and bulk textile-processing wastewaters. Filtration with bigger membranes, i.e. ultrafiltration and microfiltration, is generally not suitable as the membrane pore size is too large to prevent dye molecules passing through[57] but it can be successful as pretreatment for further nanofiltration or reverse osmosis[58]. Membrane filtration is a quick method with low spatial requirement. Another advantage is that the permeate, as well as some of the concentrated compounds, including non-reactive dyes, can be reused[59, 60]. This reuse, however, applies mostly only for smaller waste flows[61]. The disadvantages of membrane techniques are flux decline and membrane fouling, necessitating frequent cleaning and regular replacement of the modules.

1.8.4. Coagulation/flocculation

Coagulation/flocculation is often applied in the treatment of textile-processing wastewater, either to partly remove Chemical Oxygen Demand (COD) and colour from the raw wastewater before further treatment to polish the final effluents of biologically or otherwise treated wastewater even as the main treatment process[62]. The principle of the process is the addition of a coagulant followed by a generally rapid chemical association between the coagulant and the pollutants. Thus formed coagulates or flocs subsequently precipitate or are to be removed from the water phase by flotation.Various inorganic coagulants are used, mostly lime, magnesium, iron and aluminium salts. Inorganic compounds are, however, generally not very suitable to remove highly soluble (sulphonated) dyes from solution unless rather large quantities are dosed. Coagulation/flocculation with inorganic chemicals generates considerable volumes of useless or even toxic sludge that must be incinerated or handled otherwise. This presents a serious drawback of the process.

1.8.5. Electrolysis

Electrolysis is based on applying an electric current through to the wastewater to be treated by using electrodes. The anode is a sacrificial metal (usually iron) electrode that withdraws electrons from the electrode material, which results in the release of Fe(II)-ions to the bulk solution and precipitation of $Fe(OH)_2$ at the electrode surface. Moreover, water and chloride ions are oxidised, resulting in the formation of O_2, O_3 and Cl_2. The cathode is a hydrogen electrode that produces H_2 gas from water. Organic compounds like dyes react through a combination of electrochemical oxidation, electrochemical reduction, electrocoagulation and electroflotation reactions.

1.8.6 Biological methods

Biological dye removal methods are based on microbial biotransformation of dyes. As dyes are designed to be stable and long-lasting colorants, they are usually not easily biodegraded. Nevertheless, many researches have demonstrated partial or complete biodegradation of dyes by pure and mixed cultures of bacteria, fungi and algae.

1.8.7. Sorption and ion exchange

Activated carbon or other materials can be used to remove dyes from wastewater, either by adsorption (anionic dyes) or by combined adsorption and ion exchange (cationic dyes). Sorption techniques yield waste sludge, i.e. dye-saturated material that should be disposed off or regenerated. As there are nonionic, anionic and cationic dyes, most adsorbents do not remove all different dye types. Activated carbon is capable of adsorbing many different dyes with high adsorption capacity[63, 64, 65] but it is expensive and the costs of regeneration are high because desorption of the dye molecules is not easily achieved. Various other (mostly low-cost) adsorbents have therefore been investigated as an alternative to activated carbon.

1.8.8. Activated Carbon

Activated carbon is the most widely used adsorbent for adsorption method because it has a high capacity for the adsorption of organics, but its use is limited due to its high cost. This has led to a search for cheaper and more effective substitututes, such as coal, fly ash, wood, silica gel, bentonite clay, bagasse pith; maize cob, coconut shell, rice husk, and cotton waste have been tried with varying success for color removal[66]. Adsorptive capacities of several materials for color removal were investigated. Especially, natural zeolite, sepiolite and bentonite and their modified forms were used for the removal of some dyestuffs[67, 68]. Modification processes were applied whether to increase their surface area or to change their surface properties in order to improve their color removal capacities.

Table. 1.2. Advantages and disadvantages of the current methods of dye removal from industrial effluents[40]

Physical/chemical methods	Advantages	Disadvantages
Oxidation	Rapid process	High energy costs and formation of by-products
Ozonation	Applied in gaseous state: no alteration of volume	Short half life (20 min)
Photochemcal	No sludge generation	Formation of by products
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost electricity
Ion exchange	No adsorbent loss	Not effective for all dyes
Membrane filtration	Removes all dyes	Concentrated sludge production
Electrokinetic coagulation	Economically feasible	High sludge production
Adsorption	Good removal for a wide range of dyes	Adsorbent requires disposal
Activated carbon	Highly effective for various dyes	Very expensive

1.9. Research Objective

Textile industry is one of the most important industries in Bangladesh. The water consumption in textile industry, especially in dyeing and washing processes, is too high. Therefore, large amount of wastewater is produced and discharged to the receiving environment during textile production process. For controlling water pollution it is essential to treat waste 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 solid. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances.

Bangladesh is very rich in various kinds of porous natural materials, which can be used as adsorbents. They are very cheap and available in vast quantities. One of them is saw dust which is present in large quantities in all part of Bangladesh. The other adsorbents are coconut coir and jute stick, which are also available in Bangladesh. The objective of this study is to use these three adsorbents to remove reactive, direct and disperse types of dyes from textile wastewater by using prepared activated charcoal and jute stick.
Keeping this in mind, the present research has been carried out with the following aims,

1. Preparation of activated charcoal from saw dust, coconut coir and preparation of jute stick powder.
2. Characterization of the prepared activated charcoal, powder by FTIR. SEM, BET, and pH_{zpc}
3. Study of dyes removing capacities from aqueous solution using these prepared adsorbents by adsorption process.
4. Optimization of various parameters such as adsorbent dosage, pH, temperature, conc. of dye soln. etc.
5. Study of adsorption kinetics
6. Study of adsorption isotherm
7. Study of thermodynamic parameters
8. Analysis of desorption kinetics
9. Finally, the optimized methods have been applied for the removal of dyes from waste water collected from textile industries.

Significance of research

1. The research work determine the suitability of sawdust, coconut coir and jute stick as adsorbents for the removal of dyes from aqueous solution.
2. The research work was performed to find an alternative source of adsorbent rather than commercially available more expensive activated carbon.

1.10. Dyestuffs used in the research work

Name of dye	Type	Chemical Class	Abbreviations
Remazol Red	Reactive	Azo	RR
Remazol Yellow	Reactive	Azo	RY
Remazol Blue	Reactive	Anthraquinone	RB
Levafix Red	Reactive	Anthraquinone	LR
Coralene Scarlet XF	Disperse	Azo	CS XF
Coralene Blue MD	Disperse	Anthraquinone	CB MD
Congo Red	Direct	Azo	CR

Chapter - 2

Theory and Literature Survey

2.1. Wastewater Treatment

Wastewater quality can be defined by physical and chemical characteristics. Physically wastewater is usually characterized by a gray color, musty odor, and a solids content of about 0.1%. From a physical point of view the suspended solids can lead to the development of sludge deposits and anaerobic conditions when discharged into the receiving environment. Chemically wastewater is composed of organic and inorganic compounds as well as various gases. Organic components may consist of dyes, carbohydrates, proteins, fats, greases, surfactants, oils, pesticides, phenols, etc., Inorganic components may consist of heavy metals, nitrogen, phosphorus, sulfur, chlorides etc. In domestic wastewater, the organic and inorganic portions are approximately 50% for each category.

Textile industries are found in most countries and their numbers have increased, particularly in Asia. These industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring material. The annual world production of textiles is about 30 million tones requiring 7×10^5 tons of different dyes. The textile industry is one of the industries that generate a high volume of wastewater (Fig.1.1). Due to the large degree of organics present in these molecules and the greater stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal of dyes from wastewater. Many dyes are difficult to decolorize due to their complex structure and synthetic origin.

2.1.1. Biological treatments

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolonization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as, bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants[69]. However, their applications often restricted because of technical constraints. Biological treatment requires a` large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals and less flexibility in design and operation[70]. Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes[40]. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

2.1.2. Adsorption

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a solution[71].

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances[72]. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. The adsorption characteristics of a wide variety of inorganic and organic supports have been measured and their capacity to remove synthetic dyes has been evaluated[73].

The adsorption onto activated carbon is the most commonly used technique for the treatment of wastewaters. Activated carbons (granular or powdered) are widely used adsorbents because of its extended surface area, micro porous structure, high degree of surface reactivity and excellent adsorption capability for organic pollutants. Activated carbon is very effective for adsorbing cationic, mordant, acid dyes, dispersed, direct, vat and pigment and reactive dyes. However commercially available activated carbons are very expensive[74]. Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low cost adsorbents including natural materials adsorbents and waste materials adsorbents and waste materials form industry and agriculture has been proposed by several workers. Table 2.1 shows list of examples of commercial activated carbon (CAC) used in adsorption of dyes.

Table 2.1. Adsorption capacities (q_{max}) for commercial activated carbon (CAC).

Dyes	Commercial Activated Carbon (CAC) q_{max} (mg/g)	References
Reactive blue 2	217.2	Garg et al., (2004)[74]
Direct red 81	240.7	Nada et al., (2004)[75]
Reactive yellow 86	127.4	Nada et al., (2004)[75]
Reactive red	650	Walker et al., (2003)[76]
Acid blue 40	133.3	Ozacar and Sengil, (2006)[77]
Basic red 46	106	Stern et al., (2003)[78]
Acid yellow 17	57.47	Ozacar and Sengil, (2006)[77]
Basic blue	309.2	Meshko et al., (2001)[72]
Direct red 28	16.81	Fu and Viraraghavan, (2002)[79]
Direct brown 1	7.69	Mohan et al., (2002)[80]
Reactive orange 107	714	Aksu and Tezer, (2005)[81]

Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptive are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Thus, in spite of logical prediction that all surfaces are potentially capable of decreasing its free energy, it is pragmatic to assume that there must be some specificity in the nature of the surface in order that adsorption may take place. It may also be noted from obvious thermodynamic reasons that adsorption normally takes place with decrease in entropy, because by confining an adsorbate molecule to a thin surface layer, certain degrees of freedom are lost. Equation for adsorption,

$\Delta U = \Delta H - T\Delta S$

Obviously shows that ΔH is also negative, that is, adsorption in general exothermic. The main work of saturation a surface is usually accomplished by adsorption of a single layer of molecules and in such a case the phenomenon is termed unimolecular or monomolecular adsorption. However, adsorption involving the formation of several layers in by no means infrequent, and these are called multimolecular adsorption.

2.1.3. Steps in adsorption processes

Adsorption process usually occurs in the following steps[82]

I. 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.

2. Film diffusion transport

In this step, adsorbents spread from inert liquid film to the entry of the pores of the adsorbent.

3. Pore transport and adsorption

In this step, adsorb ate 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.

2.2. The Relation between Surface Tension and Adsorption

Surface reaction in adsorption process must occur at least partly as a result of like wise influence and alter the forces active within the phase boundaries, or surface boundaries; these forces result in characteristic boundary energies. Classical chemistry defines the properties of a system by the properties of its mass; for surface phenomena, however, the significant properties are those of the surface or boundary[83]. A pure liquid always tends to reduce its free surface energy through the action of surface tension, which is quantitatively equal to the amount of work that would be necessary to compensate the natural reduction in free surface energy. From a molecular point of view, enlarging a surface requires the breaking of bonds between molecules making up the liquid phase, and the forming of bonds between molecules of different phases. Hence, to increase the surface of liquid requires an input of work in excess of that necessary to merely compensate the tension at the surface. To induce frothing at a liquid-gas interface, for example, the surface tension must be over compensated[83]. It is well known that a large number of soluble materials can effectively alter the surface tension of a liquid. Detergents, for example, lower surface tension dramatically, and can thus act to cause spreading of the water drop on the flat plate, resulting in a wetting of the plate. Detergent-like substances are thus termed “wetting” agents or “surface-active” agents. If a material which tends to be active at the surface is present in a liquid system, a decrease in the tension at the surface will occur upon movement of the solute to the surface. Migration of the substance to the surface or boundary results in a net reduction of the work required to enlarge the surface area, the reduction being proportional to the concentration of adsorbate at the surface. Hence the energy balance of the system favors the adsorptive concentration of such surface-active substances at the phase interface. Stated in a manner more appropriate for the objectives of the present discussion, a solute that decreases surface tension must be concentrated at the surface because the solvent molecules have a smaller attractive force for the molecules of the solute than for each other. The phenomenon of increased concentration of the soluble material in a boundary or surface is adsorption, and any solute which lowers the surface tension of a liquid in which it is dissolved will adsorb at the boundary of the liquid phase. Conversely, any solute which increases the surface tension is “negatively adsorbed” at the boundary of the liquid phase, that is, the solute migrates away from the surface toward the center of the liquid phase[83].

2.2.1. Adsorption mechanisms

Adsorption occurs due to the interactions between ions, molecules and the adsorbent surface. These integrations depend on the types of either ions or molecules and the types of the adsorbent surfaces available. The surfaces are either inorganic or organic and the adsorbents are also either inorganic or organic. Inorganic surfaces are highly polar and in general have a positive or a negative charge. However, organic surfaces can be charged and ranged from strongly polar to non-polar.

2.2.2. 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 2.2[84].

Table 2.2. Adsorption mechanism of organic compounds

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 sulphone

2.3. Causes and Types of Adsorption

The primary driving force for adsorption may be a consequence of *lyophobic* (solvent-disliking) character of the solute relative to the particular solvent, or of a high affinity of the solute for the solid. For the majority of systems encountered in water and wastewater treatment practice, adsorption results from the combination of the two forces. The degree of solubility of a dissolved substance is by far the most significant factor in determining the intensity of *lyophobic* character of the solute[83]. The more a substance likes the solvent systems – the more *hydrophilic* in the case of an aqueous solution- the less likely it is to move toward an interface to be adsorbed. Conversely, a *hydrophobic* –water disliking-substance will more likely be adsorbed from aqueous solution. A large number of organic contaminants, such as sulfonated alkylbenzenes, have a molecular structure comprised of both hydrophilic and hydrophobic groups. In this case, the hydrophobic part of the molecule tends to be active at the surface and undergo adsorption, whereas the hydrophilic part tends to stay in the solution phase is at all possible [83].

The "solubility-amphoteric" character of the substance results in an orientation of the molecule at the interface; the hydrophobic part adsorbed at the surface, and the hydrophilic part directed toward the solvent phase. The second primary driving force for adsorption results from a specific affinity of the solute for the solid. In this context, it is desirable to distinguish between three principal types of adsorption. According to the most plausible of present concepts of adsorption, this surface phenomenon may be predominantly one of the electrical attractions of the solute to the adsorbent, of van der Waals attraction, or of a chemical nature[83].

There are two methods of adsorption namely physisorption and chemisorptions. Both methods take place when the molecules in the liquid phase becomes attached to a surface of the solid as a result of the attractive forces at solid surface (adsorbent), overcoming the kinetic energy of the contaminant (adsorbate) molecules. Adsorption of this type is sometimes referred to also as ideal adsorption. If the adsorbate undergoes chemical interaction with the adsorbent the phenomenon is referred to as chemical adsorption, activated adsorption or chemisorption. Chemically adsorbed molecules are considered not to be free to move on the surface or within the interface.

2.3.1. Physical adsorption

Physical adsorption is usually predominant at low temperature and characterized by a relatively low energy of adsorption that is the adsorbate is not held as strongly to the adsorbent as for chemical adsorption. The reversibility of physorption is dependent on the strength of attractive forces between adsorbate and adsorbent. Table 2.3 shows a comparison of physical and chemical adsorption.

2.3.2. Chemical adsorption

Chemical adsorption exhibit high energies of adsorption because the adsorbate forms strong localized bonds at active centers on the adsorbent. Chemical interaction between the adsorbent and the adsorbate is favored by higher temperature because the chemical reactions proceed more rapidly at elevated temperature than at lower temperatures.

Most adsorption phenomena are combinations of the two forms of adsorption; that is, the several forces which influence the different types of adsorption often interact to cause concentration of a particular solute at an interface. Thus it is generally not easy to distinguish between physical and chemical adsorption[83].

Table2.3. Comparison of physical and chemical adsorption [85]

Parameter	Physical adsorption	Chemical adsorption
Adsorption enthalphy(kcal/mol)	<10	>20
Adsorption rate	Diffusion controlled	Controlled by surface chemical reaction
Effect of temperature	Almost none	Positive
Specificity	Low	High
Interaction	Reversible	Irreversible
Surface covered	Complete	Incomplete
Activation energy	Small	Large
Adsorption/mass of adsorbent	Large	Small

2.3.3. Factors affecting adsorption include:

- The physical and chemical characteristics of the adsorbent, i.e., surface area, pore size, chemical composition
- The physical and chemical characteristics of the adsorbate, i.e., molecular polarity, chemical composition
- The concentration of the adsorbate in the liquid phase (solution)
- The characteristics of the liquid phase, i.e., pH and temperature
- The residence time of the system.

2.3.4. Industrial applications of adsorption

- The fundamental practical applications of adsorption are[74]
- Removal of colored and colorless organic pollutants from industrial wastewater
- Separation and purification of liquid and gas mixtures, bulk chemicals ,isomers and air
- Drying gases and liquids before loading them into industrial systems
- Removal of impurities from liquid and gas media
- Recovery of chemicals from industrial and vent gases
- Water purification

The commercial adsorption processes for separating gas and liquid mixtures are accomplished due to selective adsorption of certain substances from their mixtures. The same idea is true for purification of gas and liquid mixtures and drying of some industrial gases. For those purposes the pore system of adsorbents used is sufficiently wide to enable fast diffusion, separation is used mainly by selective adsorption that depends upon the vander Waals forces between the adsorbent and the constituents of the gas or liquid mixtures. The above processes are major unit operations in the chemical and petrochemical industries[55].

2.4. Industrial application of dye

Industrial applications of dyes are divided into two groups[42]:

I. **Textile Dyeing**:

These groups includes the following-

- Dyes for cotton, model fibres and linen: Reactive dyes, direct dyes, sulphur dyes, vat dyes, azoic colorants and pigments.
- Dyes for wool, silk and polyamide: Acid dyes, chrome dyes, metal-complex dyes and reactive dyes.
- Dyes for acetate, triacetate and polyester fibers: disperse dyes
- Dyes for acrylic fibers: cationic dyes

II. **Non-Textile Dyeing**

Non-textile dyeing includes: Leather dyes, fur dyes, hair dyes, food dyes, ink dyes, plastic dyes, photographic dyes and indicator dyes.

2.5. Factors affecting adsorption process

2.5.1. Adsorbate

The physical characteristic of the adsorbate is important for a number of reasons. First, for any homologous series of organic molecules as size increases solubility generally decreases. Molecular size is also important for the perspective that all adsorbents depend upon internal surface area for the full Use of their adsorption capabilities. If the molecular size is too large, adsorption will be hindered and adsorption capacity will decrease as very larger molecules block or cannot penetrate pores or pathways within the adsorbent[86]. Laszlo et al.[87], stated that the inner surface of adsorbent does not take part in the adsorption process for the case where the size of pollutant is larger than the pore size of adsorbent. Whether the molecule is in an ionic or natural state, whether it is a branched isomer or straight chain can have significant effect on the removal of this material from solution by adsorption. The molecular form can have consequences affecting the solubility of the adsorbate and it can also determine the energy of adsorption the force with which the particular molecule is held on the adsorbent. Further, these characteristics can affect the rate of diffusion of the molecule through the liquid. The rate of diffusion is usually a function of both molecular size and from for a given solvent[88].

The three major waste solution characteristics, which have particular impact on adsorption, are: the solution pH, its temperature; and the presence of other completion adsorbate compounds.

(a) pH of solution

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorption process through dissociation of functional groups on the adsorbent surface active sites[89]. The pH of a solution is of significance for its effect on both adsorbate and adsorbent and may have chemical characteristics which are affected by the concentration of hydrogen ions (H^+) in the solution. Some adsorbents have affinity for H^+ or OH^- ions and can directly affect the solution pH and therefore solubility and adsorption capacity. This effect must be considered during test design where large quantities of virgin adsorbent may be used per volume of solution. The pH change may not be quite so evident in full- scale operation where large volumes of solution are treated.

Adsorption from solution can be high pH sensitive in aqueous system where an adsorbate exhibits an isoelectric point or neutral point on the pH scale. It is at this point where maximum adsorption can be achieved' since solubility is minimized and the non polar-adsorbent has greatest affinity for non- ionic materials[88]. Gulnaz et al.[90], reported that the amount of basic red 18 and basic blue 9 dyes adsorbed on dried activated sludge increased with pH up 6-10 (Fig. 2.1). They also studied the reactive orange 12, reactive red 2, and reactive blue 4 dyes adsorption onto coir pith activated carbon. They reported that the amounts of reactive dyes adsorbed were high at low pH as compared to high pH.

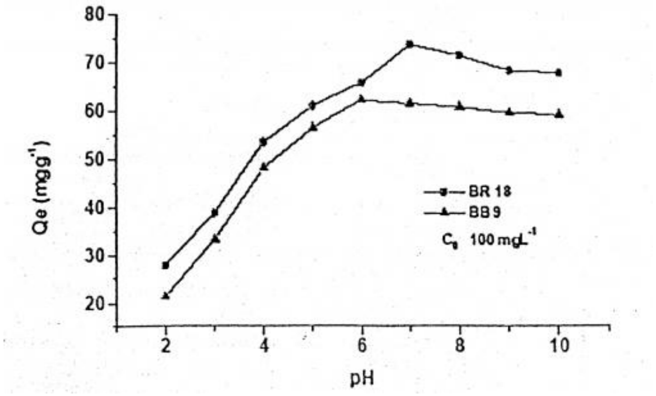


Fig. 2.1 Effect of pH on adsorption of basic dyes.

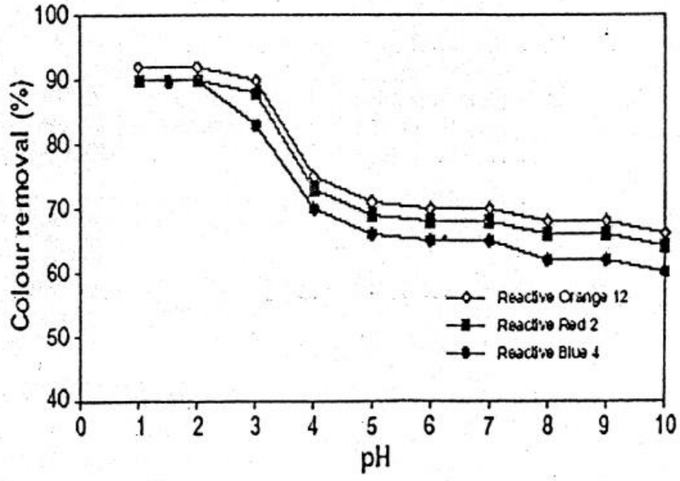


Fig. 2.2. Effect of pH on the adsorption of reactive dyes.

The increase in adsorption is due to increase of electrostatic attraction between negative charged dye molecules and positively charged active groups of coir pith activated carbon (Fig. 2.1). Malik [91] reported that the amount of direct blue 2B and direct green B dyes on sawdust carbon decreases with the increasing the pH value from 2 to 10 (Fig. 2.2). Several studies on how pH affects the adsorption process are summarized in Table 2.4.

Table 2.4. Reported studies on effect of pH on adsorption process.

Adsorbents	Adsorbates (Dyes)	Dyes removal	References
Na-bentonite and DTMA- benntonite	Acid blue 193	Decrease	Ozcan et al. [92], (2004)
Activated carbon	Direct blue 2B and direct gren B	Decrease	Malik[91], (2004)
Activated sludge	Basic blue 9 and basic red 18	Increase	Gulnaz et al. [90], (2004)
Chitosan beads	Reactive dyes (RB2, RR2, RY2, RY86),	Decrease	Kavitha et al. [93], (2007)
	Acid dyes (AO12, AR14, AO7)		
	Direct dye (DR81)		
Coir pith activated carbon	Readctive red 2 rective blue 4 and reactive orange 12	Decrease	Kavitha et al. [93], (2007)
Bagasse fly ash	Malachite green	Increase	Indra et al. [89], (2006)
Soy meal hull	Direct red 80	Decrease	Arami et al. [94], (2006)
	Direct red 80		
	Acid blue 92		
	Acid red 14		

(b) Temperature of solution

Study of the temperature dependence of adsorption gives valuable information about the enthalpy change during adsorption. The temperature of the solution affects the attraction between adsorbate and adsorbent in adsorption process[88]. Tsai et al.[95], studied the adsorption of ethyl violet or basic violet 4 dye by regenerated spent bleaching earth. The values of q_e increased from 36.1 mg/g at 15 °C to 56.5 mg/g at 45 °C. They also found that the percentage removal of acid black 1 and basic violet 3 dyes increase with the increasing of temperature from 30 to 50 °C in adsorption process using unburned carbon. The adsorption process at any particular concentration decreases with increasing temperature which is normally an exothermic process. Ozcan and Ozcan[97]reported that the amount of acid red 57 dye adsorbed on sepiolite decreases with the increasing of temperature from 20 to 50 °C. Gulnaz et al[91]reported that the adsorption capacities of dried activated sludge increased with decreasing temperatures from 50 to 20 °C which indicated that the adsorption process was exothermic. The sorption capacity of dried activated sludge was determined as 73.2, 60.1 and 43.6 mg/g for basic red 18 dye and 61.2, 46.2 and 33.6 mg/g for basic blue 9 dye at 20, 35 and 50 °C, respectively. Wu et al.[9], studied the adsorption of one basic blue 69 (BB 69) and direct red 227 (DR 227) dyes onto activated clay in the temperature range 15 - 75°C. They reported that adsorption capacity of basic blue 69 dyes on activated clay increases with increasing temperature, but that of direct red 227 dye decreases probably due to different adsorption nature; that is, the adsorption of basic blue 69 was extremely favorable and that of direct red 227 was classified as reversible adsorption. Several studies of endothermic and exothermic nature of adsorption process are summarized in Table 2.5.

Table 2.5. Studies reported by researchers on temperature effects on adsorption process.

Adsorbents	Adsorbates dyes	Temp. range (^{0}C)	Endo-thermic	Exo-thermic	References
Sepiolite	Reactive blue 221 and acid red 57	25-55	√		Ozcan et al. [96] ,(2005)
Activated carbon	Supranol yellow 4GL (acid dye)	30-50	√		Faria et al.[98] ,(2004)
Calcium-rich fly ash	Congo red	20-60	√		Noroozi,et al.[99] ,(2007)
Sawdust composite,	Methylene blue	20-30		√	Abd El-Latif et al.[100],(2010)
Activated sludge	Reactive black 5	20-50		√	Gulnaz et al.[90],(2004)
Chitosan	Reactive red 141	20-60		√	Hasan, et al.[101],(2008)
Coir pith carbon	Congo red	35-60	√		Namasivaya et al.[102],(2002)
Modified wood shavings	Methylene blue	22-60	√		Janos et al.[103],(2009)

2.5.2. Adsorbent

The physical and chemical properties of the adsorbent used to remove a pollutant from solution are quite important.

(a) Physical properties

The adsorbent can be in the form of granules or particles, which may have a density near or very different from the solution to be treated, or the adsorbent may be in very fine powdered from which may be easily suspended in the solution to be treated. These physical properties have most effect on the selection of the mode of application of the adsorption process using that particular adsorbent. Some physical properties such as surface area and size and distribution of pores in the particles directly affect adsorption performance by determining the amount of adsorbent capacity available and the molecular size which can be adsorbed [104]. Table 2.6 lists the international Union of pure and Applied Chemistry (IUPAC) classification of pores by size.

Table 2.6. Classification of pore sizes.

Type	Pore diameter, D (nm)	Characteristic
Micropore	$D < 2$ nm	Superimposed wall potentials
Mesopore	$2 \text{ nm} < D < 50$ nm	Capillary condensation
Macropore	$D > 50$ nm	Effectively flat walled

There are at least two types of surface involved, internal within the pores and an external surface similar to that of non-porous solids. The surface area and pore size are usually measured using Autosorb I, Brunauer, Emmett, and Teller (BET) using nitrogen adsorption at 77 K.)

(b) Chemical properties

Includes the degree of ionization of the surface of the adsorbent, the types of functional groups which are present on the adsorbent and the degree to which these properties may be changed by contact with the solution. The presence of the ionized or otherwise active functional groups on the adsorbent surface allow chemical interactions of chemisorptions which usually produces various affects.These affects are different form and less reversible than physical adsorption. This effect may be advantageous or not, depending on a chemical nature of the adsorbent to change the chemical characteristics of the solution to be treated can also have either beneficial or adverse effects on the adsorption process. Physical and chemical treatment can significantly change the adsorption capacity[105]. The resultant samples were characterized in terms of their surface chemistry and textural-properties, and subsequently tested in the removal of different classes of dyes. This is particularly important where the treated solution is to be reused, or is for human consumption [88].

Surface Interaction

Surface area is one of the principle characteristics affecting the adsorptive capacity of an adsorbent since the adsorption process results in a concentration of solutes at the surface. Adsorption at a surface is largely the result of binding forces between the individual ions or molecules of an adsorbate and the surface[71].

2.5.3. Selectivity of Adsorbent

To be suitable for commercial applications, adsorbents should have[106]

1. Reasonably high surface area or micro pore volume
2. Surface chemistry
3. High selectivity to enable sharp separations
4. High capacity to minimize the amount of adsorbent needed
5. Favorable kinetic and transport properties for rapid sorption
6. Chemical and thermal stability, including extremely low solubility in the contacting fluid to preserve the amount of adsorbent and its properties
7. Hardness and mechanical strength to prevent crushing and erosion
8. The Capability of being regenerated when used with commercial feed stocks that contain trace quantities of high- molecular-weight species that are strongly adsorbent and difficult to adsorption
9. Relatively low cost.

Adsorbents including natural materials and waste materials from industry and agriculture such as saw dust, rice husk, jute stick powder, coconut husk, fly ash, bagasse fly ash, zeolites, chitin and chitosan are used to remove pollutants from aqueous solution. Zeolites have high ion- exchange capacity and relatively high specific surface areas and more importantly the relatively cheap prices make zeolites attractive adsorbents. Their price is about US$ 0.03-0.12/kg depending on the quality of the mineral. Chitin and chitosan adsorbents are efficient adsorbents and have an extremely high affinity for many classes of dyes[107]. Fly ash is a waste material originating in great amounts in combustion processes. Although it may contain some hazardous substances, such as heavy metals it is widely utilized in industry in many countries. Fly ash a surface area of 15.6 m^2/g. Its properties are extremely variable and depend strongly on its origin [108]. Bagasse fly ash adsorbent generated in the sugar industry does not contain large amounts for toxic metals and has been widely used for adsorption of dyes[80].

2.6. Desorption

Desorption is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption (that is, either adsorption or absorption). This occurs in a system being in the state of sorption equilibrium between bulk phase (fluid, i.e. gas or liquid solution) and an adsorbing surface (solid or boundary separating two fluids). When the concentration (or pressure) of substance in the bulk phase is lowered, some of the sorbed substance changes to the bulk state.

In chemistry, especially chromatography, desorption is the ability for a chemical to move with the mobile phase. The more a chemical desorbs, the less likely it will adsorb, thus instead of sticking to the stationary phase, the chemical moves up with the solvent front.

After adsorption, the adsorbed chemical will remain on the substrate nearly indefinitely, provided the temperature remains low. However, as the temperature rises, so does the likelihood of desorption occurring. The general equation for the rate of desorption is:

$$R = rN^x,$$

Where r is the rate constant for desorption, N is the concentration of the adsorbed material, and x is the kinetic order of desorption.

Usually, the order of desorption can be predicted by the number of elementary steps involved:

Atomic or simple molecular desorption will typically be a first-order process (i.e. a simple molecule on the surface of the substrate desorbs into a gaseous form). Recombinative molecular desorption will generally be a second-order process (i.e. two hydrogen atoms on the surface desorbed and form a gaseous H_2 molecule).

The rate constant r may be expressed in the form

$$r = Ae^{-E_a/kT}$$

Where A is the "attempt frequency", the chance of the adsorbed molecule overcoming its potential barrier to desorption, E_a is the activation energy of desorption, k is the Boltzmann constant, and T is the temperature[109].

2.7. Surface charge (pH_{zpc} and pH_{ss}) of solid

Normally, solid surface carries two types of charges. The generation of surface charge when a solid is in contact with aqueous selection is common to almost all system. Some charges diffuse in the medium when they come in contact with aqueous solution and some do not instead remain in contact on the surface. pH of solid surface(pH_{ss}) measures the amount of former charges, while pH of zero point charge measure the later. The pH_{zpc} of solid surface naturally depends on the relative numbers of each type of grouping and on their respective dissociation constants[110]. Adsorption largely depends on the pH of the bulk. If pH of the bulk is higher then pH_{zpc} (zero-point charge), the surface become negative and the lowering the pH of the bulk the pH_{zpc}, surface become positive. Knowing the value of pH_{ss} and pH_{zpc} experimental conditions may be chosen.

2.8. 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[111]. The adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature[83]. In general, the adsorption isotherm describes how adsorbates will interact with adsorbents and so is critical in optimizing the use of adsorbents[66].

2.8.1. Langmuir isotherm

Assumes monolayer coverage of adsorbate over a homogenous adsorbent surface, graphically a plateau characterizes the Langmuir isotherm. Therefore, at equilibrium a saturation point is reached where no further adsorption can occur. Sorption is assumed to take place at specific homogenous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site[111].

Langmuir equation is given in equation 2.1[112].

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \qquad (2.1)$$

Rearranging equation

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \qquad (2.2)$$

Where q_e is the equilibrium dye concentration on the adsorbent (mg/g), C_e is the equilibrium dye concentration in solution (mg/l), q_{max} is the monolayer capacity of the adsorbent (mg/g), and K_L is the Langmuir adsorption constant (l/mg). Therefore, plots C_e/q_e vs. C_e it is possible to obtain the value of qmax from the slope, which is $(1/q_{max})$ and the value of K_L from the intercept which is $(1/K_L q_{max})$. The Langmuir equation is applicable to homogenous sorption where the sorption of each molecule has equal sorption activation energy. The equation is thermodynamically consistent and follows Henrys Law at concentrations approaching zero[66].

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given below[71].

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

Where K_L is the Langmuir isotherm constant andC_0 is the highest initial dye concentration (mg/l). The value of separation factor R_L, indicates of the adsorption process as given[71]

- Unfavorable ($R_L > 1$)
- Linear ($R_L = 1$)
- Favorable ($0 < R_L < 1$)
- Irreversible ($R_L = 0$)

2.8.2. Freundlich isotherm

The Freundlich equation is an empirical equation employed to describe heterogeneous systems in which it is characterized by the heterogeneity factor 1/n. Hence, the empirical equation can be written[113] as

$q_e = K_F C_e^{1/n}$

Where q_e is the equilibrium dye concentration on adsorbent (mg/g), C_e, is the equilibrium dye concentration in solution (mg/I), K_F is Freundlich constant $(mg/g)(I/mg)^{1/n}$ and 1/n is the heterogeneity factor. This expression is characterized by the heterogeneity factor K_F and 1/n so the Freundlich isotherm may be used to describe heterogeneous systems. For favorable adsorption value of 1/n must be between 0 and. The Freundlich equation agrees well with the Langmuir over moderate concentration ranges but, unlike the Langmuir expression it does not reduce to the linear isotherm (Henrys' Law) at low surface coverage. Both of these theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with a single set of constants. To determine the constants K_F and n, the linear form of the equation 2.3 shown below may be used to produce a graph of $\ln q_e$ against $\ln C_e$.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (2.3)$$

Therefore, plots $\ln q_e$ vs. $\ln C_e$ it is possible to obtain the value of K_F from the slopes and the value of 1/n from the intercepts. Where K_F $(mg/g)(l/mg)^{1/n}$ and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent respectively. Table 2.7 summaries Freundlich Constants for different dye/adsorbent systems.

Table 2.7. Summaries of the adsorption capacities of different adsorbents obtained from Langmuir isotherm model.

Dyes	Adsorbents	Langmuir isotherm		Freundlich isotherm		References
		q_{max} mg/g	K_L L/mg	K_F	n	
Reactive blue 114	Calcined alunite	170.7	0.050	13.7	1.742	Ozacar and Sengil[77], (2006)
Reactive yellow 64	Calcined alunite	236	0.017	6.28	1.373	Ozacar and Sengil[77], (2006)
Reactive red 124	Calcined alunite	153	0.084	19.2	1.995	Ozacar and Sengil[77], (2006)
Acid brilliant blue	Banana Pith	4.3	0.13	01	2.63	Namasivayam et al.[114], (1998)
Acid violet	Coir pith	1.6	0.746	2.87	2.35	Namasivayam et al.[102], (2002)
Acid blue 29	Coir pith	16.6	0.03	0.47	0.42	Namasivayam et al.[102], (2002)
Acid blue 29	Peat	13.95	0.178	3.69	2.841	Konduru et al.[115], (1997)
Basic blue 9	Fly ash	15.17	1.862	1.36	1.09	Konduru et al.[115], (1997)
Basic blue 9	Bentonite	46.30	36.0	43.7	6.30	Konduru et al. [115], (1997)
Dispersed red 1	Fly ash	54.05	0.007	0.43	1.09	Konduru et al.[115], (1997)
Dispersed red 1	Peat	49.73	0.094	5.18	1.71	Konduru et al.[115], (1997)
Dispersed red 1	Bentonite	22.73	8.445	37.7	1.49	Konduru et al.[115],(1997)

2.9. Adsorption kinetic

2.9.1. Pseudo first-order kinetic

The first-order rate expression of Lagergren[116]based on the sorption capacity of adsorbent is generally expressed as follows

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (2.4)$$

Where q_t is the amount of adsorbed pollutant on the adsorbent at time t and k_1 is the rate constant of Lagergren first-order adsorption. After integration and applying boundary conditions t = 0 to t = t and qr = 0 to $q_t = q_t$, the integrated form of equation 2.4 becomes

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2.5)$$

Where q_e and q_t are the amount of adsorbed (mg/g) at equilibrium and at any time t, k_1 is the rate constant (min^{-1}). The plot of log (q_e-q_t) versus t gives a straight line for the first-order adsorption kinetics. The value of the first-order rate constant k_1 is obtained from the slope of the straight line. The k_1 values and the correlation coefficients R^2 and the predicted and experimental q_e values for different adsorbent /dye combinations are given Table 2.8.

2.9.2. Pseudo Second - order kinetic

The pseudo second-order equation is also based on the sorption Capacity of the solid phase [117]. Contrary to the other model it predicts the behavior over the whole range of concentration. The pseudo second-order kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2.6)$$

Where k_2 is the pseudo-second-order rate constant (min g/mg), q_e and q_t represent the amount of dye adsorbed (mg/g) at equilibrium and at any time t. Separating the variables in equation 2.6 gives

$$\frac{dq_t}{(q_e - q_1)^2} = k_2 t \qquad (2.7)$$

Where k_2 is the rate constant of second-order adsorption. For the boundary conditions t = 0, t = t and q_t = 0 q_t = q_t the integrated and linear form of equation 2.7 becomes

$$\frac{t}{q_1} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (2.8)$$

If second-order kinetic is applicable, the plot of t/q_1 against t of equation 2.8 should give a linear relationship, from which q_{eq} and k_2 can be determined from the slope and intercept. Table 2.8 lists values of k_2 and q_e together with their R^2 values for different dye/adsorbent system.

Table 2.8. Comparison of the pseudo first-order and second-order adsorption rate constants some dyes on various adsorbents.

Dyes	**Qe.exp (mg/g)**	**Pseudo first-order kinetic model**			**Pseudo second-order kinetic model**			**References**
		Qe.exp (mg/g)	k_1 (1/min)	R^2	$Q_{e.\ cal}$ (mg/g)	k_2 (min g/mg)	R^2	References
Reactive blue 114	63.50	33.89	2.58×10^{-2}	0.98	67.11	1.54×20^{-3}	0.99	Mahmoodi et al.[118], (2011)
Reactive yellow 64	57.20	56.22	4.61×10^{-2}	0.97	62.50	1.12×10^{-3}	0.99	Mahmoodi et al.[118], (2011)
Reactive red 124	66.90	50.21	4.61×10^{-2}	0.97	70.42	1.85×10^{-3}	0.99	Mahmoodi et al.[118], (2011)
Basic red 18	22.30	6.14	1.10×10^{-2}	0.77	6.46	0.42×10^{-2}	0.97	Gulnaz et al.[90], (2004)
Basic blue 9	19.50	6.16	0.85×10^{-2}	0.73	6.14	0.43×10^{2}	0.98	Gulnaz et al.[90], (2004)
Direct blue 2B	496	141.00	0.03	0.73	500	0.11	0.99	Malik[91], (2004)
Direct green B	298.20	91.80	0.03	0.99	303	0.09	0.99	Malik[91], (2004)
Acid red 14	109.89	7.91	0.33	0.73	67.57	0.12	0.99	Arami et al.[94], (2006)
Acid blue 92	114.94	13.51	0.08	0.33	97.09	0.15	0.99	
Direct red 80	178.57	111.25	0.78	0.98	185.19	0.01	0.99	

2.9.3. 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[55].

- 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.

Adsorption dsorption elementary processes in this case adsorption rate is expected to be proportional to the first power of concentration; it means that this step is a first-order process and can be defined as [87]

$$\frac{dc}{dt} = k_1 C^2 \qquad (2.9)$$

Where C is pollutant concentration in the wastewater remaining at each contact time and k_1 is the first-order reaction-rate constant. After integration and applying boundary conditions t t = 0 to t = t and C = C_0 to C = C; the integrated form of equation 2.9 becomes

$$\log \frac{C_0}{C} = \frac{1}{2.303} k_1 t^2 \qquad (2.10)$$

Where C_0 is the initial pollutant concentration. If intra-particular diffusion is involved in the sorption process, the model developed by Weber and Morris can be used to find the region where intra-particle diffusion is rate-limited and to determine intra-particular diffusion rate. In this model the rate of intra-particular diffusion is a function of tm and can be defined as follows[87]

$$q_1 = \int \left(\frac{D_1}{r_p^2} \right)^2 = k_{dif}\, t^{1/2} + C \qquad (2.11)$$

Where r_p^2 is particle radius, D_1 is the effective diffusivity of solute within the particle and k_{dif} intra-particular diffusion rate constant (mg/ $h^{1/2}$ g). If intra-particle diffusion is rate-limited; then a plot of adsorbate uptake (q) versus the square root of time ($t^{1/2}$) would result in a linear relationship and k_{dif} and C value can be obtained from this plot. Moreover the particle diffusion would be the rate-controlling step if the line passes through the origin.

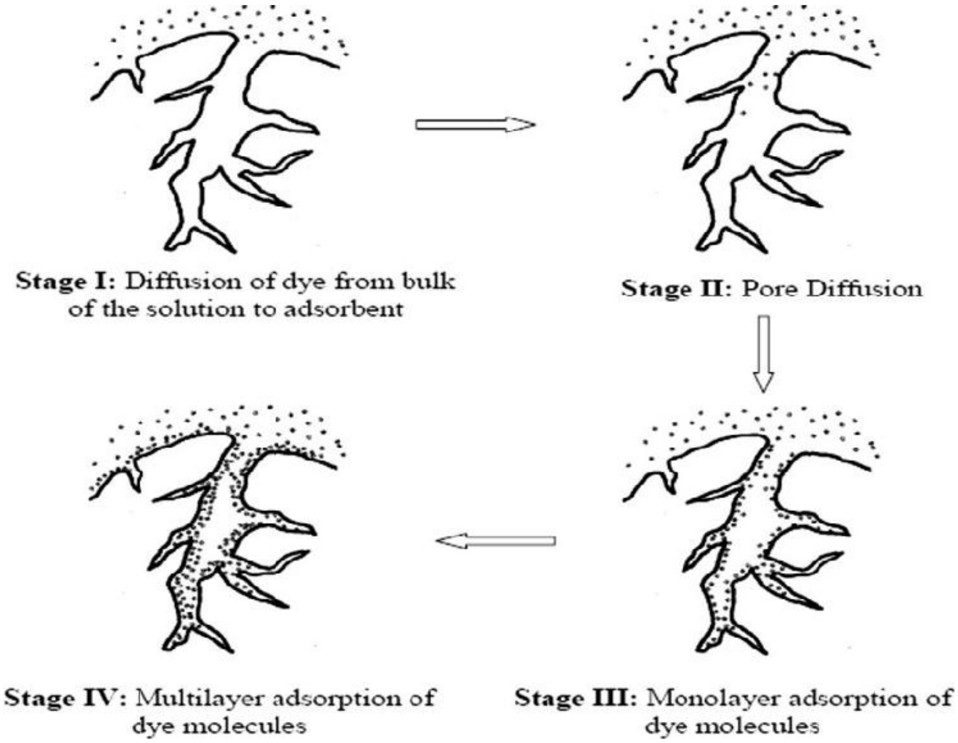


Fig. 2.3. Proposed four-stage mechanism of dye adsorption[119] (Sivakumar and Palanisamy 2010)

In many cases the kinetics of adsorption based on overall adsorption rate by adsorbents are described by the first-order Lagergren and pseudo second-order kinetic models[81]. Aksu studied Intra-particle diffusion rate constant k_{dif} of adsorption of two organic acids (tannic acid and mimic acid) and two dyes (methylene blue and reactive dyes) using composite beads, activated clay and chitosan beads. It was found that adsorption of all adsorbates onto activated clay follows the intra-particle diffusion model best among various adsorbents. The intra-particle diffusion model is better fitted for activated clay and/or chitosan flakes because they are denser solids and have more apparent mass transfer blockage than other adsorbents.

2.10. Sorption Kinetics in Batch Method

Molecular diffusion is one of several phenomena contributing to establishment of rates of transfer of adsorbed materials from the exterior sites of a porous adsorbent to surfaces bounding inner pore spaces. For many applications of adsorption and ion exchange, the rate of intraparticle transport in turn governs the overall rate of removal of solute from solution. For example, although it is certain that adsorptive forces govern positions of equilibrium attained for adsorption of phenol and sulfonated alkylbenzene compounds on porous granular carbon, results of the studies of adsorption of these substances from a dilute solution indicate that in rapidly stirred, batch-type systems the rate of uptake is controlled primarily by rate at which adsorbate is transported from the exterior to the interior sites of the adsorbent particles. There is much further experimental evidence to support the theory that "diffusion" in the pores of solid adsorbents or resins is the ratecontrolling step in many adsorption and ion-exchange processes[83]. Pore diffusion kinetics deriving from intraparticle transport process are particularly pertinent in batch reactors operated at levels of mixing or agitation sufficient to render resistance to film transport less than that for pore transport. Intraparticle transport phenomena may derive from the net action of several molecular forces. For most systems of interest in water and waste treatment applications these may be enumerated as follows: adsorption, two-dimensional micelle formation, three-dimensional micelle formation, electrokineticinteractions, and molecular diffusion[83].

Adsorption, resulting from attractive forces between adsorbate and surfaces of capillary walls and repulsive forces between adsorbate and the aqueous solvent, serves to withdraw adsorbate temporarily from solution. Withdrawal by adsorption retards the transfer of an individual molecule or ion of adsorbate and, at the same time, reduces the effective cross section of the capillary to inhibit diffusion of other molecules. An individual molecular species continually undergoes an exchange process at the surface, alternately, adsorbing at the wall and returning to the solution within the pore space to continue net movement in the direction of decreasing concentration. The detention time at the surface may be increased substantially by the formation of two-dimensional micelles in the adsorbed film, thus further inhibiting free diffusion. Elektrokinetic interaction between adsorbate and adsorbent or between adsorbate and other solutes in a given system may be an important factor in intraparticle transport phenomena, particularly in ion-exchange processes. Carbon surface are generally considered to bear net negative charges; some interference with the movement of ions through the pores of activated carbon may therefore be anticipated.

2.11. Thermodynamic parameters

The pseudo-second order rate constant of dye adsorption is expressed as a function of temperature by the Arrhenius type relationship

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (2.12)$$

Where E_a is the Arrhenius activation' energy of sorption, representing the minimum energy that reactants must have' for the reaction to proceed A is the Arrhenius factor; R is the universal gas constant and T is the solution temperature. When lnk; is plotted versus 1/T a straight line with slope -Ea/R is obtained (Table 2.9). The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5-40 KJ/mol while higher activation energies (40-800 KJ/mol) suggest chemisorption [92].

Table 2.9. The activation energy of dyes adsorption onto various adsorbents

Adsorbents (Dyes)	Adsorbents	Activation energy E_a (KJ/mol)	References
Methylene blue (MB)	Managanese-oxides-modified diatomite (MOMD)	99.80	Ansari et al.[120], (2010)
Reactive black		- 6.74	
Reactive yellow N (RY)		56.65	
Acid red 57	Acid-activated bentonite	29.3	Ozcan and Ozcan[92], (2004)
Acid blue 294	Activated bottom ash	14.6	
Malachite green	Activated bottom ash	3.219×10^2	Gupta et al.[121], (2004)
Methyl violet	Perlite	13.2	Dogan et al.[122], (2009)

Wu et al.[97], studied the adsorption of one basic dye (BB 69) and one direct dye onto activated clay in the temperature range 15-75 ^{0}C. The apparent activation energies for adsorption of BB 69 and DR 227 were found as 8.03 and 17.5 KJ/mol, respectively.

In any adsorption process, both energy and entropy considerations must be taken into account in order to determine what process will occur spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process.

The thermodynamic parameters such as change in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined by using the following equation 2.13 and 2.14,

$$\ln K_c = - \Delta H^0 / RT + \Delta S^0 / R \tag{2.13}$$

$$\Delta G = \Delta H - T\Delta S \tag{2.14}$$

Where R (8,314 J/mol K) is the universal gas constant, T (K) is the absolute temperature. K_C (l/g) is the standard thermodynamic equilibrium constant defined by q_e/ C_e. By plotting a graph of $\ln k_c$ versus 1/T the values ΔH^0 and ΔS^0 Can be estimated from the slope and intercept (see Table 2.10). Table 2.10 lists a composition of thermodynamic parameters of some dyes on various adsorbents.

Table 2.10. Thermodynamic parameters of some dyes on various adsorbents.

Adsorbates	**Adsorbents**	**ΔH^0 (KJ/mol)**	**ΔS^0 (J/mol K)**	**References**
Crystal violet	Fly ash	36.51	209.64	Mohan et al.[80], (2002)
Basic red 9	AC (slurry)	53.06	264	Gupta et al.[121], (2004)
Methylene blue	Red mud	- 31.0	-59.1	Gupta et al.[121], (2004)
Malachite green	Waste slurry blast furnace slag	10.87 18.70	134 163	Gulnaz et al.[90], (2004)
Methylene blue	Bottom ash	24.103	97.712	Gupta et al.[121], (2004)
Congo red	Fullers earth chitin chitosan	158 129 128 127	920 1010 1060 1080	Kumar et al.[123], (2005)
Acid red 57 and Acid blue 294	Modified diatomite		271.5 - 111.9	Ozcan and Ozcan[92],(2004)

2.12. Literature Survey

The use of adsorption process to remove dyestuffs from textile industry wastewaters has been popular in recent years. Many treatment processes have been applied for the removal of dye from waste water. Among treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. 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 sorbate[124]. Activated carbon is the most widely used adsorbent for dye removal because of its extended surface area, 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, baggase, 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.

Hameed et al.[125] studied papaya seeds a novel nonconventional low-cost adsorbent for the removal of (cationic dye) 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 intraparticle 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.

Ponnusami et al.[126] studied Gulmohar (Delonix regia) as adsorbent for the removal of Methylene blue from aqueous solution. The materials were studied without chemical treatment. Authors found the adsorption was favorable at higher pH and lower temperature. The equilibrium data were well fitted by the Langmuir isotherm an appreciable Langmuir capacity of 0.3 mg g-1 was found out.

Immich and Ulson de Souza et al.[127] 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.

Oil palm trunk fiber as an adsorbent was investigated by **Hameed and El-Khaiary** [128] who studied the removal of Malachite green, thereby making an attempt to overcome the economic disadvantages of activated carbon. The adsorbent was studied without any pretreatment and was sieved into different size ranges prior to use. The monolayer coverage of Malachite green on oil palm trunk fiber was found to be 149.35 mg g-1 at 30 ^{0}C.

Wang et al.[129] reported on the capacity and mechanism of adsorption of two basic dyes, namely Malachite green and Methylene blue by rice bran and wheat bran. Rice bran and wheat bran are by-products. 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.

Groundnut shell, an agricultural solid waste has been used as an adsorbent by **Malik** et al.[130] for the removal of Malachite green from aqueous solution. The material is largely available and can be used as a potential sorbents due to their physico-chemical characteristics and low cost. Groundnut shell is easily available at zero prices. Nut shell is carbonaceous, fibrous solid waste, which creates a disposal problem and is generally used for its fuel value.

Abdullah et al.[131] 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.

EI-Khaiary et al.[132] studied the kinetics and mechanism of mehtylene blue adsorption from aqueous solution by nitric acid created water-hyacinth. The experiments were conducted to evaluate the adsorption characteristics of a cataionic dye (mehtylene blue) onto nitric acid created water-hyacinth. Results showed that N-WH can remove MB effectively from aqueous solution. The adsorption kinetics at room temperature could be expressed by the pseudo second order model.

The adsorption kinetics and equilibrium of methylene blue (MB) onto reticulated formic Lignin (RFL) from sugar cane bagasse was studied by **Filho** et al[133]. The adsorption process is *pH*, temperature and ionic strength (μ) dependent.

Dulman and Cucu-Man[134] 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 (pH\pHzpc), the percentage color removal of hydrolyzed reactive dyes was relatively high.

Malik et al.[135] investigated Mahogany sawdust and rice husk as adsorbents for the removal of (acidic dye) Acid yellow 36. The adsorbents were activated by means of steam. The kinetics of the process was found to be dependent on contact time, adsorbent dose and pH. The authors found that an acidic pH is favorable for the adsorption of acid dye. It was observed that adsorption obeys both Freundlich andLangmuir isotherms and the intraparticle diffusion of dyemolecule within the particle is the rate-limiting step.

A Phoenix tree leaf has also been studied as an adsorbent by **Han** et al.[136] 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-1 at 295, 305 and323 K, respectively, makes it an adsorbent of a little importance for dye removal from wastewater.

Namasivayam et al.[104] investigated coir pith, an agricultural solid waste, as an adsorbent for the adsorption of Rhodamine B and Acid violet dyes. The adsorbent was used after drying, sieving and carbonizing at 700 ^{0}C. It was found that Rhodamine B adsorption reached equilibrium stage at 5, 7, 10 and 10 min for dye concentration 10, 20, 30 and 40 mg L-1, respectively, while crystal violet (CV) was found to have equilibrium time of 40 min for all the concentrations. The adsorption capacity was found to be 2.56 and 8.06 mg g-1 of adsorbent for Rhodamine B and Acid violet, respectively.

Coir pith has also been investigated as an adsorbent by **Kavitha and Namasivayam**[95] for the removal of Procion Orange from wastewater. The sorption capacity of 2.6 mg g-1 makes it an adsorbent of little importance for dye removal from wastewater.

Mall et al.[137] utilized bagasse fly ash for the removal of Orange-G (OG) and Methyl violet (MV) from aqueous solution. Results indicated that OG is strongly adsorbed at pH 4.0, whereas MV is strongly adsorbed at pH 9.0. The percentage of dye removal was higher at low initial concentration and increased in amount of adsorbent used. The adsorption data have been correlated with Freundlich, Langmuir, Redlich–Peterson, Dubinin–Radushkevich and Tempkin adsorption models. The authors observed that the Freundlich isotherm gave the best correlation for the adsorption of Orange-Green-bagasse fly ash system and Redlich–

Peterson isotherm better fits the Methyl violet-bagasse fly ash system. The adsorption of Methylene violet and Orange Green followed pseudo-second-order kinetics.

Manaskorn et al.[138] studied bagasse pith from sugarcane industry without any pretreatment for the removal of three reactive dyes, Remazol Black B, Remazol Brilliant Blue and Remazol Brilliant Red from aqueous solutions. High percentage removal was observed for the adsorption of reactive dyes in the order of 58.48–98.03 % for RR Black, 46.15–93.47 % for RB Blue and 46.30–94.60 % for RB Red, respectively.

Muhammad J. iqbal et al.[139] studies the adsorption of industrially important dyes namely Bromophenol blue, Alizarin red, MB, Ericrome black-T, Phenol red, malachite green and methyl violet from aqous media on activated charcoal has been investigated.

Kung, King His. et al.**[140]** studied the adsorption of ten chlorophenols on synthetic naturally occurring Fe and Al oxides to elucidate the mechanism of bonding and relative bond strength of the Cl^- substitutes phenols on oxide surfaces.

D. K. Shing et al.[141] investigated the adsorption of phenol on oxide-coated sand as an adsorbent. Rate of adsorption and break through curves were studies. The adsorption of phenols remains same in the pH range 3-6. The adsorption behavior of 2,4-diclorophenol on alumina**,** manganese (IV) oxideand zinc oxide were investigated at different pH of the solvent, different temperature and using different electrolytes.

Muhammad Naeem Ashiq et al.[142] investigated that the adsorption of industrially important dyes namely Alizarin red, MB, Phenol red, Malachite green Bromophenol blue, Ericrome black-T, and Methyl violet from aqous media on activated charcoal.

Agricultural solid waste such as seed hull has been used as adsorbents for the removal of dye from wastewater. These materials are available in large quantities and may have potential as adsorbents due to their physico–chemical characteristics and low cost. Sunflower seed hull activated with sulphuric acid has been used for the removal of Acid violet 17 by **Thinakaran** et al.[143]. The Langmuir adsorption capacity was found to be 116.27 mg g-1.

The review of **K. S. Bharathi**[144] evaluates different agricultural waste materials as low-cost adsorbents for the removal of dyes from wastewater. The review also outlines some of the fundamental principles of dye adsorption on to adsorbents.

Garg et al.[75] studied Rose wood sawdust a low-cost adsorbent for the removal of Malachite green from aqueous solution. Further, in order to know the effect of chemical treatment and to improve its efficiency the authors also tested the potential of the adsorbent by treating it with formaldehyde and sulphuric acid. Besides this, studies on the effect of pH, initial concentration, adsorbent dose and contact time were also carried out by Garg et al.

Turabik[69] investigated the removal of Basic Blue 3 from a synthetic wastewater by adsorption onto bentonite. The effects of contact time, initial dye concentrations, and mass of adsorbent, agitation speed, pH and temperature on adsorption were examined in this study. Turabik stated that the adsorption capacity of bentonite increases with a decrease of particle size and initial dye concentration. Langmuir Isotherm was applied and adsorption capacity of bentonite was obtained as 75.18 mg/g. Turabik found that the effects of agitation speed and temperature on adsorption were not important. Also, different pH values gave similar adsorption capacities except for pH at 12 at which a slightly lower adsorption capacity was achieved.

Norlisa Harruddin et al.[145] studied reactive dye of Black B was separated using the supported liquid membrane process. Commercial polypropylene membrane was used as a support of the kerosene–tridodecylamine liquid membrane.

Kartik H. Gonawala et al.[146] investigation is carried out on colarane blue BGFS Anthraquinone dye. Powdered Fe_2O_3 has been used for dye removal practical. It was observed that maximum dye removal efficiency at pH 2 with Fe_2O_3 dosage of 0.3 gm and initial concentration is 125 ppm. Practicals were also carried out on actual wastewater.

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Chapter - 3

Removal of Remazol Red from Textile Waste Water Using Treated Sawdust : An Effective Way of Effluent Treatment

Abstract

Activated carbon prepared from sawdust is endeavored as adsorbent for the removal of reactive dye, namely Remazol Red (RR) from aqueous media. The adsorption of RR has been studied onto activated sawdust at various particle size, adsorbent dose, temperature and pH values. The adsorptions of the above mentioned dye were designed for the Langmuir and Freundlich Isotherms. Pseudo first and second order kinetic models were used to calculate the amount adsorbed at equilibrium condition (q_e). The calculated values of q_e for pseudo-second order equation were found to be in good agreement with those of experimental values. The monolayer capacity (q_m) for treated sawdust (8.00 mg g $^{-1}$) is greater than for commercial charcoal (0.074 mg g $^{-1}$). It is established that treated sawdust is a better adsorbent for the removal of RR as compared to commercial charcoal.

3.1. Introduction

Industrial effluents are one of the major pollutants of water. Many dyes are carcinogenic and affect the life of aquatic organisms[1, 2]. Removal of azo dyes from the effluent generated by textile industries is rather difficult. Azo dyes represent a major class of synthetic colorants that are both mutagenic and carcinogenic[3]. Reactive dyes are extensively used in textile industry and due to their large size they have high affinity to bind with cellulosic fiber. The worldwide annual growth rates of reactive dyes are four times as much as for conventional dyes[4]. Vinyl sulfone dyes are a class of reactive dyes effectively used for cotton, silk and wool. They are also known as remazol dyes after the trademarked name under which they were first introduced. Vinyl sulfone dyes are less reactive than other dyes and therefore major part of these dyes remains in dyeing bath or drained off as industrial effluents. It has been reported that up to 30% of the used dyestuff remains in the spent dye-bath after the dying process[5]. Presence of such dyes in effluents causes a lot of pollution in water. Various challenges have been made to remove these harmful dyes from industrial wastes[6, 7, 8].

Adsorption is one of the cheapest and most effective techniques [9, 10]. Different adsorbents are used for the removal of dyes from aqueous solutions such as alumina, crushed bricks, peat, sand, charcoal bentonite, silica, apricot etc[11, 12, 13, 14]. The most widely used adsorbent for the removal of dyes are commercial charcoal which is expensive and not easily available. Therefore, the interest is growing to find out an alternative adsorbent to commercial charcoal. The removal efficiency of untreated sawdust for RR is 45-55% but for treated sawdust, it is around 96%.

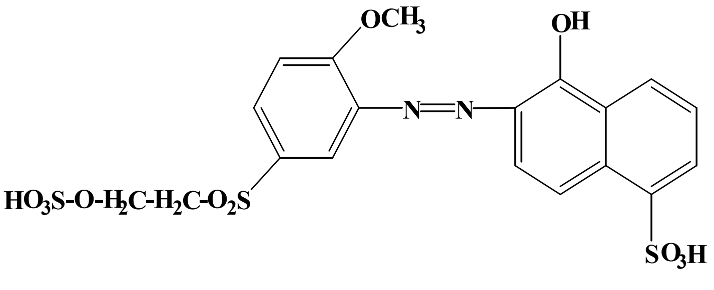


Fig. 3.1. Structure of Remazol Red.

The objective of this work is to study the feasibility of activated charcoal prepared from sawdust as alternate adsorbents to commercial charcoal[15, 16] for the removal of Remazol Red (RR, Fig.3.1). The adsorption results of RR onto saw dust are also compared with that of commercial charcoal.

3.2. Experimental

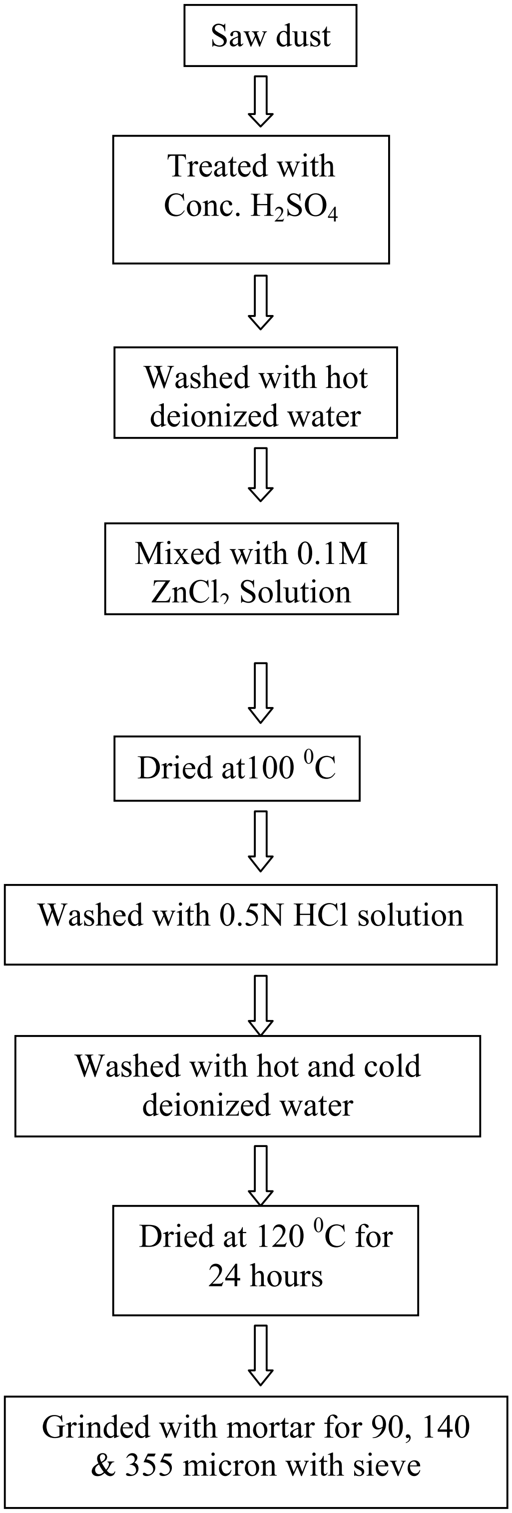
3.2.1. Materials and Methods

3.2.1.1. Preparation of activated charcoal (Treated sawdust)

There are two different methods for the preparation of activated carbon: physical activation and chemical activation[6]. In comparison to physical activation, chemical activation provides advantages. The process of dye removal was applied in batch mode. Adsorption experiments were performed by suspending charcoal in the effluent and analyzing the supernatant by spectroscopic method.

Sawdust (*Shegun, Tectona grandis*) was collected from local carpentry workshop (Rampura, Dhaka, Bangladesh). This was washed with double distilled water to remove water-soluble impurities and surface-adhered particles. Then the adsorbent was oven-dried at 60 ^oC to remove the moisture and other volatile impurities. Then, part of the dried sawdust was soaked in concentrated H_2SO_4 in an amount sufficient to cover the material completely, agitated at 120 rpm in a shaking incubator for 30 min, and then left for 2h. After being mixed, the slurry was subjected to drying at 100 ^oC for 24 h. Chemical activation of the sawdust was performed with $ZnC1_2$. Ten grams of sawdust was mixed well with 100 ml of 10% $ZnC1_2$solution. The mixing was performed at 50 ^oC for 1 h. After mixing, the slurry was subjected to vacuum-drying at 100^o C for 24 h[7, 15]. The resulting impregnated solids was placed in a stainless steel tubular reactor and heated(5^0C min^{-1}) to a temperature of 300 ^oC under nitrogen flow at a rate of 150 cm^3 min^{-1} at STP for 1 h. Nitrogen entering the reactor was first heated to 250-300 ^oC in a preheater. The products were washed sequentially with 0.5 M HCI, hot water, and finally cold distilled water to remove residual organic and mineral materials and then dried at 110 ^oC. In all experiments, the heating rate and nitrogen flow were kept constant. The preparation of the activated charcoal has been presented in the following flowchart:

Flow chart for the preparation of activated charcoal from saw dust



3.2.1.2. Preparation of Dye Solution

Remazol Red (RR) was used in the experiment. It is a reactive dye supplied by Dye Star Ltd., Dhaka, Bangladesh. This dye form covalent bond with the fiber, usually cotton, although it is used to a small extent on wool and nylon. This class of dyes first introduced commercially in 1956 and made it possible to achieve extremely high washing fastness properties by relatively simple dyeing methods. A stock solution of 1000 ppm RR was prepared by dissolving appropriate amount of dye in water. The required concentration was prepared for the various steps of the investigation by dilution.

3.2.1.3. Study of Batch Adsorption Process

Equilibrium isotherms for adsorption onto the selected carbons determined by using 1 g of adsorbent per 50 ml of aqueous solution for initial dye concentrations in the range of 50-200 ppm. For these experiments, the bottles were shaken at constant temperature (25 ^{o}C) and agitation speed (120 rpm), for the minimum contact time required to attain equilibrium, as determined from the kinetic measurements. The effectiveness of the treatment was evaluated by measuring concentration by UV-Visible spectroscopic method at 520.5 nm. The influence of pH was studied by adjusting the reaction mixture to different initial pH values and analyzing the residual color at the equilibrium contact time. The pH values were adjusted with dilute sulfuric acid and sodium hydroxide solutions. Then the percentage of dye removal was calculated by,

$$R = \frac{(C_0 - C_e)}{C_0} \text{x } 100\% \qquad (3.1)$$

The amount of dye adsorbed onto the activated carbons, q_e (mg/g), was calculated according to:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (3.2)$$

Where C_0 and C_e are the initial and the final dye concentrations (mg/L), respectively, and W is the amount of adsorbent (g), V is the volume of the solution (L).

3.3. Results and Discussion

3.3.1. The physical properties of treated sawdust

The physical properties of the treated sawdust have been shown in the Table 3.1. From the table it is found that the BET surface area [17] is 5.69 m^2/g and the average pore diameter is 99.60 A^0. The point of zero charge (pzc) of the above mentioned adsorbent is 3.7.

Table 3.1. Physical properties of treated sawdust (Activated charcoal)

Properties	**value**
Particle size (µm)	<140
BET surface area (m^2/g)	5.69
Average pore diameter (A^0)	99.60
Micro pore volume(cc/g)	0.014
Micro pore area (m^2/g)	2.37
Bulk density (g/mL)	0.84
pzc	3.7

3.3.2. Characterization of adsorbent (Treated sawdust) by FTIR

In order to obtain complementary evidence for the interaction of ions onto the surface, FTIR spectra of untreated saw dust, treated saw dust, and loaded treated saw dust were recorded in the region of 500-4000 cm^{-1} as shown in the following Fig. 3.2, 3.3 and 3.4.

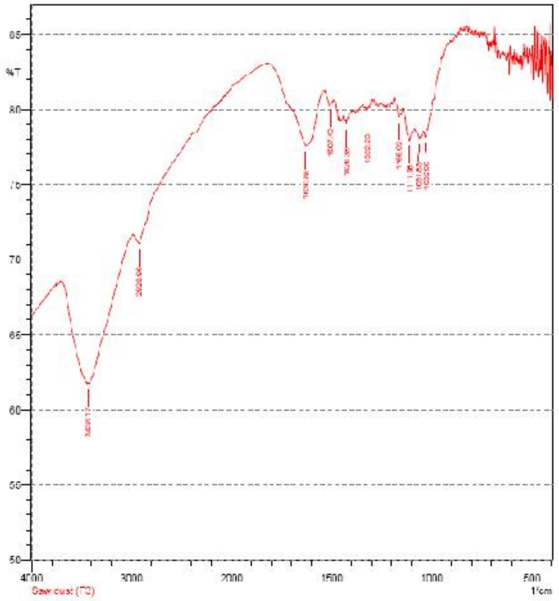


Fig. 3.2. FTIR spectra of untreated saw dust

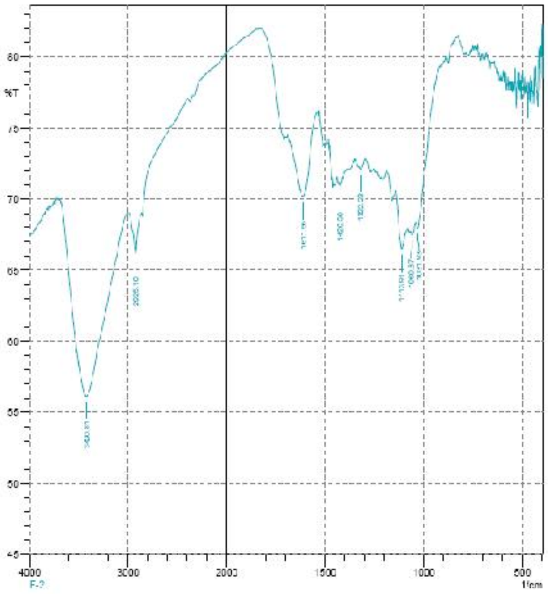


Fig. 3.3. FTIR spectra of treated saw dust

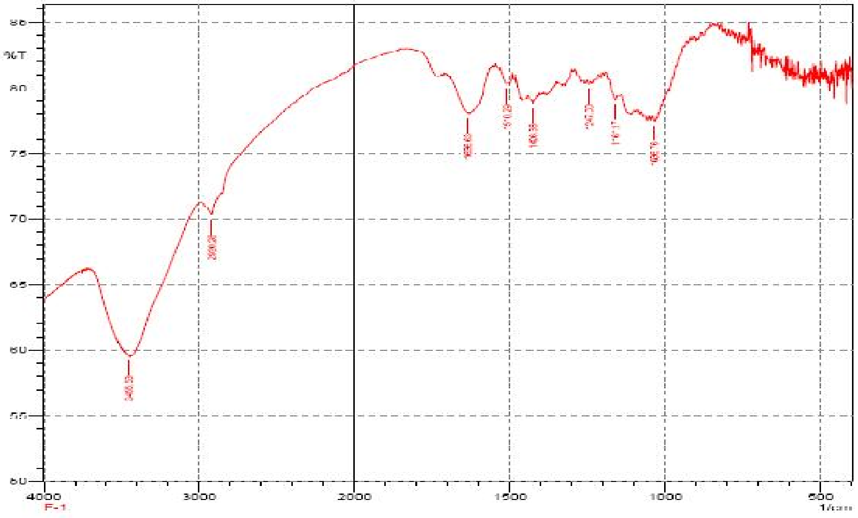


Fig. 3.4. FTIR spectra of treated saw dust after adsorption.

Table 3.2. The observed bands are given below:

Wave no. (cm^{-1})	Region (cm^{-1})	Type of vibration	Group
3455	3300-3460	O-H str.	Intermolecular hydrogen bonded OH
2925	2500-3000	O-H str.	Carboxylic acids
1636	1610-1650	C=O str.	Carboxylic acids
1426	1420-1430	CH_2 str.	Cellulose and lignin
1322	1315-1330	C-H str.	Cellulose and hemicelluloses
1113	1100-1180	S=O str.	Sulfonic acid
1036	1010-1115	M-O str.	Alumina, K, Ca ,Mg etc

FTIR spectra of untreated sawdust, treated sawdust and treated sawdust after adsorption were shown in Fig.3.2, 3.3, 3.4. FTIR peak was analyzed for the presence of different bonds (Si-O, Zn=O, C-C, C-H bending, C-H stretching and O-H) according to standard data[18, 19] and presented in Table 3.2. From the FTIR analysis it was found that O-H peak shifted from 3438 cm^{-1} to 3420 cm^{-1} for treated sawdust. In addition, O-H peak shifted to 3466 cm^{-1} for adsorbed charcoal.

3.3.3. Optimization of Contact time

The contact time between dye and adsorbent is of significant importance in waste water treatment by adsorption methods. A rapid removal of pollutants and establishment of equilibrium in a short period signifies the efficacy of the adsorbent. The effect of shaking time for the adsorption of dye onto charcoal prepared from sawdust was determined at 25 ^{o}C. The fixed concentration of RR was shaken after adding 1g of adsorbent in each time. Color removal was rapid at initial stage but decreased with the increase of time (Fig. 3.5). Initially rapid increase was due to the presence of large number of vacant site and with the passage of time, number of active sites decreased which were responsible for the reduction of adsorption rate. The optimum contact time was observed for 12 hours for the adsorbent.

3.3.4. Optimization of adsorbent amount

For optimizing the amount of adsorbents, experiments were performed using 50 ml aqueous solution of RR and was shaken for 120 minutes after adding different amount of adsorbents (0.5-3.0 g). Absorbance of the filtrate was noted using spectrophotometer at max λ of the dye. It was observed that adsorption of dye increased with the increase of the amount of adsorbents and then attained constant value at equilibrium (Fig. 3.6). The optimum amount was found to be 1.0g which was used for all subsequent adsorption.

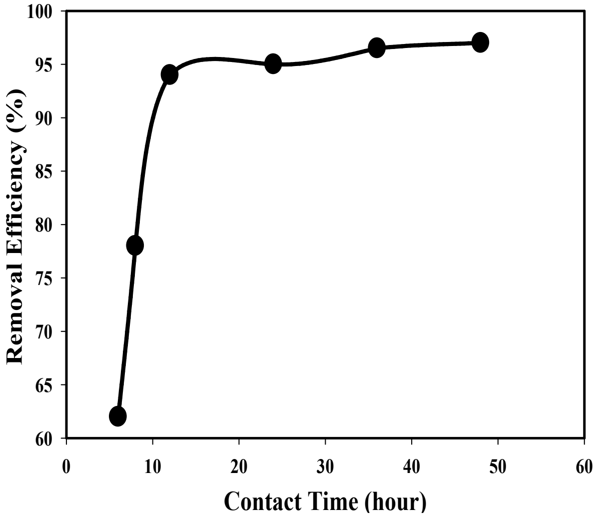


Fig. 3.5. Effect of contact time on the removal of RR**.** Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

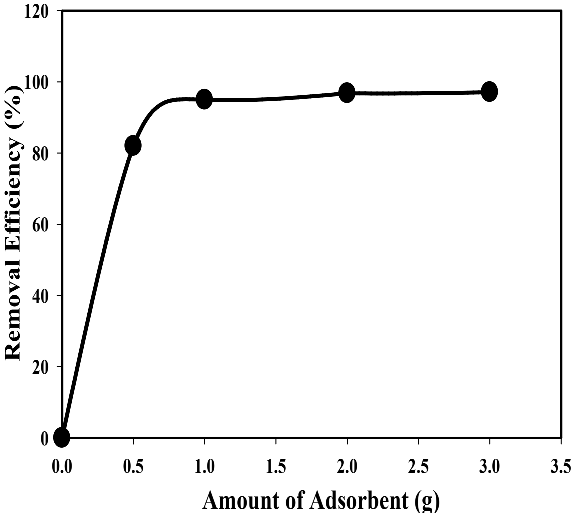


Fig. 3.6. Effect of adsorbent amount on the removal of RR. Particle size: 140µm; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Contact time: 12 hours; Temp.: 25 ^{0}C.

3.3.5. Effect of pH

Hydrogen and hydroxy1 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 of RR decreased with increase in pH (Fig.3.7). 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 (Equation 3.3), adsorption of dye decreases at higher pH values.

$$ASO_3\ Na \overset{H^+-OH^-}{\Longleftrightarrow} ASO_3^-Na^+ \tag{3.3}$$

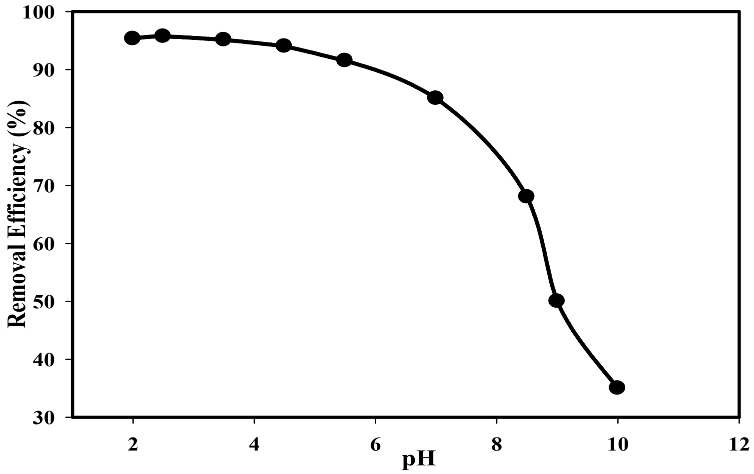


Fig. 3.7. Effect of pH on the adsorption capacity of saw dust for RR. Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; Contact time: 12 hours; Temp.: 25 ^{0}C.

The amount of dye adsorbed on the surface of the adsorbent decreases with the increase of pH is in good agreement with the data reported earlier [15].

3.3.6. Effect of Particle Size

From the Fig. 3.8, it is clear that lower is the particle size higher is the adsorption efficiency. When the size of the TSD particles increase, the adsorption of dye solution decrease. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites. Therefore, particle size <140µm was chosen for the next experiment.

3.3.7. Optimization of Initial Concentration

The removal efficiency is highly dependent on the initial concentrations of dye solution. The effect of the initial sample concentration on the removal of dye with saw dust (SD) was investigated. The initial concentration was evaluated in the range of 50-150 mg/L and the results were illustrated in Fig. 3.9. The removal efficiency decreased with increasing of initial concentration of sample solution. From this experiment, it is observed that higher removal efficiency was achieved using 50g/L of dye solution.

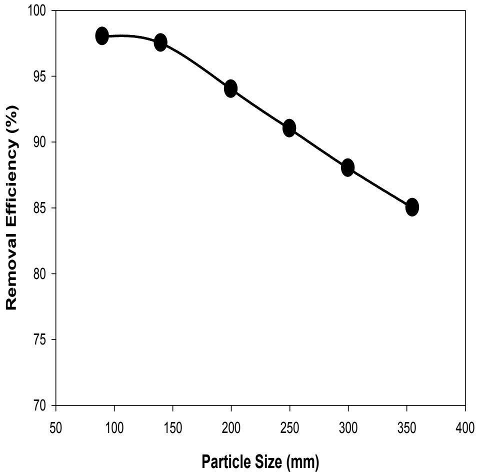


Fig. 3. 8. Effect of particle size on the removal of RR. Contact time: 12 hours; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

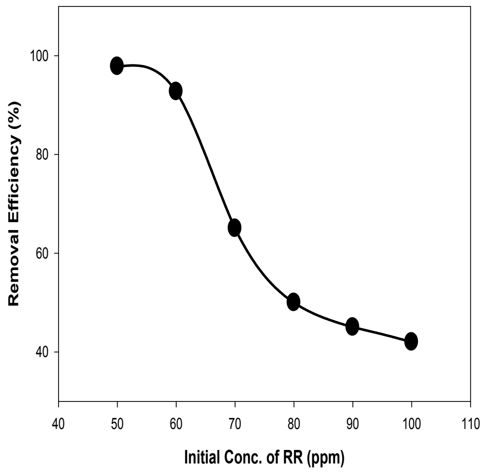


Fig. 3. 9. Effect of initial concentration of dye RR. Particle size: 140μm Adsorbent amount: 1.0 g; Initial volume: 50 mL; pH: 7.0; Contact time: 12 hours; Temp.: 25 ^{0}C.

3.3.8. Optimization of the initial volume of dye solution

Different initial volumes with optimized concentration 50 mg/ L of dye solution were observed onto treated saw dust. It shows clearly that removal efficiency decreases with increase of initial volume. The removal efficiency varied from 95 to 75 % with initial volume 25 mL to 80 mL. Decrease of the removal efficiency suggests that it happened due to the decrease of contact of dye with active sites on saw dust. At lower volume of dye solution, most of the dye might get available adsorbent sites.

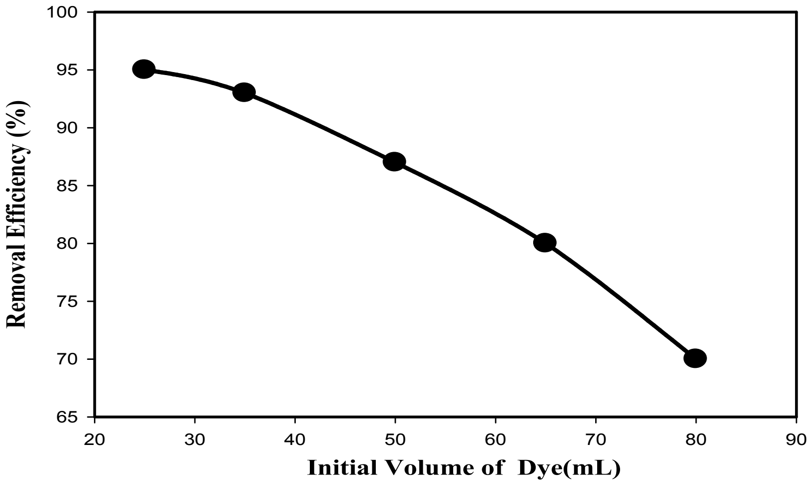


Fig.3.10. Effect of initial volume on the removal of RR. Particle size: 140µm ; Adsorbent amount : 1.0 g; Initial conc.: 50 mg/L ; pH: 7.0; Contact time: 12 hours; Temp.: 25^{0}C

3.3.9. Adsorption Isotherms

The adsorption isotherms of RR on sawdust were found to be L-type in each case [6]. The initial sharp rise in the degree of adsorption with increasing dye concentration is due to the availability of higher adsorption sites on the surface of the adsorbents. When the concentration of dye solution increases, adsorption sites are decreased. As a result, the dye molecules find difficulty to access the remaining vacant surface. Adsorption of RR is found to be slightly increased with increase in temperature then remain almost constant (Fig. 11). This indicates that desorption process is more favorable at lower temperature and is expected to be an endothermic process.

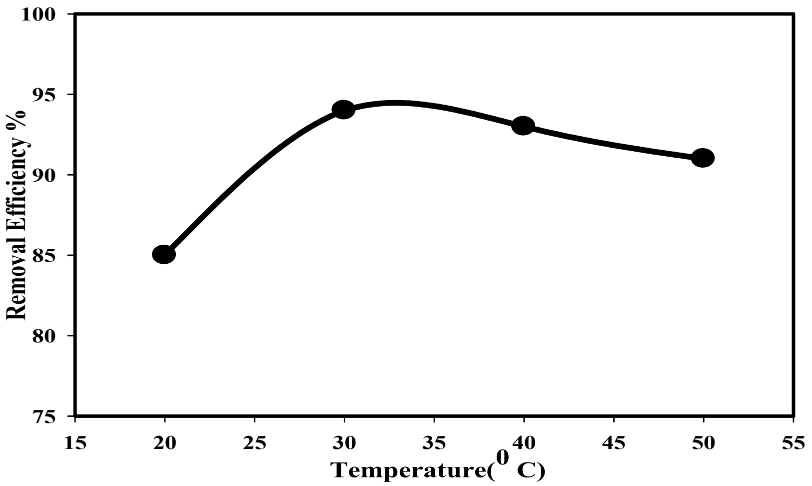


Fig.3.11. Effect of temperature on the removal of RR .Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7; Contact time: 12 hours.

Adsorption data for Remazol Red onto activated sawdust (charcoal) was fitted to the linear forms of Freundlich (3.4) and Langmuir (3.5) equations

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(K_F) \qquad (3.4)$$

Where q_e(mg/g) is the amount adsorbed per unit mass of the adsorbent, C_e is the equilibrium concentration, K_F and 1/n are constants, being indicative of the extent of adsorption and degree of non-linearity between solution concentration and amount of dye adsorbed respectively.

From Freundlich plot (Fig.3.12.), the constants K_F and n are calculated from the intercepts and slopes of linear plots of $\log(q_e)$ versus $\log(C_e)$, respectively and their values are given in Table 3. If $n = 1$, adsorption is homogeneous and there is no interaction between the adsorbed species. If $n < 1$, the adsorption is unfavorable and if $n > 1$, then the adsorption is favorable. In present studies, we have found that n is greater than unity for the given adsorbents which indicates that adsorption is favorable. It has also been reported that the value of K_F gives rough estimation about the degree of adsorption. In the present studies it was observed that the value of K_F for the adsorption of RR onto treated saw dust (1.71 mg g^{-1}) is greater than those for commercial charcoal

(1.41 mg g^{-1}), (Table 3.3). Greater value of K_F for activated sawdust reflects that it is better adsorbent for the removal of RR than commercial charcoal.

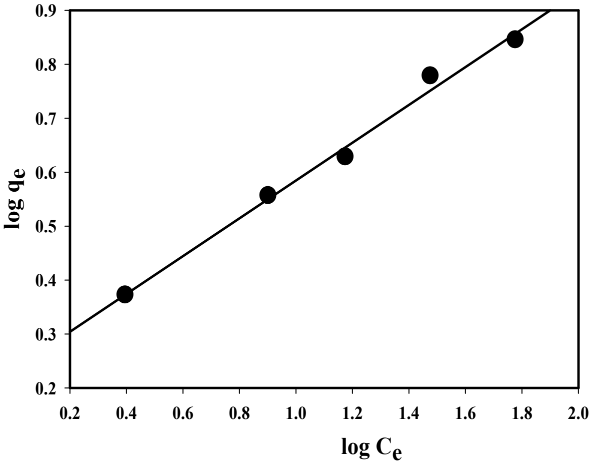


Fig. 3.12. Freundlich isotherms of RR on saw dust at 25 ^{0}C

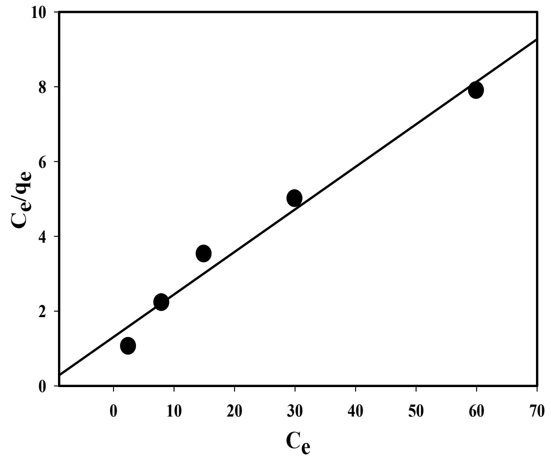


Fig. 3.13. Langmuir isotherms of RR on sawdust at 25 ^{0}C.

Table 3.3. Freundlich parameters for Remazol red on Sawdust and commercial activated carbon at 25 ^{0}C.

Adsorbents	**n**	**K_F(mg/g)**	**R^2**
Prepared activated saw dust	2.85	1.71	0.991
Commercial activated carbon	1.79	1.41	0.998

Langmuir equation is given as

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \tag{3.5}$$

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(K_L q_m)$, where C_e is the equilibrium concentration (mg/dm^3), q_e is the amount of dye sorbed (mg/g), q_m is q_e for a complete monolayer (mg/g), and K_L is the sorption equilibrium constant (dm^3/mg).The essential characteristics of Langmuir eqn. can be expressed in terms of separation factor R_L[20].

Where $R_L = 1/(1+K_L.Co)$.

* $R_L > 1$; Unfavorable.

* $0 < R_L < 1$; Favorable.

* $R_L = 1$; Linear.

* $R_L = 0$; Irreversible.

Table 3.4. Langmuir Parameters and Separation factor R_L for Adsorption of RR on treated sawdust.

Adsorbent	**K_L/ L mg^{-1}**	**q_m/ mg g^{-1}**	**R^2**	**R_L**
Prepared activated saw dust	0.105	8.00	0.988	0.045
Commercial activated carbon	7974.8	0.074	0.9448	0.351

3.3.10. Adsorption Kinetics

In order to investigate the adsorption processes of Remazol Red onto sawdust two kinetic models were used. Pseudo-first order kinetic equation is given as[6]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{1.303}t \qquad (3.6)$$

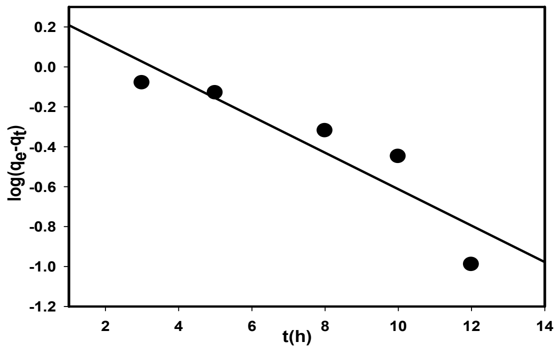
Where, q_t is the amount of dye adsorbed at time t (mgg^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}), $k_1$is the pseudo-first order rate constant (min^{-1}) and t is the contact time (min).

Values of the constants, k_1 and q_e for the adsorption of dye on the adsorbents were determined from the slopes and intercepts of the plots $\log(q_e - q_t)$ against t, respectively and their values are given in Table 3.5.

Pseudo-second order model can be represented in the following form

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e}t \qquad (3.7)$$

Where, k_2 is the Pseudo-second order rate constant (g $mg^{-1}min^{-1}$). The values of the q_e and k_2 were determined by potting a graph between t/qt and time.



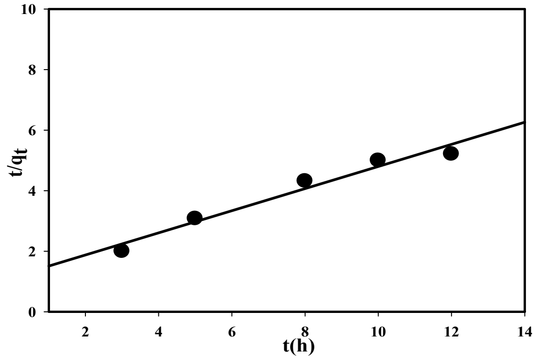


Fig. 3.14. Pseudo first order kinetics plot for the adsorption of Remazol Red on treated saw dust at 25 ^{0}C.

Fig.3.15.Pseudo second order kinetics plot for the adsorption of Remazol Red on treated saw dust at 25 ^{0}C.

3.3.11. Intra-particle diffusion

Weber and Morris[21] proposed the intra-particle diffusion model to identify diffusion mechanisms of adsorption process. The effect of intra-particle diffusion resistance on adsorption can be determined by the following relationship.

$$q_t = k_{id}\, t^{1/2} + C$$

Where k_{id} is the intra-particle rate constant (g mg^{-1} min$^{-1/2}$), and the intra-particle rate constant k_{id} is a function of equilibrium concentration in solid phase qe and intra-particle diffusivity. Adsorption mechanism follows the intra-particle diffusion model, a plot of q_t against $t^{1/2}$ should give a linear line with slope kid and intercept *C*. Values of *C give* information about the thickness of the boundary layer, i.e. the larger intercept the greater is the boundary layer effect. If the plot of uptake, q_t, versus square root of time, $t^{1/2}$ passes through the origin, the intra-particle diffusion will be the sole rate limiting process.

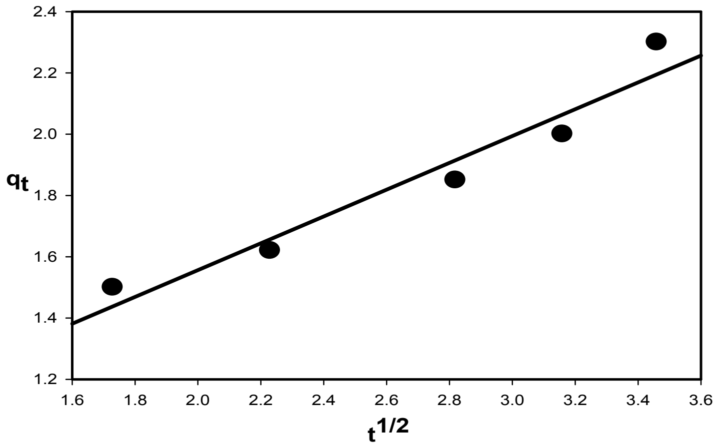


Fig. 3.16. Intra-Particle Diffusion Model of Remazol Red

The results of adsorption kinetics were processed based on the three kinetic models: pseudo-first order, pseudo-second and intra-particle diffusion models. Theoretical and experimental data for the adsorption kinetics are given in Table 3.5. The experimental values of q_e are closer to the calculated values for second order kinetics than those of first order kinetics. The value of correlation coefficient (R^2) for second order is also closer to unity as compared to that of first order (Table 3. 5). Therefore, the adsorption of selected dye on treated sawdust more appropriately followed pseudo second order kinetic model. The intra-particle diffusion plots for adsorption of dyes were linear but did not pass through the origin, indicated that the pore diffusion isn't the rate limiting step of the studied adsorption process.

Table 3. 5. Kinetics parameters for the adsorption of Remazol Red on sawdust.

Pseudo first order Kinetic model			**q_e exp. mg/g**	**Pseudo second order Kinetic Model**			**Intra.Diff. Cons.**
q_e (mg/g)	k_1 (h^{-1})	R^2		q_e (mg/g)	k_2 (h, g/mg)	R^2	k_{id}
2.62	o.26	0.83	2.36	2.73	0.092	0.96	0.437

3.3.12. Desorption kinetic

Desorption process usually done by mixing a suitable solvent with the dye-saturated substrate and shaken together for fixed time, until the dye extract on the solvent and then using filtration to separate the adsorbent. The dye–solvent mixture dried at high temperature to evaporate the solvent. The desorbed dye then determine in spectrophotometer. The results obtained are shown in Fig.3.17, which shows that the amount of desorption increases with time. This also indicates that the adsorption is physical in nature, which is consistent with thermodynamic study.

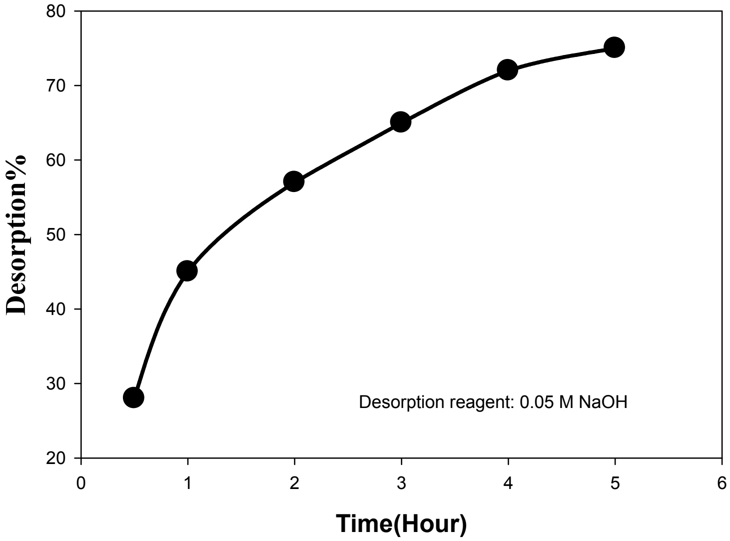


Fig. 3.17. Plot of desorption of Remazol Red vs. time

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dyes. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. If hydrochloric acid or alkaline water desorp the dyes, then the adsorption is by ion exchange. If organic acids, like acetic acid desorp the dyes, then the dye is attached to the adsorbent through chemisorption. The effect of various reagents used for desorption studies (Table 3.6) shows that sodium hydroxide is a better reagent for desorption, because we could get more than 75% removal of adsorbed dyes. The reversibility of adsorbed dyes in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of dyes by mineral acids and alkaline medium indicates that the dyes are adsorbed onto the activated carbon by physisorption. The effect of various reagents used for desorption studies (Table 3.6) shows that sodium hydroxide is a better reagent for desorption, because we could get more than 77 % removal of adsorbed dyes.

Table 3.6. Results of different reagent on desorption

Adsorbent	**Regenerant solvent**	**Desorption%**
Treated Sawdust	Distilled Water	18
	HCl (0.05 M)	8
	NaOH(0.05 M)	77.22

3.4. Conclusion

In the present investigation activated charcoal prepared from saw dust was found to be better adsorbent for the removal of Remazol Red from aqueous media as compared to commercial charcoal. Adsorption of the investigated dye decreases with the increase in pH and slightly increases with temperature of the solution. It was observed that adsorption process followed pseudo-second order kinetic model. Values of q_e calculated from pseudo second order plots are in good agreement with the experimental values. This developed method will be very successful for selectively separating the present dye contaminants, regenerating the exhausted biomass, recovering the sorbed dye and designing to continuous dye treatment systems.

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Chapter - 4

Application of activated Coir dust for efficient removal of Remazol Blue from aqueous solution of dye

Abstract

The adsorption of Remazol Blue (RB) dye on activated charcoal prepared from coir dust was investigated in a batch process. The effects of adsorbent dosages, contact time, pH and solution temperature were evaluated. The adsorption equilibrium and kinetic were found to follow Freundlich isotherm models and pseudo-second-order kinetic model, respectively. Results from thermodynamic adsorption show that interaction for RB dye was found to be feasible, nonspontaneous, and endothermic. Furthermore, it was found that a maximum uptake of Remazol Blue was ~95% by activated charcoal prepared from Coir dust. This result indicates that activated carbon (Coir dust) could be employed as low-cost alternatives to commercial activated carbon for the removal of reactive dyes (RB) from wastewater.

4.1. Introduction

The effluents from the dyestuff manufacturing and textile industries, in particular, are highly colored with a large amount of suspended organic solids and considered as important sources of water pollution. When the quality of the environment is considered, removal of synthetic dyes becomes a must, because some of these dyes and their degradation products may be carcinogenic and toxic. Consequently, their treatment cannot solely depend on biodegradation alone[1]. Indeed, removal of dyes is nowadays regarded as an important practice in textile wastewater treatment.

Numerous physiochemical and biological methods have been used to decolorize dye bearing effluents, often in combinations as one single treatment may not be sufficient to remove certain classes of synthetic dyes[2, 3]. Adsorption has been found to be an efficient and economic method for dyes removal. One of the advantages is the possibility to use a large variety of solid materials: synthetic to natural low-cost materials (natural as well as wasted materials from different industries and agriculture) as suitable adsorbents for decolorization of industrial effluents[4]. Various types of activated carbon[5, 6] and polymeric ion-exchange resin[7] have been used to remove a wide range of dyes from water. However, these adsorbents are not so efficient. As a consequence, there has been considerable effort directed toward development of low cost and highly efficient adsorbents for color removal[8]. The most widely used adsorbent for the removal of dyes are charcoal prepared from saw dust which is inexpensive and easily available. Recently, Jahan Ara et al. developed a dye removal method with activated charcoal prepared from saw dust [9]. The developed method only applied for the removal of remazol red (RR) from wastewater. The efficacy of the adsorbent, however, varies from one material to another. It was also found that uptake of RB was very poor by natural coir dust(30-40%).Therefore, the present work is undertaken with a view to develop activated charcoal from coir dust for the removal of Remazol blue from waste water. The objective of the work is to study the feasibility of activated charcoal prepared from coir dust as alternate adsorbents to commercial charcoal for the removal of Remazol blue (RB). In this study activated charcoal was prepared from coir dust by sulfuric acid and zinc chloride. Finally, it was used as adsorbent to remove Remazol Blue dye from aqueous solutions. Remazol Blue (RB), (Fig.4.1.) is a reactive dye which is extensively used in textile industry [10].

4.2. Experimental

4.2.1. Preparation of activated charcoal

Natural coir dust shows very poor removal efficiency (30-40%).Therefore chemical activation was considered to increase the removal efficiencies of dye. There are two different processes for the preparation of activated carbon: physical activation and chemical activation[11]. In comparison to physical activation, chemical activation provides advantages. The process of dyes removal was applied in batch mode. Coconut coir is a fibrous material found between the leathery covering and the shell of a coconut**.** Adsorption experiments were performed by suspending coir dust in the effluent and analyzing the supernatant by spectroscopic method. Coir dust was collected from Luxmipur district. This was washed repeatedly with distilled water to remove adhering dirt and soluble impurities. Then it was oven-dried at 90 ^{o} C to remove the moisture and other volatile impurities. Then, part of the dried coir dust was soaked in concentrated H_2SO_4 in an amount sufficient to cover the raw material completely, agitated at 120 rpm in an incubator shaker for 30 min, and then left for 2h. After being mixed, the slurry was subjected to drying at 100 ^{o}C for 24 h.

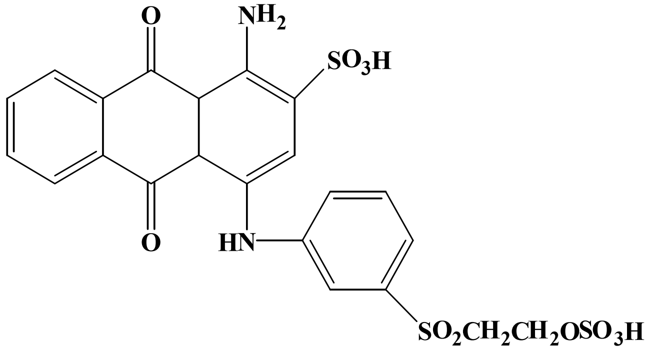

Fig. 4.1. Chemical structure of Remazol Blue.

Chemical activation of the coir dust was performed with $ZnCl_2$. Ten grams of coir dust was well mixed with 100 ml of a concentrated solution that contained 10 g of $ZnCl_2$. The mixing was performed at 50 ^{o}C for 1 h. After being mixed, the slurry was also be subjected to drying at 100 ^{o}C for 24 h[12, 13]. The resulting impregnated solids were placed in a stainless steel container and heated (5 ^{o}C min^{-1}) to a temperature of 300 ^{o}C for 1 h. The products were washed sequentially with 0.5 N HCI, hot water, and finally cold distilled water to remove residual organic and mineral materials and then dried at 110 ^{o}C. Dried coir dust then passed through sieves of various sizes.

4.2.2. Point of Zero charge

Determination of pH_{zpc} was done to investigate how the surface charge of adsorbent material depended on pH. The point of zero charge (pH_{ZPC}) for the coir dust was determined by the following procedure: 100 mL of deionized water was added to an Erlenmeyer flask, which was then capped with cotton. The deionized water was heated until boiling for 20 min to eliminate the CO_2 and dissolved ions in the water. The CO_2 free water was cooled as soon as possible, and the flask was immediately capped. Now this water is free from both cations and anions, and it is considered to be a neutral one. On the other hand, 0.5 g of activated carbon (coir dust) was weighed and placed in a 25 mL Erlenmeyer flask to which 10 mL of CO_2 free deionized water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at 25 °C. The pH of the solution was measured, and this value is the point of zero charge [9].

4.2.3. Preparation of dye solution

A widely used dye Remazol Blue (RB) was used in this experiment. It is a reactive dye supplied by dye star Ltd., Dhaka, Bangladesh. Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive dyes are highly used for dyeing of cotton, wool, nylon, silk etc. This class of dyes first introduced commercially in 1956, made it possible to achieve extremely high washing fastness properties by relatively simple dyeing methods. The chemical structure of dye is shown in Fig.4.1. A stock solution of RB was prepared by dissolving necessary amount of dye in water. The required concentration was prepared for various steps of the investigation by dilution.

4.2.4. Study of Batch Adsorption Process

Aqueous solutions of reactive dye were prepared by dissolving the dye in distilled water to the required concentrations (50-250ppm). Equilibrium isotherms for adsorption onto the selected carbons determined by using 1 g of adsorbent per 50 ml of aqueous solution. For these experiments, the bottles were shaken at constant temperature (25 ^{o}C) with agitation speed (120 rpm), for the minimum contact time required to attain equilibrium, as determined from the kinetic measurements. The effectiveness of the treatment was evaluated by measuring concentration by UV-Visible spectroscopic method at 607 nm. BET surface area and other properties of the activated charcoal were measured by Surface area analyzer (Quanthachrome Nova 2200 e, USA). The influence of pH was studied by adjusting the reaction mixture to different initial pH values and analyzing the residual color at the equilibrium contact time. The pH values were adjusted with dilute sulfuric acid and sodium hydroxide solutions.

Table 4.1. Physical properties of activated charcoal prepared from Coir dust.

Properties	**Value**
Particle size	<140 µm
BET Surface Area (m^2/g)	5.96
Average Pore Diameter (A^0)	95.12
Micro Pore Volume(cc/g)	0.016
Micro Pore Area (m^2/g)	2.27
Bulk Density (g/mL)	0.79
pH_{zpc}	5.11

Then the percentage of dye removal was calculated by,

$$R = \frac{(C_0 - C_t)}{C_0} \text{ x } 100\% \tag{4.1}$$

The amount of dye adsorbed onto the activated carbons, q_e (mg/g), was calculated according to:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{4.2}$$

Where C_0 and C_e are the initial and the final dye concentrations (mg/L), respectively, and W is the amount of adsorbent (g), V is the volume of the solution (L).

4.3. Results and discussion

4.3.1. Physical Properties of the activated charcoal

The physical properties of the activated charcoal prepared from coir dust have been presented in Table 4.1. From the table it is found that the BET surface area is 5.96 (m^2/g) and the average pore diameter is 95.12 A^0. The point of zero charge of the prepared activated charcoal is 5.11.

4.3.2. Effect of Adsorbent Dosage

For optimizing the amount of adsorbents, experiments were performed using 50 mL aqueous solution of RB and were shaken for 120 minutes after adding different amount of activated charcoal (0.5−2.5g). Absorbance of the filtrate was noted using spectrophotometer at λmax of the dye. It was observed that adsorption of the dye increased with increase of the amount of adsorbent and then attained constant value at equilibrium as shown in Fig. 4.2. Fig. 4.2 shows that about 94% of dye was removed with 1.0 g charcoal. With increasing the amount of adsorbents (from 0.5 g to 2.5g) removal efficiency also increased. However, 1.0−2.5g of adsorbent showed almost the similar removal efficiency with same particle size of <140μm. This was due to the agglomeration of the particles themselves so that the removal efficiency was not significantly increased with amount of adsorbents. Therefore 1.0 g of adsorbent was chosen for all the subsequent adsorption studies.

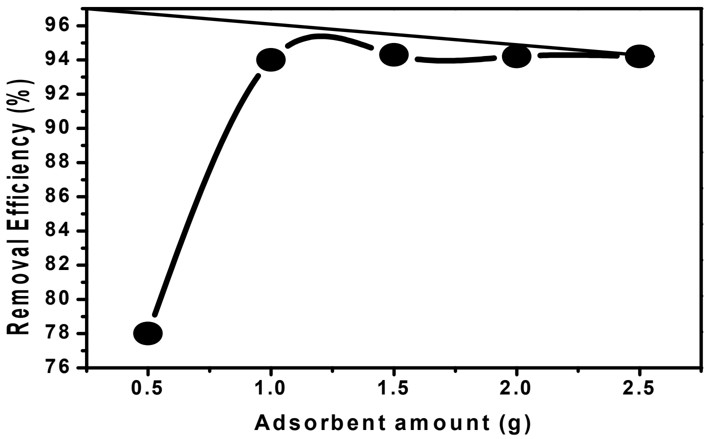

Fig. 4.2. Effect of adsorbent amount on the removal of RB. Particle size: 140μm; Initial concentration: 50 mg/L; Initial volume: 50mL ; pH: 7.0; Contact time: 6 hours; Temp.: 25 ^{0}C.

4.3.3. Effect of Contact Time

The contact time is one of the factors affecting the development of surface charges at the solid solution interface. The effect of period of contact on the removal of Remazol Blue (RB) by the activated charcoal was determined by keeping other conditions (initial concentration of the dye, initial volume, pH and temperature) constant. The effect of contact time was investigated by treating 1.0 g of the activated charcoal with 50 mL of 50 mg/L RB solution at pH value of 7. The mixture was agitated with mechanical shaker for different periods of contact time (1-8 h). The results are presented in Fig. 4.3. It was observed that the removal efficiency of RB dye increase with contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material. As the data shows the adsorption process was rapid for the first 4 h. Therefore, 3.0 h contact time was chosen for all the subsequent adsorption studies.

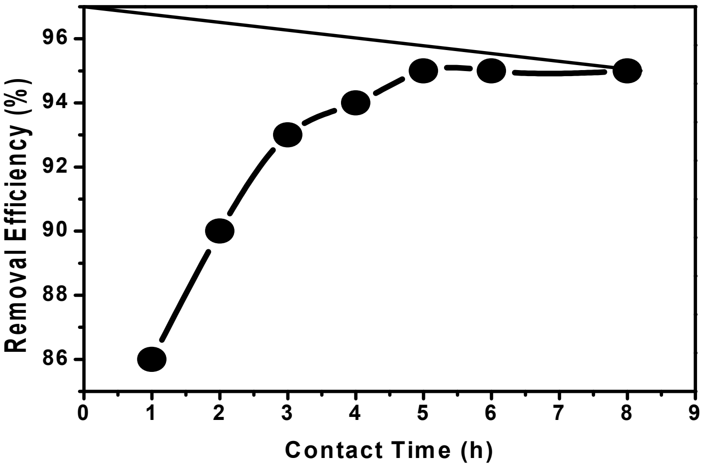

Fig. 4.3. Effect of contact time on the removal of RB. Particle size : 140μm ; Adsorbent amount : 1.0 g; Initial conc.: 50 mg/L ; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

4.3.4. Effect of Particle Size

From the Fig. 4.4, it is clear that lower the particle size higher the adsorption efficiency. The size of the coir particles increased the adsorption of dye solution decreased. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites. Therefore**,** particle size <140µm was chosen for the next experiment.

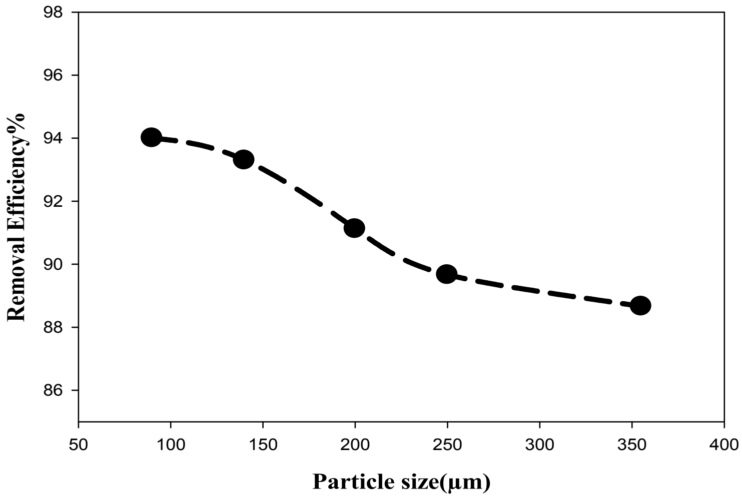

Fig. 4.4. Effect of particle size for the removal of RB. Contact time: 6 hours; Adsorbent amount : 1.0 g; Initial conc.: 50 mg/L ; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C

4.3.5. Effect of initial concentration of dye

The removal efficiency is highly dependent on the initial concentrations of dye solution. The effect of the initial sample concentration on the removal of dye with coir dust (CD) was investigated. The initial concentration was evaluated in the range of 50-200 mg/L and the results were illustrated in Fig. 4.5. The removal efficiency decreased with increasing of initial concentration of sample solution. From this experiment, it is observed that higher removal efficiency was achieved using 50g/L of dye solution. Therefore, 50mg/L dye solution was chosen for the next experiment.

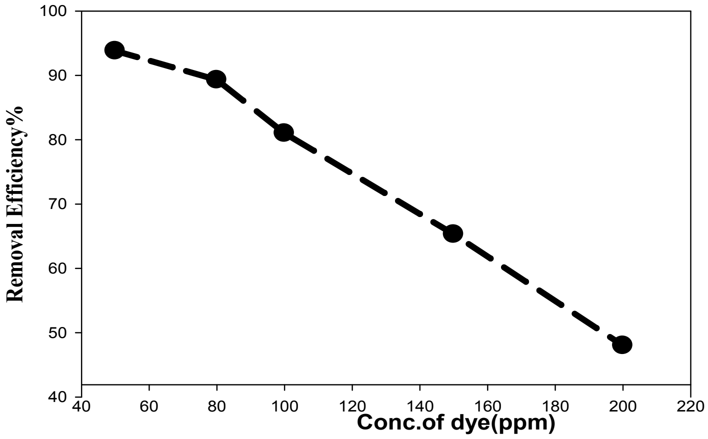

Fig. 4.5. Effect of initial concentration of dye on removal of RB. Contact time: 6 hours; Adsorbent amount : 1.0 g; Particle size : 140μm; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

4.3.6. Effect of pH

In the present work, the pHzpc of the activated charcoal (coir dust) was found to be 5.11. Different species may present divergent ranges of suitable pH depending on which adsorbent is used. When pH of the solution is less than pHzpc, the surface of the activated charcoal is positively charged and attractive to anions [14, 15]. In this study, the effect of pH on the percentage of removal of Remazol Blue (RB) dye using activated carbon was evaluated as shown in Fig. 4.6. To investigate the effect of pH, the experiment of adsorption of dye solution was carried out at different pH value (2.0—12.0) by using 0.01 M HCl and 0.01M NaOH aqueous solution.

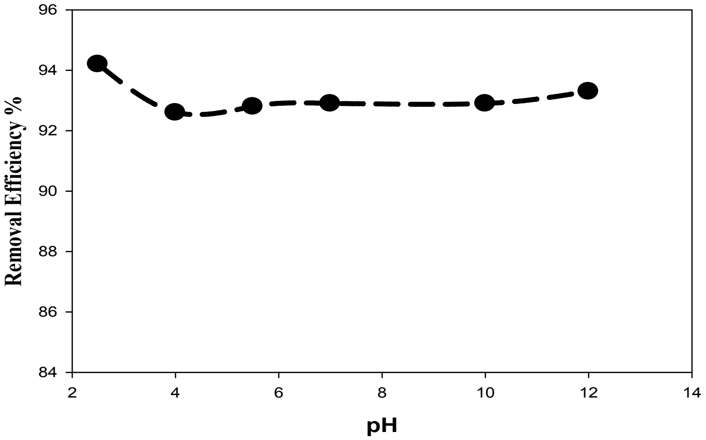

Fig. 4.6. Effect of pH on the removal of RB. Particle size: 140μm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL Contact time: 6 h; Temp.: 25^{0}C.

It could be seen that at lower pH the adsorption of dye is slightly high. After this adsorption of dye remain unchanged for variation of pH. So, the maximum uptake was observed at the pH ranges 3-12. At pH 2.5-3.5, the attributed electrostatic interactions between the positively charged of activated charcoal and the negatively charged of RB dye prefer to give highest removal percentage (95%).

4.3.7. Optimization of the initial volume of dye solution

As it is desired to obtain the optimum conditions for the development of a noble method for dye removal; the effect of initial volume was also investigated. Different initial volumes with optimized concentration 50 mg/ L of dye solution were treated onto treated coir dust and results were summarized in Fig.4.7 respectively. It shows clearly that removal efficiency decreases with increase of initial volume. The removal efficiency varied from 97 to 75 % (For CD) with initial volume 25 mL to 100 mL. Decrease of the removal efficiency suggests that it happened due to the decrease of contact of dye with active sites on coir dust. At lower volume of dye solution, most of the dye might get available adsorbent sites. Moreover, increasing volume of the dye solution, active adsorbent sites were unavailable due to fill by the previous dye solution.

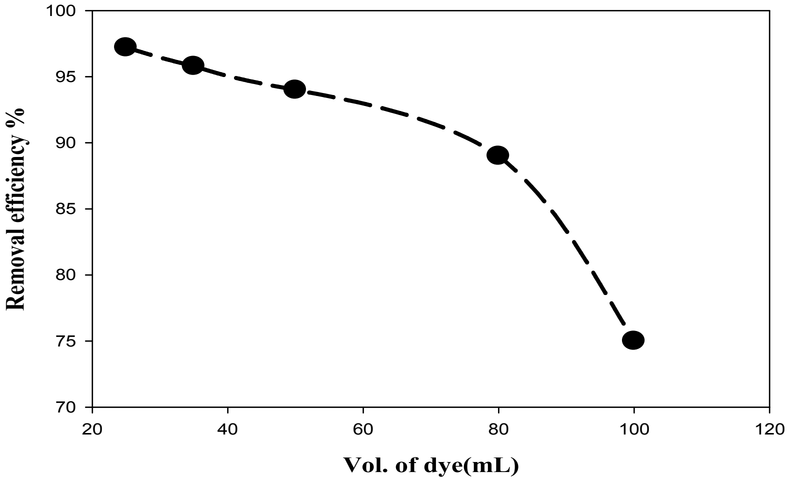

Fig. 4.7. Effect of initial volume of dye on the removal of RB. Particle size : 140µm ; Adsorbent amount : 1.0 g ;Initial conc.: 50 mg/L ; Contact time: 6 h; Temp.: 25^0C.; pH: 7.0.

4.3.8. Effect of Temperature

To determine the equilibrium temperature for the maximum uptake of dye solution (RB), the adsorption onto activated carbon was studied for the above optimized condition as a function of temperature (25—50 ^{0}C) is presented in Fig.4.8. A study of the temperature dependence of adsorption process gives valuable information about the enthalpy change during adsorption. Fig.4.8 indicates that the removal efficiency increases slightly with increasing temperature from 20 ^{0}C to 50 ^{0}C which indicates that the adsorption process was in endothermic nature. Increasing the temperature has increased the diffusion of dye molecule to across the external and internal boundary layer of sample due to decrease in solution[16]. In addition, at higher temperature more dye molecules have sufficient energy to undergo an interaction with active sites of adsorbent and enhance the dye mobility to penetrate inside the adsorbent's pores[17].

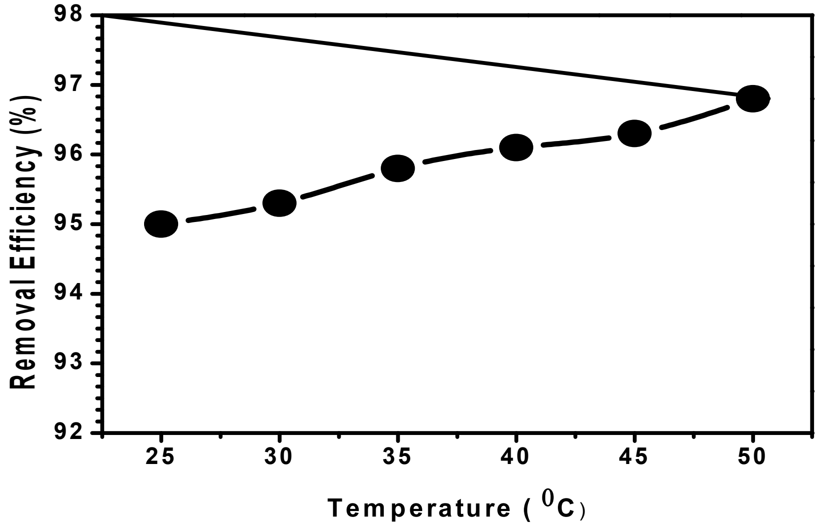

Fig. 4.8. Effect of temperature on the removal of RB. Particle size: 140µm; Adsorbent amount: 1.0g; Initial conc.: 50 mg/L ; Initial volume: 50 mL; Contact time: 6 h; pH: 6.

4.3.9. Adsorption Isotherm

The adsorption isotherm used to show the adsorption molecules distribute between the solid phase and liquid phase at adsorption equilibrium state. The Langmuir and Freundlich isotherms are the most frequently employed models. The linear regression is used to determine the best-fitting isotherm and the pertinences of isotherm equations is compared by evaluating the correlation coefficients, R^2. Langmuir's isotherm model is based on the theory that adsorption energy is constant and uptake occurs on homogeneous surface by monolayer adsorption.

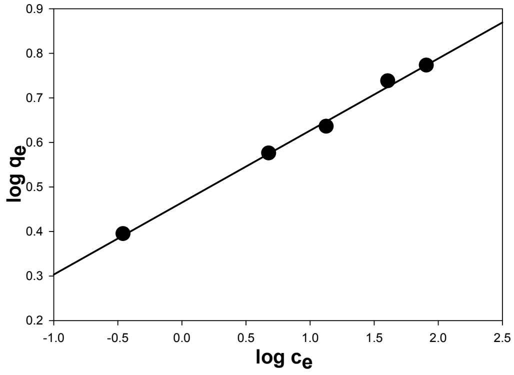

Fig. 4.9. Freundlich isotherms of remazol blue on activated carbon at 25 °C.

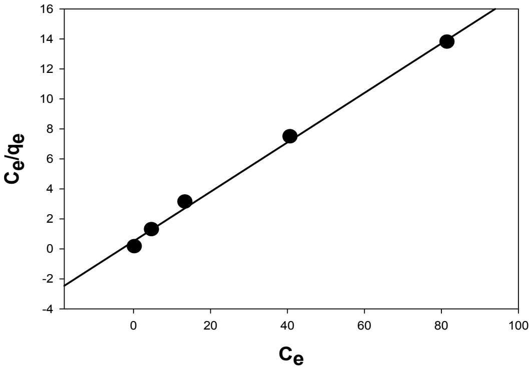

Fig. 4.10. Langmuir isotherms of remazol blue on activated carbon at 25 °C.

When the surface is covered by monolayer of adsorbate, the adsorption goes on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs[18]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \qquad (4.3)$$

Where, C_e (mg/L) is the RB equilibrium concentration and q_e (mg/g) is the amount of RB adsorbed per unit mass of adsorbent, q_m(mg/g) is the Langmuir constant related to adsorption capacity and K_L (L/mg) is rate of adsorption. The values of q_m and K_L were calculated from the intercept and slope of linear plot and are presented in Table 4.2.

Freundilch model[19] is an empirical expression that is the earliest known relationship describing the adsorption equation. This isotherm takes into account a heterogeneous surface and multilayer adsorption to the binding sites on the surface of the adsorbent. The Freundlich model is expressed in the following equation:

$$\log(q_e) = \frac{1}{n} \log(C_e) + \log(K_F) \qquad (4.4)$$

Where, K_F and n are indicative isotherm parameters of adsorption capacity and adsorption intensity, respectively. Generally, n >1 illustrates that adsorbate is favorably adsorbed on the adsorbent. The higher of n values favors the adsorption process as well as intensify the adsorption[20]. From the Freundilch and Langmuir plot (Fig. 4.9 and Fig. 4.10), the isotherm results are presented in Table 4.2. From the Table 4.2, it was found that Freundlich model gave higher R^2 values (0.989) than Langmuir model (0.966), which indicate that RB adsorption by activated carbon was made up of heterogeneous surface and multilayer adsorption [21]. This result is similar to other works on reactive dye adsorption by activated carbon prepared from coir pith[22].

Table 4.2. Freundlich and Langmuir parameters for Remazol Blue on activated carbon prepared from coir dust

Freundlich isotherm			**Langmuir isotherm**			
K_F	n	R^2	q_m	K_L	R^2	R_L
2.916	6.184	0.989	6.064	0.325	0.996	0.015

4.3.10. Adsorption Kinetics

Kinetics adsorption data of RB dye on activated charcoal was analyzed using two kinetic models: pseudo-first-order and pseudo-second order. The pseudo-first-order kinetic model is shown by the following equation [11]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{1.303}t \qquad (4.5)$$

Where, q_t is the amount of dye adsorbed at time t (mgg^{-1}), q_e is the amount adsorbed at equilibrium ($mg\ g^{-1}$), $k_1$is the pseudo-first order rate constant (min^{-1}) and t is the contact time (min).

The values of the constants, k_1 and q_e for the adsorption of dye on the adsorbents were determined from the slopes and intercepts of the plots $\log(q_e - q_t)$ against t, respectively and their values are given in Table 4.3.

Pseudo-second order model can be represented in the following form

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e}t \qquad (4.6)$$

Where, k_2 is the Pseudo-second order rate constant ($gmg^{-1}min^{-1}$). The values of the q_e and k_2 were determined by potting a graph between t/q_t and time. The applicability of the pseudo first order and pseudo second order model can be examined by linear plot shown in Fig. 4.11 and 4.12.The linearity of this plot indicates the applicability of the two models. However the correlation coefficient, R^2 shows that second order model fits the experimental data better than the pseudo first order model.

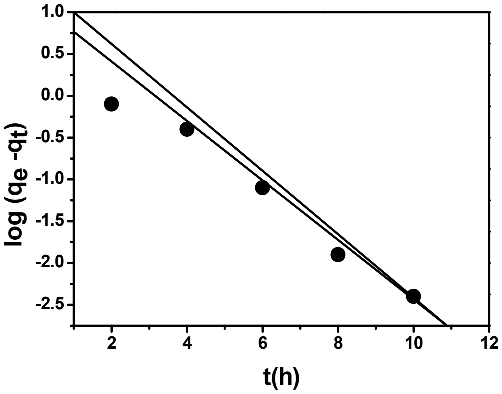

Fig.4.11. Pseudo first order kinetics of RB

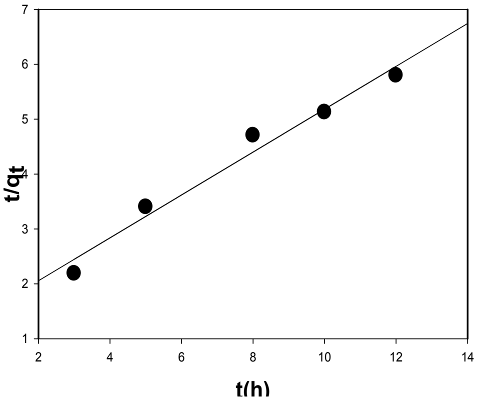

Fig.4.12. Pseudo second order kinetics of RB

4.3.11. Intra-particle diffusion

Weber and Morris[23] proposed the intra-particle diffusion model to identify diffusion mechanisms of adsorption process. The effect of intra-particle diffusion resistance on adsorption can be determined by the following relationship.

$$q_t = k_{id}\, t^{1/2} + C$$

Where *k*id is the intra-particle rate constant (g mg^{-1} $min^{-1/2}$), and the intra-particle rate constant *k*id is a function of equilibrium concentration in solid phase q_e and intra-particle diffusivity. Adsorption mechanism follows the intra-particle diffusion model, a plot of q_t against $t^{1/2}$ should give a linear line with slope kid and intercept *C*. Values of *C give* information about the thickness of the boundary layer, i.e. the larger intercept the greater is the boundary layer effect. If the plot of uptake, q_t, versus square root of time, $t^{1/2}$ passes through the origin, the intra-particle diffusion will be the sole rate limiting process. The intra-particle diffusion plots (Fig.4.13) for adsorption of dyes were linear but did not pass through the origin indicated that the pore diffusion isn't the rate limiting step of the studied adsorption process.

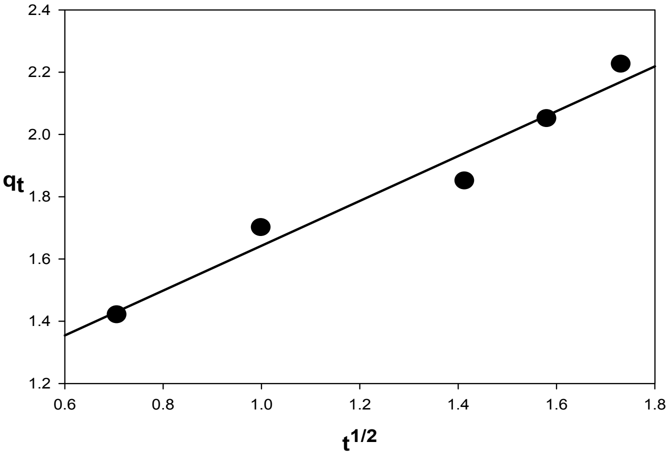

Fig. 4.13. Intra-Particle Diffusion Model of RB

4.3.12. Desorption kinetic

In the desorption studies, the loaded adsorbent was separated from solution by centrifugation and dried. The results obtained are shown in Fig-4.14, which shows that the amount of desorption increases with time. This also indicates that the adsorption is physical in nature, which is consistent with thermodynamic study.

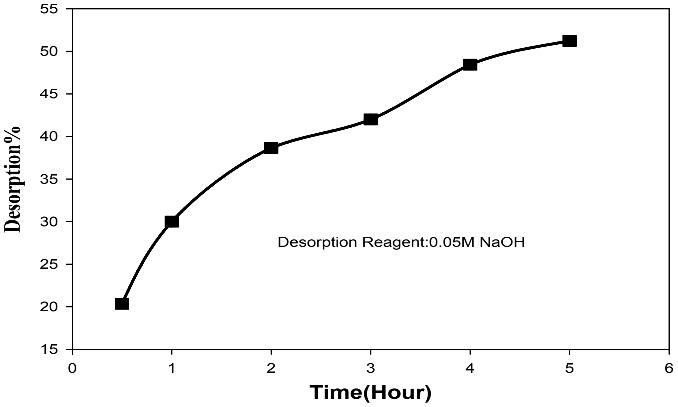

Fig. 4.14. Plot of desorption vs time for RB

Extensive investigation is perhaps needed to find out more suitable condition for desorption. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. Since the adsorbents used for dye removal are rather cheap and readily available, regeneration does not seem to be really necessary and it can also be burnt with the sorbed dye as a source of energy. The effect of various reagents used for desorption studies shows that sodium hydroxide is a better reagent for desorption, because we could get more than 50% removal of adsorbed dyes. Poor desorption% then other adsorbents implies strong interaction between RB and coir dust.

Table 4.3. Kinetic parameters for the adsorption of Remazol Blue on activated carbon prepared from coir dust.

Pseudo first order Kinetic model			**q_e exp. mg/g**	**Pseudo second order Kinetic model**		
q_e (mg/g)	k_1 (h^{-1})	R^2		q_e (mg/g)	k_2 (h , g/mg)	R^2
1.57	0.856	0.97	2.48	2.85	0.641	0.99

4.4. Conclusion

The adsorption of RB on activated charcoal prepared from Coir dust was favoured at neutral medium. The Freundlich model was fits well to the adsorption equilibrium.The results indicated that the pseudo-second order equation provided the best correlation with the experimental data. Thermodynamic adsorption studies indicated that the adsorption process was physically controlled. The use of this low-cost biosorbent is recommended since this are relatively cheap or of no cost, easily available and show high affinity for dyes. Such advantages make it suitable method for the removal of dyes such as RB from textile wastewaters.

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Chapter - 5

Effect of Salts on the removal of Remazol Yellow by using activated Charcoal prepared from Sawdust

Abstract

The effect of electrolyte on the activated charcoal (Treated sawdust) for the removal of Remazol Yellow (RY) dye was studied. The maximum percentage of dye removal was obtained as 94% with 1.0 g/50 mL of NaCl electrolyte. The Langmuir showed the best fit with equilibrium isotherm data. The interactions were evaluated with respect to both pseudo-first-order and pseudo-second-order reaction kinetics. The adsorption process was found to follow the pseudo-second-order model. To optimize the operating conditions, the effect of pH, temperature, adsorbent dosage, and initial dye concentration and initial volume of dye solutions were investigated. The obtained results indicated that the utilization of activated charcoal produced from saw dust played an important role in the removal of RY dye from aqueous solutions. In addition, saw dust was low cost and easily available material. It can be used an alternative adsorbent precursor for more expensive adsorbents used for the removal of Remazol Yellow.

5.1. Introduction

Globally, thousands of dyes stuffs are being synthesized daily and also being released in the environment in the form of effluents during synthesis and dyeing process [1]. Reactive dyes are the most common dyes used due to their favorable characteristics of bright color, water fastness, simple application techniques, and low energy consumption. They exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups[2,3]. They are not easily biodegradable, thus, the colour may remain in the effluent even after extensive treatment[4, 5]. If waste products are improperly managed, public health and the environment could be threatened[6, 7].

To remove dyes and other contaminants from waste water, several physical, chemical and biological methods have been developed, such as membrane separation, flocculation coagulation, adsorption, ozonization and aerobic/anaerobic treatments[8,9,10]. However, these technologies are generally unsuccessful in colour removal, expensive, and less adaptable to a wide range of dye wastewaters [11, 12]. The low cost, simple design, easy handling, and sludge-free cleaning operations have established the adsorption technique as more effective and convenient in comparison to other techniques[13].

Adsorption now plays a key role in modern industries, mainly in the field of environmental protection engineering, with the increasing environmental consciousness of people all over the world. Adsorption processes are being employed widely for large scale biochemical, chemical, and environmental recovery and purification applications[14]. Over the last few decades, adsorption has been recognized as an influential separation process and has become an attractive option for the removal of dyes from industrial effluents [15]. Among various adsorbents, activated carbons are the most effective because of their excellent adsorption capacity for organic targets[15]. Many studies have been undertaken to investigate the use of low cost adsorbents such as peat, wood shavings, silica[11,16-18,] coir pith[19], sugar beet pulp[20], sugar cane bagasse pith[21], jute fiber[22], soybean[23], and wheat husk[24] for colour removal. Unfortunately, these low cost adsorbents have generally low adsorption capacities and require large amounts of adsorbents. Therefore, a need arises to find new, economical, easily available, and highly effective adsorbents[11].

Wood industries in Bangladesh produce a lot of saw dust as by products. These byproducts are usually disposed of by burning or by deposition in landfills, but conversion to higher-value products would be preferable. One such product could be activated carbon. Previously, we have studied the removal of Remazol Red with activated charcoal prepared from saw dust[25]. However, no information is available on removal of Remazol Yellow with activated charcoal prepared from saw dust. In this present research, the effects of salts on the removal of Remazol Yellow by activated charcoal prepared from saw dust was studied. Without salt Removal efficiency of RY was 83% but it was 94% in presence of salt. Effects of various experimental parameters were investigated in batch mode to measure the removal efficiency of dye. The isothermal data could be well described by the Langmuir and Freundlich isotherm. The kinetic data were well fitted to pseudo-second order model.

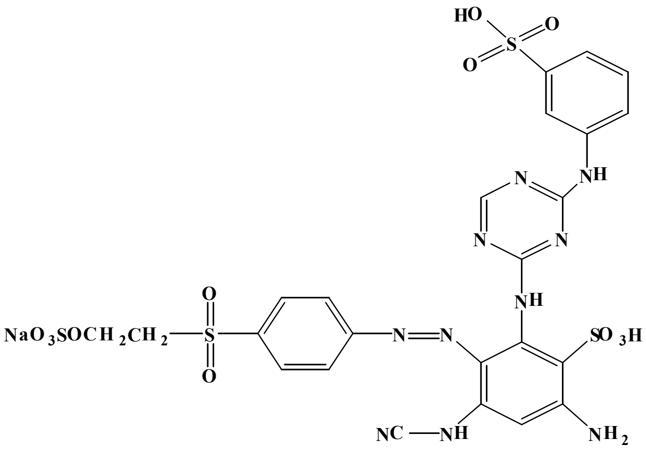

Fig. 5.1. Chemical structure of Remazol Yellow.

5.2. Experimental

5.2.1. Preparation of activated charcoal

Saw dust is a by-product of saw mills, where it is produced from the cutting of wood. Utilization of low cost sawdust deserves more attention in the field of waste water treatment. There are two different processes for the preparation of activated carbon: physical activation and chemical activation[26]. The process of dyes removal was applied in batch mode. Adsorption experiments were performed by suspending Saw dust in the effluent and analyzing the supernatant by spectroscopic method. Saw dust was collected from nearby sources. This was washed with distilled water to remove water-soluble impurities and surface-adhered particles. Then, it was oven-dried at 60 ^{o}C to remove the moisture and other volatile impurities. Then, part of the dried saw dust was soaked in concentrated H_2SO_4 in an amount sufficient to cover the raw material completely, agitated at 120 rpm in an incubator shaker for 30 min, and then left for 2h. After being mixed, the slurry was subjected to vacuum-drying at 100 ^{o}C for 24 h. Chemical activation of the Saw dust was performed with $ZnC1_2$. Ten grams of Saw dust was well mixed with 100 ml of a concentrated solution that contained 10 g of $ZnC1_2$. The mixing was performed at 50 ^{o}C for 1 h. After being mixed, the slurry was also be subjected to drying at 100 ^{o}C for 24 h[27]. The resulting impregnated solids were placed in a porcelain dish and heated (5 ^{o}C min^{-1}) to a temperature of 300 ^{o}C for 1 h. After cooling, the products were washed sequentially with 0.5 N HCl, hot water, and finally cold distilled water to remove residual organic and mineral materials and then dried at 110 ^{o}C.

5.2.2. Chemicals and dye solution

Deionized water and high purity reagents were used for all standard and sample solution. Remazol Yellow (RY) was used as dye in the experiment. It's a reactive dye supplied by dye star Ltd., Dhaka, Bangladesh .Such reactive dye utilize a chromophore containing substituent that is capable of directly reacting with the fibre substrate. This dye form a covalent bond with the fiber, usually cotton, although they are used to small extent on wool and nylon. This class of dyes first introduced commercially in 1956, made it possible to achieve extremely high washing fastness properties by relatively simple dyeing methods[2]. The chemical structure of dye is shown in Fig. 5.1. A stock solution of Remazol Yellow was prepared by dissolving the necessary amount of dye in water.

5.2.3. Point of Zero charge

This is the point where the surface charge of adsorbent is zero. The point of zero charge (pH_{ZPC}) for the sawdust was determined by the following procedure: 100 mL of deionized water was added to an Erlenmeyer flask, which was then capped with cotton. The deionized water was heated until boiling for 20 min to eliminate the CO_2 and dissolved ions in the water. The CO_2 free water was cooled as soon as possible, and the flask was immediately capped. Now this water is free from both cations and anions, and it is considered to be a neutral one. On the other hand, 0.5 g of activated carbon was weighed and placed in a 25 mL Erlenmeyer flask to which 10 mL of CO_2 free deionized water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at 25 °C. The pH of the solution was measured, and this value is the point of zero charge[25]. The pH_{ZPC} of the above mentioned adsorbent is 3.7.

5.2.4. Study of Batch Adsorption Process

Equilibrium isotherms for adsorption onto the activated carbons determined by using 1 g of adsorbent per 50 ml of aqueous solution for initial dye concentrations in the range of 50-200ppm. For these experiments, the bottles were shaken at constant temperature (25 ^{o}C) with agitation speed (120 rpm), for the minimum contact time required to attain equilibrium, as determined from the kinetic measurements. The effectiveness of the treatment was evaluated by measuring concentration by UV-Visible spectroscopic method at 416 nm. The influence of pH was studied by adjusting the reaction mixture to different initial pH values and analyzing the residual color at the equilibrium contact time. The pH values were adjusted with dilute sulfuric acid and sodium hydroxide solutions. Then the percentage of dye removal was calculated by,

$$R = \frac{(C_0 - C_e)}{C_0} \text{x } 100\% \qquad (5.1)$$

The amount of dye adsorbed onto the activated carbons, q_e (mg/g), was calculated according to:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (5.2)$$

Where C_0 and C_e are the initial and the final dye concentrations (mg/L), respectively, and W is the amount of adsorbent (g), V is the volume of the solution (L).

5.3. Results and discussion

5.3.1. Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter for the adsorption process as it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The adsorption experiments were carried out at different solid/liquid ratios for 24 hr. At an initial dye concentration of 50 mg/L adsorption results obtained for various adsorbent dosages are given in Fig. 5.2.

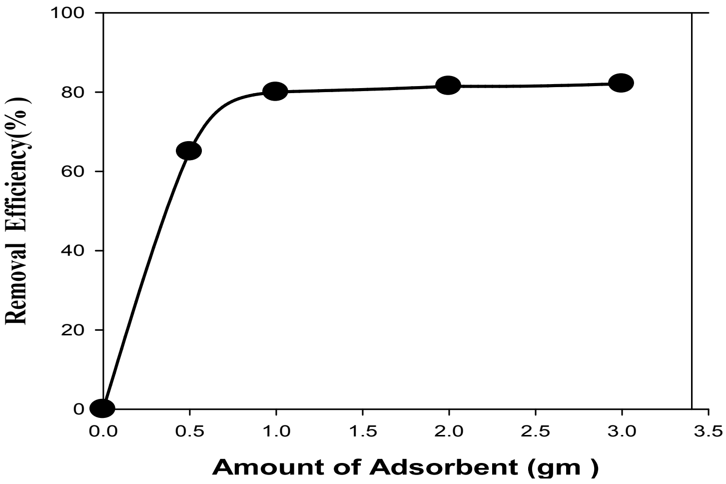

Fig. 5.2. Effect of adsorbent amount on the removal of Remazol Yellow(RY). Particle size: 140µm; Initial concentration: 50 mg/L; Initial volume: 50mL; pH: 7.0; Contact time: 6 hours; Temp.: 25 ^{0}C.

Fig. 5.2 shows that about 80% of dye was removed with 1.0 g of adsorbent. With increasing the amount of adsorbents (0.05g to 3.0 g) removal efficiency was increased. However, 1.0, 2.0 and 3.0 g of adsorbent showed almost similar removal efficiency with same particle size of <140µm. This was due to the agglomeration of the particles themselves so that the removal efficiency was not significantly increased with amount of adsorbents. Therefore 1.0 g of adsorbent was chosen for the next experiment.

5.3.2. Effect of Contact Time

The adsorption of Remazol Yellow was studied as a function of contact time in order to determine the equilibrium time. The experiments were conducted at 25 ^{0}C in an isothermal water bath shaker with initial dye concentration of 50 mg/L. A rapid adsorption can be seen at the initial stage of the contact period (Fig.5.3). This is most likely due to a large number of surface sites for adsorption. However, it gradually slowed down until it reached equilibrium. After a lap of time, the remaining surface sites are difficult to be occupied because of the repulsion between the solute molecules of the solid and bulk phases. Thus, adsorption took long time to reach equilibrium. At the point of dye removal reached a constant value where no more dye was removed from the solution. The amount of dye being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of dye desorbed from the adsorbent. Form the Fig. 5.3, it was found that the contact time is needed for dye solution with initial concentration of 50 mg/L to reach equilibrium was 24 hours. The maximum removal percentage of Remazol Yellow was found as 82%.

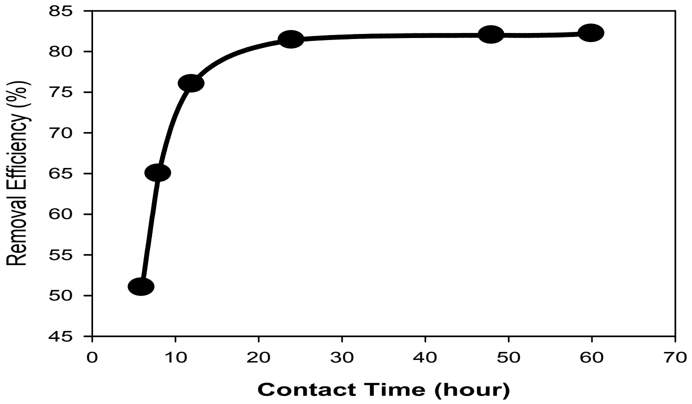

Fig. 5. 3. Effects of Contact time on the removal of Remazol Yellow. Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Temp.:25 ^{0} C.

5.3.3. Effect of particle size

About 81.00-82.00 % dye were removed by 1.0 g of TSD with the particle size of <90µm as shown in Fig. 5.4. From the Fig. 5.4, it is clear that lower the particle size higher the adsorption efficiency. The size of the TSD particles increased, the adsorption of dye decreased. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites. Therefore, particle size <140µm was chosen for the next experiment.

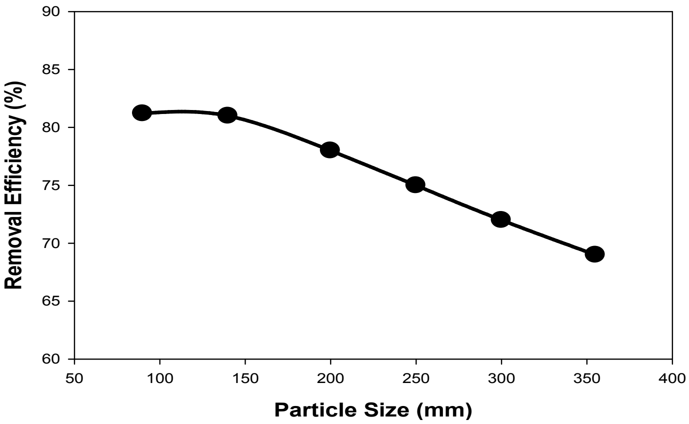

Fig. 5.4. Effect of particle size for the removal of RY. Contact time: 6 hours; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

5.3.4. Optimization of initial concentration of dye

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 40 to 100 mg/L. The removal efficiency is highly dependent on the initial concentrations of dye solution. These phenomena might due to the fact that at low concentration, most of the dye solution might contact with active sites of adsorbents. However, at higher concentration, most of the dye was not able to contact with the active surfaces because the sites might have been occupied by the other species present in the solution. The higher removal efficiency was achieved using 50mg/L of dye solution.

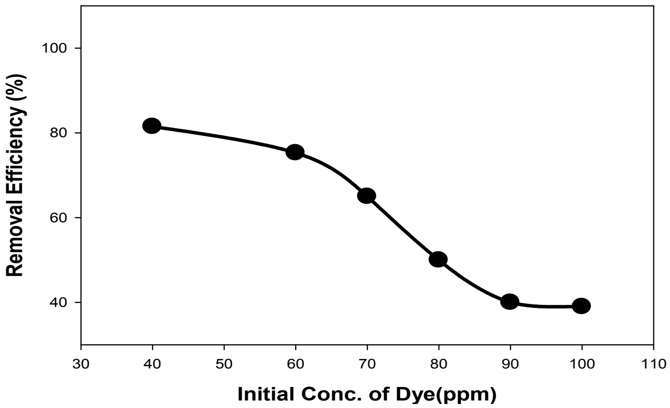

Fig. 5.5. Effect of initial concentration of dye on removal of RY. Contact time: 6 hours; Adsorbent amount: 1.0 g; Particle size: 140μm; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

5.3.5. Effect of initial volume of dye

The removal efficiency varied from 80.5 to 59.6 % (For TSD) with initial volume 25 mL to 80 mL. Decrease of the removal efficiency suggests that it happened due to the decrease of contact of dye with active sites on saw dust. At lower volume of dye solution, most of the dye might get available adsorbent sites. Moreover, increasing volume of the dye solution, active adsorbent sites were unavailable due to fill by the previous dye solution.

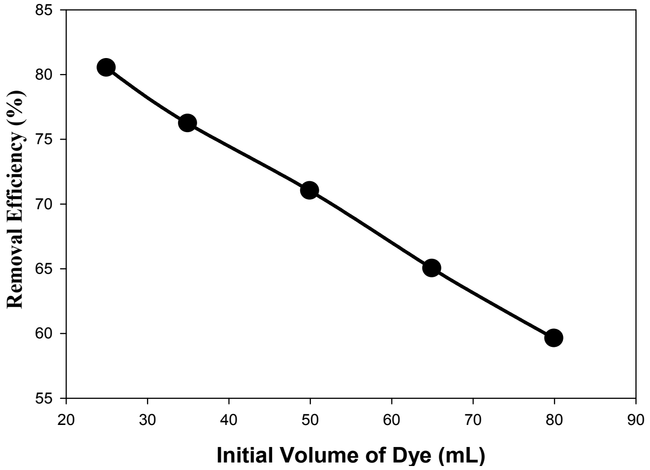

Fig. 5.6. Effect of initial volume of dye on the removal of RY. Particle size: 140μm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Contact time: 6 h; Temp.: 250C.; pH: 7.0.

5.3.6. Effect of pH

The pH of the dye solution plays an important role in the adsorption capacity, where it affects both the degree of ionization of the dye as well as the surface properties of the adsorbent. In this work, the influence of pH on the dye adsorption was studied as presented in Fig. 5.7. The effect of pH on adsorption of dye was studied within pH range 2-10. After 24 hours equilibration at various pH values illustrated that the percentage adsorption slightly decreases for Remazol Yellow when pH increased from 2 to 8 (Fig. 5.7). But after pH 8, adsorption rapidly decreases to almost zero. Thus the pH value 2 was selected as the optimum for performing the adsorption studies. The pH_{pzc} value of the activated carbon was determined which was 3.7. At lower solution pH (less than pH_{pzc}), the activated carbon may get positively charged, which enhances the negatively charged reactive dye anions through electrostatic forces of attraction and hence increase the adsorption capacity[25]. Also, this behavior of dye is in accordance with the known fact that the adsorption decreases with increasing pH for anionic dyes (as the Remazol Yellow in the present case), while it increases with increasing pH for cationic dyes.

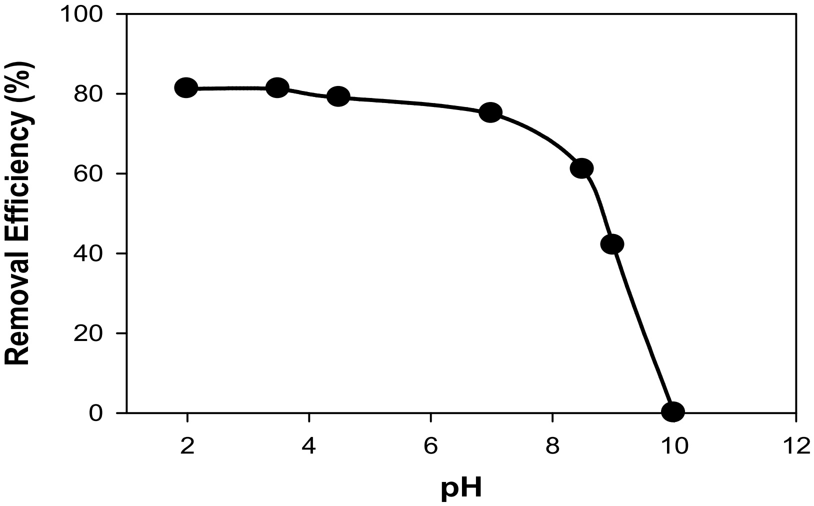

Fig. 5.7. Effect of pH on the removal of Remazol Yellow. Particle size: 140μm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; Contact time: 24 hours; Temp.: 25 ^{0}C.

5.3.7. Effect of Temperature

To determine the equilibrium temperature for the maximum uptake of dye solution (Remazol Yellow), the adsorption onto activated carbon was studied for the above optimized condition as a function of temperature (20, 30, 40 and 50 ^{0}C). A study of the temperature dependence of adsorption process gives valuable information about the enthalpy change during adsorption. Fig. 5.8. indicates that removal efficiency increases with increasing temperature from 20 ^{0}C to 40 ^{0}C. The improvement of adsorption with temperature may be related to an increase in the number of active surface sites available for adsorption on adsorbent, in the porosity, and the total pore volume of the adsorbent. It could be the due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature. Therefore, mass transfer resistance of adsorbate in the boundary layer decreases. In addition, this can be a result of an increase in their kinetic energy and the enhanced rate of intra-particle diffusion of sorbate with the rise of temperature[28]. The results indicated that the adsorption reaction of RY adsorbed by activated carbon prepared from saw dust was an endothermic process in nature.

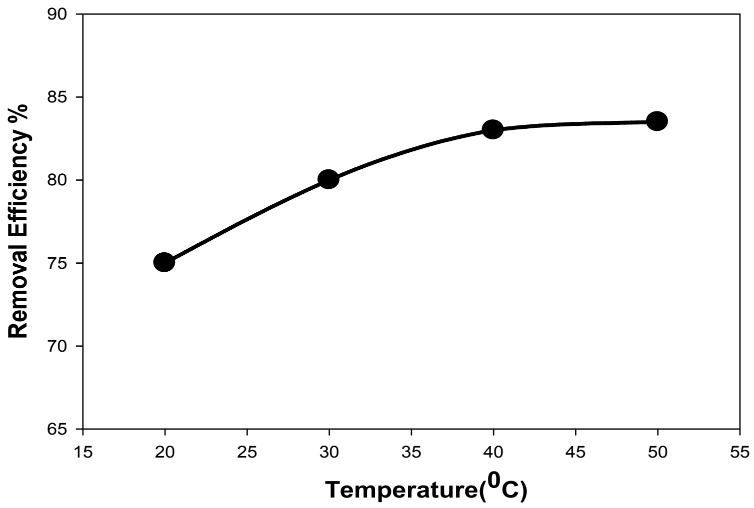

Fig. 5.8. Effect of Temperature on the removal of Remazol Yellow. Particle size: 140μm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 2; Contact time: 24 hours.

5.3.8. Effect of electrolytes

Reactive dyes are the major cause for complaint. Exhaust reactive dyeing required high salt concentration (up to 80 g/L of NaCl); salt is added to shift the equilibrium of dye from the aqueous phase to solid (fiber) phase[29]. Thus, effects of different electrolytes (NaCl, KCl, $CaCl_2$, $AlCl_3$ etc.) on the adsorption kinetics were investigated as shown in Fig. 5.9. It was found that the addition of these electrolytes to dye solution increased the percentage of dye removal, which is compared in Fig. 5.9. The colour removal was also dependent on the concentration of added electrolytes. From the Fig. 5.9, it was found that the removal efficiency gradually decrease with increasing of salt's concentration from 0.01-0.05M. It can be preferred that the salt cations neutralize the negative charge of the carbon surface enabling the adsorption of more molecules or the cations to act directly on the negative adsorbate ion[30]. As seen from the Fig.5.9, The removal efficiency increases in the order of $NaCl < KCl < CaCl_2 < AlCl_3$. Removal efficiency decreases as in the case of divalent and trivalent salt. Therefore, considering the cost and efficiency, NaCl is the best electrolyte for the removal of Remazol Yellow.

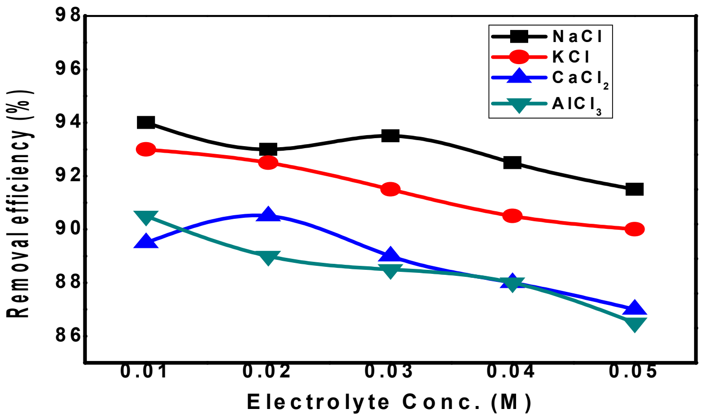

Fig 5.9. Effect of Various Salt on the removal of Remazol Yellow. Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; Contact time: 24 hours; Temp.: 25 ^{0}C.

5.3.9. Effect of NaCl

From the Fig. 5.9, it was found that, NaCl is the best electrolyte for the removal of Remazol Yellow. Presence of NaCl shows significant effect on removal efficiency of RY, where the removal efficiency was 94% with 0.01 M NaCl but without salt it was 83% (Fig. 5.10). Here the salt ions force the dye molecule to aggregate and migrate towards the adsorbent surface which increases removal efficiency.

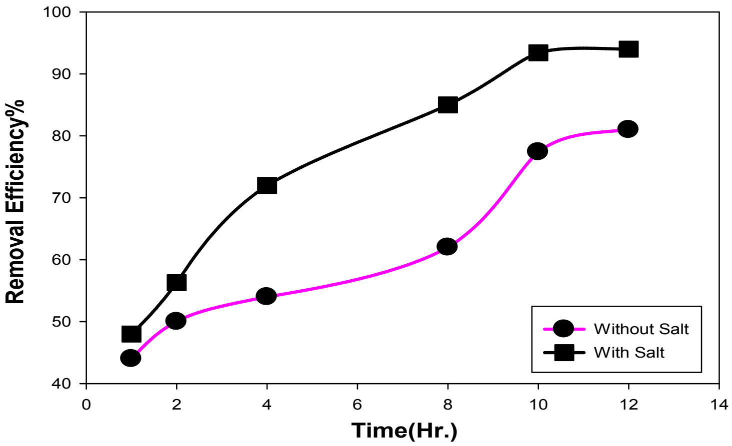

Fig. 5.10. Effect of Salt (NaCl) on the removal of RY. Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; Contact time: 24 hours; Temp.: 25 ^{0}C.

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5.3.10. Adsorption Isotherm

Adsorption isotherms, describe how adsorbate molecules interact with adsorbent particles. In the present study, experimental data were compared by using two well-known and widely applied isotherm models equations, namely Langmuir and Freundlich. The linear regression is used to determine the best-fitting isotherm and the pertinence of isotherm equations is compared by evaluating the correlation coefficients, R^2. Langmuir's isotherm model is based on the theory that adsorption energy is constant and uptake occurs on homogeneous surface by monolayer adsorption. When the surface is covered by monolayer of adsorbate, the adsorption goes on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs [31]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \qquad (5.3)$$

Where, C_e (mg/L) is the equilibrium concentration of remazol yellow, q_e (mg/g) is the amount of remazol yellow adsorbed per unit mass of adsorbent, q_m(mg/g) is the Langmuir constant related to adsorption capacity and K_L (L/mg) is rate of adsorption. The values of q_m and K_L were calculated from the intercept and slope of linear plot and are presented in Table 5.1.

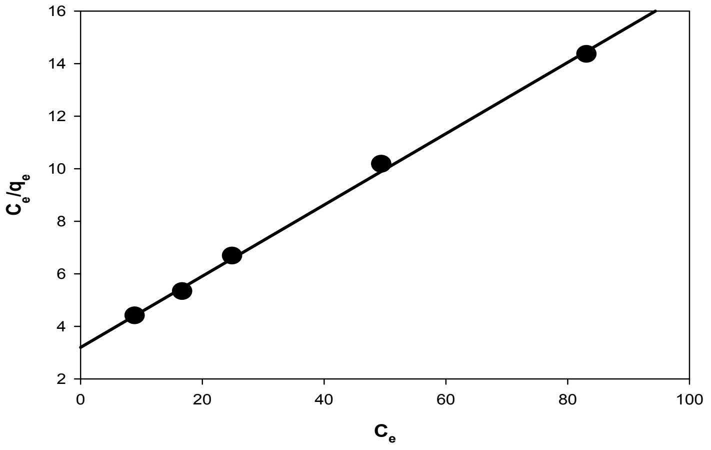

Fig. 5.11. Langmuir isotherm of Remazol Yellow

Freundilch model[32] is an empirical expression that is the earliest known relationship describing the adsorption equation. This isotherm takes into account a heterogeneous surface and multilayer adsorption to the binding sites on the surface of the adsorbent. The Freundlich model is expressed in the following equation:

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(K_F) \qquad (5.4)$$

Where, K_F and n are indicative isotherm parameters of adsorption capacity and adsorption intensity, respectively. Generally, n>1 illustrates that adsorbate is favorably adsorbed on the adsorbent. The higher of n values favors the adsorption process as well as intensify the adsorption[33].

From the Freundilch and Langmuir plot (Fig. 5.12 and Fig.5.11), the isotherm results are presented in Table 5.1. From the Table 1, it was found that Freundlich model gave higher R^2 values (without salt: 0.989; with salt: 0.995) than Langmuir model (Without salt: 0.978; with salt: 0.989), which indicate that remazol yellow adsorption by activated carbon in presence of electrolyte was made up of heterogeneous surface and multilayer adsorption[34]. This result is similar to other works on reactive dye adsorption by activated carbon prepared from coir pith[35].

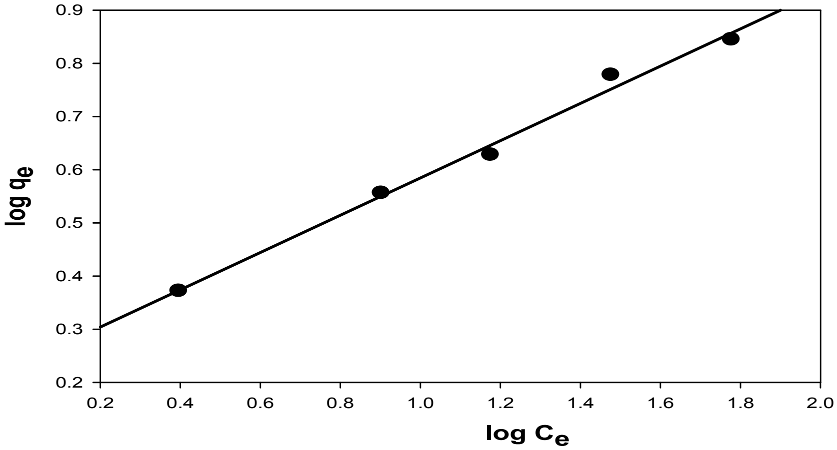

Fig. 5.12. Freundlich isotherm of Remazol Yellow.

Table 5.1. Freundlich and Langmuir Parameters and Separation factor R_L for Adsorption of RY on treated sawdust**.**

	Freundlich isotherm			Langmuir isotherm			
	K_F	n	R^2	q_m	K_L	R^2	R_L
Without Salt	1.71	2.85	0.989	8.00	0.105	0.978	0.045
With Salt (NaCl)	1.90	4.12	0.995	8.98	0.132	0.989	0.039

5.3.11. Adsorption Kinetics

Kinetics adsorption data of RY dye on activated charcoal was analyzed using two kinetic models: pseudo-first-order and pseudo-second order. The pseudo-first-order kinetic model is shown by the following equation[26]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{1.303} t \tag{5.5}$$

Where, q_t is the amount of dye adsorbed at time t (mgg^{-1}), q_e is the amount adsorbed at equilibrium ($mg\ g^{-1}$), $k_1$is the pseudo-first order rate constant (min^{-1}) and t is the contact time (min).

The values of the constants, k_1 and q_e for the adsorption of dye on the adsorbents were determined from the slopes and intercepts of the plots $\log(q_e - q_t)$ against t, respectively and their values are given in Table 5.2.

Pseudo-second order model can be represented in the following form[26]:

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{1}{q_e} t \tag{5.6}$$

Where, k_2 is the Pseudo-second order rate constant ($gmg^{-1}min^{-1}$). The values of the q_e and k_2 were determined by potting a graph between t/q_t and time. The applicability of the pseudo first order and pseudo second order model can be examined by linear plot shown in Fig 5.13 and 5.14.The linearity of this plot indicates the applicability of the two models. However the correlation coefficient, R^2 shows that second order model fits the experimental data better than the pseudo first order model.

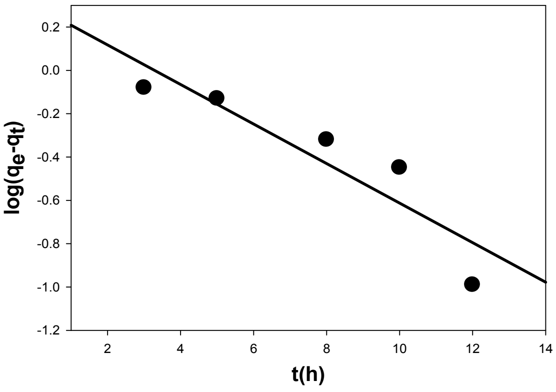

Fig. 5.13. Pseudo first order Kinetics of remazol yellow.

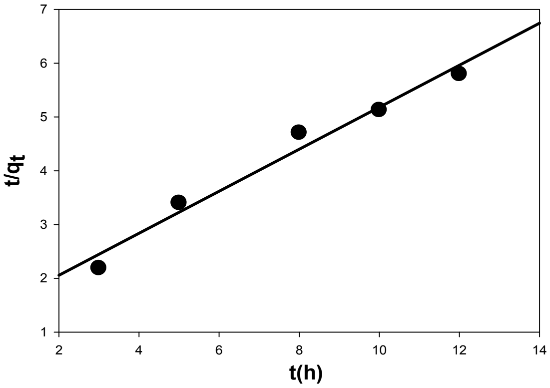

Fig. 5.14. Pseudo second order Kinetics of remazol yellow.

Table 5.2. Pseudo first order & second order rate constants, calculated & experimental q_e values for Adsorption of remazol yellow on treated sawdust at 298K

	Pseudo first order Kinetic model			**q_e exp. mg/g**	**Pseudo second order Kinetic model**		
	q_e(mg/g)	$k_1(h^{-1})$	R^2		q_e (mg/g)	k_2 (h , g/mg)	R^2
Without Salt	2.62	0.25	0.83	2.36	2.73	0.092	0.960
With Salt (NaCl)	3.75	0.655	0.89	2.34	2.59	0.411	0.997

5.4. Conclusion

Activated charcoal produced by chemical activation of saw dust with an activation agent KCl was capable of removing Remazol Yellow dye molecules from aqueous solutions. The removal was an adsorption process which was favored at acidic medium with pH value 2 and adsorption efficiency % (removal efficiency) was also found to increase with increase in adsorbent dosage, contact time, temperature, and addition of electrolyte. The kinetic study showed that dye-activated charcoal adsorption systems followed by pseudo-second-order model with high correlation coefficients and the process was endothermic. The equilibrium data was in good agreement with the Langmuir model and dimensionless separation factors (R_L values) within the range of zero to one showed that the adsorption favorable. From this study, activated charcoal which is produced from chemical activation of saw dust could be employed as an effective and low cost adsorbent. Therefore, this prepared adsorbent could be considered as an alternative to commercial activated charcoal for the removal of Remazol Yellow dye from aqueous solutions.

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Chapter - 6

Adsorption study of Levafix Red, a reactive dye on treated Jute Stick Powder

Abstract

The adsorption of Levafix Red (LR) dye from waste water via batch adsorption onto treated jute stick powder was investigated. Studies concerning the factors influencing the adsorption such as adsorbent dosage, pH, contact time and temperature were systematically investigated and discussed. The results revealed that the maximum removal of Levafix Red was ~91% from water. The kinetics data were analyzed using pseudo-first order and pseudo-second order models. It was best described by the pseudo-second order model. The adsorption equilibrium follows Langmuir isotherm. This result indicates that treated jute stick powder could be employed as low-cost alternatives to commercial activated carbon for the removal of Levafix Red from waste water.

6.1. Introduction

The effluents from the dyestuff manufacturing and textile industries, in particular, are highly colored with a large amount of suspended organic solids and considered as important sources of water pollution. When the quality of the environment is considered, removal of synthetic dyes becomes a must, because some of these dyes and their degradation products may be carcinogenic and toxic. Consequently, their treatment cannot solely depend on biodegradation alone[1]. Indeed, removal of dyes is nowadays regarded as an important practice in textile wastewater treatment.

Textile industrial sector is one of the most important and largest industrial sectors of Bangladesh with regard to production source of foreign exchange and labor force employment. About 78% of the total export earning comes from textile and textile related goods. The textile industries are estimated to consume as much as two-third of the total annual production of dyes[2]. Over 10% of the dye used in textile processing does not bind to the fibers and is therefore, released to the environment[3]. Many industries, such as the textile, dyestuffs, plastics, leather, and paper industries, discharge colored wastewaters and dyes that remain in the effluents, undergo chemical changes, consume dissolved oxygen, and may cause carcinogenic and genotoxic effects[4]. Dyes with striking visibility in recipients may affect photosynthetic activity in aquatic environment due to the reduced light penetration[5]. Therefore, it is necessary to remove dyes from wastewater before it is discharged into the environment.

It is difficult to treat dye containing wastewater by conventional methods as most of the dyes have complex aromatic structure of synthetic origin and thus hardly amenable to biodegradation[6, 7]. In chemical methods coagulation produced high concentration of sludge production. A secondary pollution problem can also arise because of excessive chemicals used in treatment processes.

Numerous physiochemical and biological methods have been used to decolorize dye bearing effluents, often in combinations as one single treatment may not be sufficient to remove certain classes of synthetic dyes[8, 9]. Adsorption is considered to be an effective method for the removal of dye due to the ease of operation and comparable low cost of application[11]. At present, the most commonly used adsorbent in wastewater treatment is activated carbon, which has also been studied for the dye removal[12]. But the extensive application of activated carbon is still in difficulty due to its high cost. Therefore, it is necessary to explore cheaper adsorbent for the removal of dye from wastewater.

Recently, an effect of the salt concentration on the dye sorption was studied in several research works. It was observed a certain increase in the azo dye adsorption onto starch-based polymers in the presence of inorganic salts (NaCl) and explained this phenomenon as a result of the charge reduction on the adsorbent surface[13]. Similarly, the adsorption of reactive (acid) dyes on activated carbon increased in the presence of NaCl (0.1 – 0.5 mol l^{-1})[14]. In addition, the presence of NaCl salt makes a major effect on the range of acidic dyes adsorption by Bentonite adsorbent[15]. Adsorption capacity of natural jute stick is 55-60%. Therefore, the objective of the work is to study the feasibility and potentiality of the NaCl treated jute stick as bioadsorbent for the removal of Levafix Red (reactive dye) from wastewater.

6.2. Experimental

6.2.1. Preparation of adsorbent

Jute is an abundant agricultural product of Bangladesh, used as low cost fuel. Jute stick was collected from the local market, and then it was cut into small pieces and washed with water to remove any adhering substances and dried at 110 °C. Finally, it was ground into powder. About 2.0g of jute sticks powder was mixed with 0.5 g NaCl, and then 25 ml water was added into it. The mixed solution was placed into a shaker for shaking about 1 hour. After Shaking it was kept another one hour in room temperature for settlement, and filtered. Then it was heated into an oven for dryness approximately 6 hours at 90 °C.

Fig. 6.1. Jute stick

Fig. 6.2. Jute stick powder

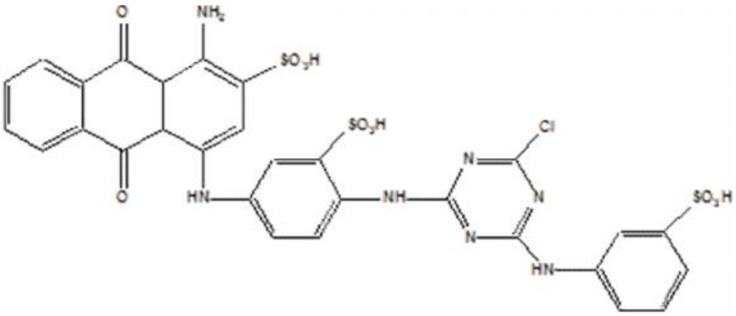

Fig. 6.3. Chemical structure of Levafix Red.

6.2.2. Point of Zero charge

This is the point where the surface charge of adsorbent is zero. The point of zero charge (PZC) for the treated jute stick powder was determined by the following procedure: 100 mL of deionized water was added to an Erlenmeyer flask, which was then capped with cotton. The deionized water was heated until boiling (20 min.) to eliminate the CO_2 and dissolved ions in the water. The CO_2 free water was cooled as soon as possible, and the flask was immediately capped. Now this water is free from both cations and anions, and it is considered to be a neutral one. On the other hand, 0.5 g of treated jute stick powder was weighed and placed in a 25 mL Erlenmeyer flask to which 10 mL of CO_2 free deionized water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at 25 °C. The pH of the solution was measured, and this value is the point of zero charge[12].

Table 6.1. Physical properties of treated jute stick powder.

Properties	Value
Particle size	<140 µm
BET Surface Area (m^2/g)	5.38
Average Pore Diameter (A^0)	99.40
Micro Pore Volume(cc/g)	0.013
Micro Pore Area (m^2/g)	2.17
Bulk Density (g/mL)	0.89
pH_{pzc}	4.65

6.2.3. Preparation of dye solution

Stock solution of Levafix Red (LR) was prepared by dissolving the appropriate amount of solid substance in water. 1000 mg LR was taken in a 250.0 mL volumetric flask and it was dissolved by deionized water. Then deionized water was added up to the mark to prepare 1000 ppm solution of LR. Further dilution was made whenever necessary. The concentration range used for experiment was 50 ppm to 250 ppm. The required concentration was prepared by dilution.

6.2.4. Study of Batch Adsorption Process

Equilibrium isotherms for adsorption onto the selected carbons determined by using 1 g of adsorbent per 50 ml of aqueous solution for initial dye concentrations in the range of 50-200 ppm. For these experiments, the bottles were shaken at constant temperature (25 ^oC) and agitation speed was (120 rpm), for the minimum contact time required to attain equilibrium, as determined from the kinetic measurements. The effectiveness of the treatment was evaluated by measuring concentration by UV-Visible (UV-1800, Shimadju, Japan) spectroscopic method at 513 nm.

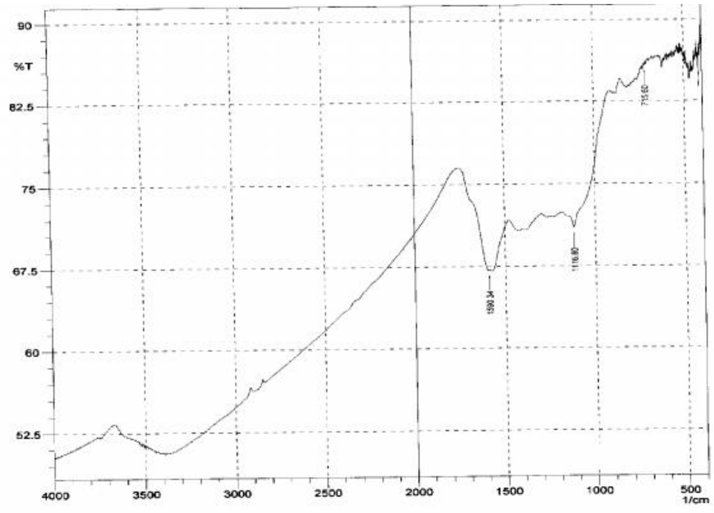

Fig.6.4. FTIR of Treated jute sticks powder.

The influence of pH was studied by adjusting the reaction mixture to different initial pH values and analyzing the residual color at the equilibrium contact time. The pH values were adjusted with dilute sulfuric acid and sodium hydroxide solutions. Then the percentage of dye removal was calculated by,

$$R = \frac{(C_0 - C_e)}{C_0} \text{x } 100\% \qquad (6.1)$$

The amount of dye adsorbed onto the activated carbons, q_e (mg/g), was calculated according to:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (6.2)$$

Where C_0 and C_e are the initial and the final dye concentrations (mg/L), respectively, and W is the amount of adsorbent (g), V is the volume of the solution (L).

6.3. Results and discussion

6.3.1. Physical Properties of the treated jute stick

The physical properties of the jute stick powder have been presented in Table 6.1. From the table it is found that the BET surface area is 5.38 (m^2/g) and the average pore diameter is 99.40 A^0. The point of zero charge of the prepared jute stick powder is 4.65.

BET surface area and other properties of Jute sticks powder were measured by Surface area analyzer (Quanthachrome Nova 2200 e, USA).

6.3.2. Surface characterizations

Infrared spectra of treated sawdust were measured with Fourier transform infrared spectrometer (IR Prestige-21, Shimadju, Japan) to elucidate the functional group present in jute stick powder. The FTIR spectra of treated Jute stick powder as shown in Fig. 6.4 exhibited peak at 3400 cm^{-1}, which can be attributed to the stretching of OH groups. These broad bands indicate high concentration of phenol and alcohol. A greater number of OH groups on the glucose units of the cellulose polymers broaden the peak. The peak at 1590 cm^{-1} was assigned to the C=O bonds. The bands at 1116 cm^{-1} is the contribution from the C─H stretching of cellulose and hemicelluloses. The band between 500 and 600 cm^{-1} shows the presence of the C-Cl groups. The Cl comes from the treatment of Jute stick powder with NaCl solution.

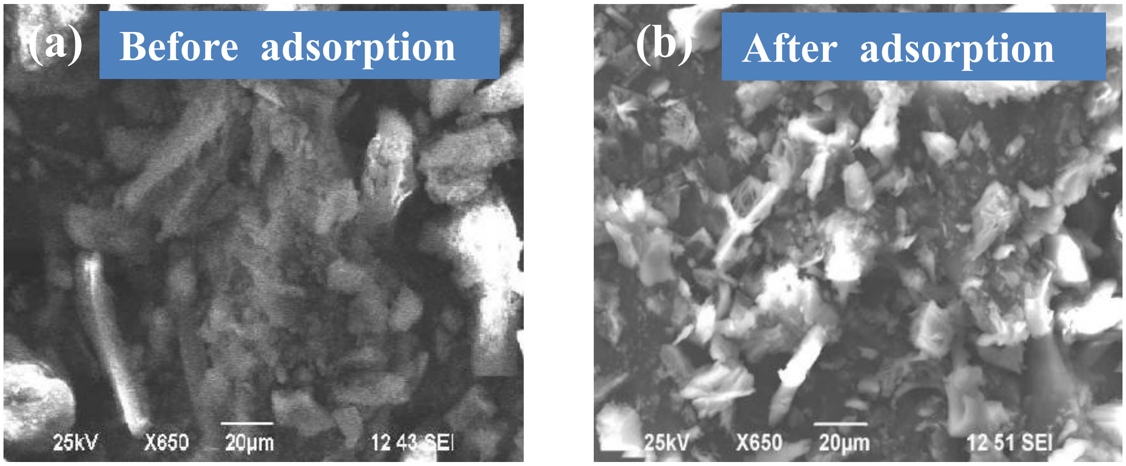

Fig. 6.5. SEM of treated jute sticks (a) before and (b) after adsorption of levafix red dye.

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. SEM of adsorbent material was taken before and after dye adsorption on activated charcoal is presented in Fig. 6.5. From the figure it is clear, there is a good possibility for dyes to be trapped and adsorbed into these pores. The SEM pictures of adsorbed samples show very distinguished dark spots which can be taken as a sign for effective adsorption of dye molecules in the cavities and pores of this adsorbent.

6.3.3. Effect of Adsorbent Dosage

For optimizing the amount of adsorbents, experiments were performed using 50 mL aqueous solution of LR (Levafix Red) and were shaken for 120 minutes after adding different amount of jute stick powder (0.5−3.0 g). Absorbance of the filtrate was noted using spectrophotometer at λmax of the dye. It was observed that adsorption of the dye increased with increase of the amount of adsorbent and then attained constant value at equilibrium as shown in Fig. 6.6. Fig. 6.6 shows that about 81% of dye was removed with 1.5 g jute stick powder. With increasing the amount of adsorbents (from 0.5 g to 3.0g) removal efficiency slightly increased. However, 1.5−3.0g of adsorbent showed almost the similar removal efficiency with same particle size of <90μm. This was due to the agglomeration of the particles themselves so that the removal efficiency was not significantly increased with amount of adsorbents. Therefore 1.5 g of adsorbent was chosen for all the subsequent adsorption studies.

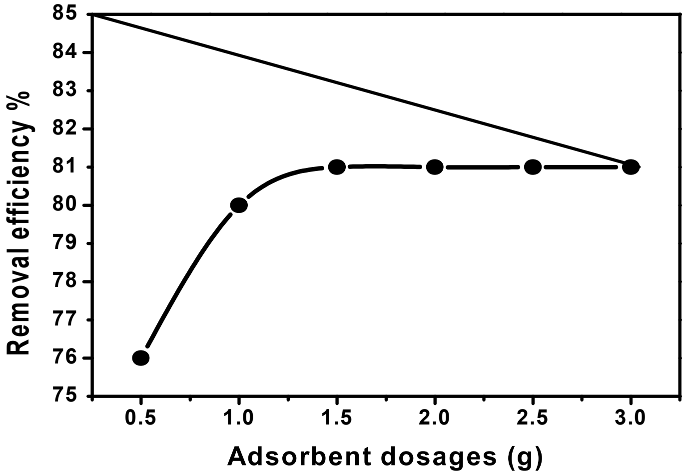

Fig.6.6. Effect of adsorbent dose for the removal of Levafix Red; Particle size: 90μm; Initial concentration: 50 mg/L; Initial volume: 25 mL; pH: 4.0; Contact time: 5 hours; Temp.: 25 ^{0}C.

6.3.4. Effect of Contact Time

In this investigation, fixed amounts of adsorbents (1.0 g) were agitated with constant volumes of dye solutions (50 mL). The of contact time on the removal of LR by the treated jute stick powder was determined by keeping other conditions (initial concentration of the dye, initial volume, pH and temperature) constant. The effect of contact time was investigated by treating 1.0 g of the jute stick powder with 50 mL of 50 mg/L LR solution at pH value of 7. The mixture was agitated with mechanical shaker for different periods of contact time (1-8 h). The results are presented in Fig. 6.7.

It was observed that the rate of removal of LR dye increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material. As the data show the adsorption process was rapid for the first 6 h. Therefore 6 h contact time was chosen for all the subsequent adsorption studies.

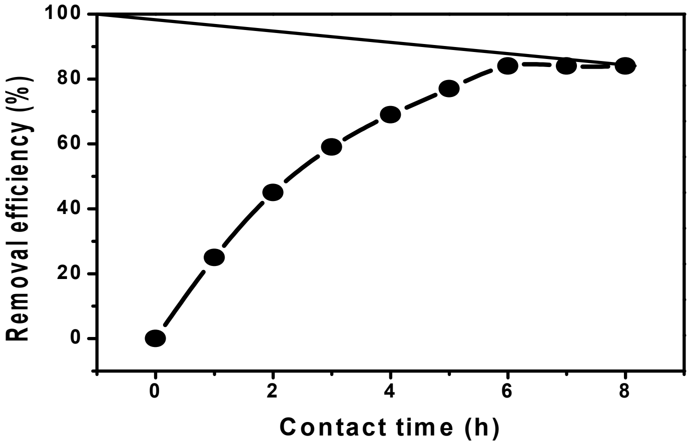

Fig. 6.7. Effect of contact time for the removal of Levafix Red. Particle size: 90μm; Initial concentration: 50 mg/L; Initial volume: 25 mL; pH: 4.0; Temp.: 25 ^{0}C.

6.3.5. Effect of pH

In the present work, the pHzpc of the jute stick powder was found to be 4.65. At a pH of solution below the pHzpc of the adsorbent, the surface of the activated charcoal is positively charged and can attract anions from the solution. When pH of the solution is less than pHzpc, the surface of the activated charcoal is positively charged and attractive to anions[16, 17].

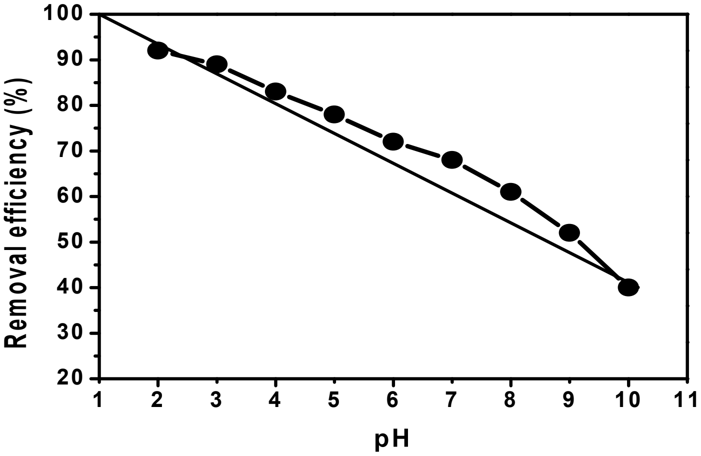

Fig.6.8. Effect of pH for the removal of Levafix Red. Particle size: 90μm; Initial concentration: 50 mg/L; Initial volume: 25 mL; Temp.: 25^{0}C; Contact time: 6 h.

In this study, the effect of pH on the percentage of removal of Levafix Red (LR) dye using jute stick powder was evaluated as shown in Fig. 6.8. To investigate the effect of pH, the experiment of adsorption of dye solution was carried out at different pH value (2.0—12.0) by using 0.01 M HCl and 0.01M NaOH aqueous solution. It could be seen that as the pH increased the adsorption of dye decreases. The maximum uptake was observed at the pH range 2.0 - 3.0. At pH below 4.6 the attributed electrostatic interactions between the positively charged of jute stick powder and the negatively charged of LR dye prefer to give the LR percentage removal (93%). Since pH 2.0 was highly acidic condition therefore pH 3.0 was selected for optimized condition for further adsorption study.

6.3.6. Effect of Temperature

Temperature is an important parameter affecting the biosorption process as various dye effluents are discharged at relatively high temperature. To determine the equilibrium temperature for the maximum uptake of dye solution (LR), the adsorption onto jute stick powder was studied for the above optimized condition as a function of temperature (25-40 ^{0}C) is presented in Fig. 6.9. Fig. 6.9, indicates that the removal efficiency decreases gradually with increasing temperature from 25 ^{0}C to 50 ^{0}C. As the temperature increases, rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increases[18]. This may be the cause of increased dye adsorption of jute stick at low temperature. But the adsorption was decreased at higher temperature due to increase of interval pores which induce diffusion and reduce levafix red (LR) dye retention.

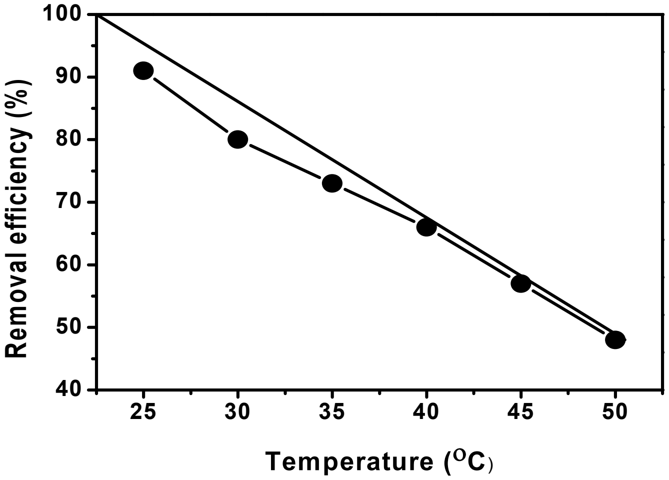

Fig.6.9. Effect of temperature for the removal of Levafix Red. Particle size: 90µm; Initial concentration: 50 mg/L; Initial volume: 25 mL; pH: 3; Contact time: 6 h.

6.3.7. Adsorption Isotherm

The adsorption isotherm used to show the adsorption molecules distribute between the solid phase and liquid phase at adsorption equilibrium state. The Langmuir and Freundlich isotherms are the most frequently employed models. The linear regression is used to determine the best-fitting isotherm and the pertinency of isotherm equations is compared by evaluating the correlation coefficients, R^2. Langmuir's isotherm model is based on the theory that adsorption energy is constant and uptake occurs on homogeneous surface by monolayer adsorption. When the surface is covered by monolayer of adsorbate, the adsorption goes on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs[19]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \qquad (6.3)$$

Where, C_e (mg/L) is the Levafix Red (LR) equilibrium concentration and q_e (mg/g) is the amount of LR adsorbed per unit mass of adsorbent, q_m (mg/g) is the Langmuir constant related to adsorption capacity and K_L(L/mg) is rate of adsorption. The values of q_m and K_L were calculated from the intercept and slope of linear plot and are presented in Table 6.2.

Freundilch model[20] is an empirical expression that is the earliest known relationship describing the adsorption equation. This isotherm takes into account a heterogeneous surface and multilayer adsorption to the binding sites on the surface of the adsorbent. The Freundlich model is expressed in the following equation:

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(K_F) \tag{6.4}$$

Where, K_F and n are indicative isotherm parameters of adsorption capacity and adsorption intensity, respectively. Generally, n>1 illustrates that adsorbate is favorably adsorbed on the adsorbent. The higher the number of n, the more favorable the adsorption and stronger the adsorption intensity[21]. From the Freundilch and Langmuir plot the isotherm results are presented in Table 6.2.

Table 6.2. Freundlich and Langmuir parameters for LR on treated jute stick powder

Freundlich isotherm			Langmuir isotherm			
K_F	n	R^2	q_m	K_L	R^2	R_L
1.221	1.996	0.986	6.788	0.144	0.66	0.996

From the Table 6.2, it was found that Langmuir model gave higher R^2 values (0.996) than Freundlich model (0.986), which indicate that LR adsorption by jute stick powder was made up of heterogeneous surface and multilayer adsorption[22]. This result is similar to other works on reactive dye adsorption by activated carbon prepared from coir pith[23]. For all the experiments, the value of 'n' is greater than one which indicates good adsorption of LR onto treated jute stick powder.

6.3.8. Adsorption Kinetics

Kinetics adsorption data of LR dye on activated charcoal was analyzed using two kinetic models: pseudo-first-order and pseudo-second order. The pseudo-first-order kinetic model is shown by the following equation[24]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{1.303}t \qquad (6.5)$$

Where, q_t is the amount of dye adsorbed at time t (mgg^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}), k_1 is the pseudo-first order rate constant (min^{-1}) and t is the contact time (min).

The values of the constants, k_1 and q_e for the adsorption of dye on the adsorbents were determined from the slopes and intercepts of the plots $\log(q_e - q_t)$ against t, respectively and their values are given in Table 6.3. Pseudo-second order model can be represented in the following form[25]:

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e}t \qquad (6.6)$$

Where, k_2 is the Pseudo-second order rate constant (gm g^{-1}min^{-1}). The values of the q_e and k_2 were determined by potting a graph between t/q_t and time. The applicability of the pseudo first order and pseudo second order model can be examined by linear plot.The linearity of this plot indicates the applicability of the two models. However the correlation coefficient, R^2 shows that second order model fits the experimental data better than the pseudo first order model.

Table 6.3. Kinetic parameters for the adsorption of Levafix Red on jute stick powder

Pseudo first order Kinetic model			**q_e exp. mg/g**	**Pseudo second order Kinetic model**		
q_e (mg/g)	k_1 (h^{-1})	R^2		q_e(mg/g)	k_2 (h , g/mg)	R^2
1.82	0.838	0.975	2.64	2.85	0.634	0.996

6.3.9. Desorption

After completing the adsorption the residue was dried in air and then used to investigate desorption. The desorption results shows that the amount of desorption increases with time. This also indicates that desorption is physical in nature. Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dyes. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. The effect of various reagents used for desorption studies shows that sodium hydroxide is a better reagent for desorption, because we could get more than 90% removal of adsorbed dyes. The reversibility of adsorbed dyes in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of dyes by mineral acids and alkaline medium indicates that the dyes are adsorbed onto the treated jute sticks by physisorption.

6.3.10. Thermodynamic study

One process of elucidation of dye adsorption mechanism on adsorbent (Jute stick) is to calculate apparent thermodynamic parameters. Using the values of Binding Freundlich constant, K_c, and following equation(6.7), (6.8) and (6.9), the variations of apparent enthalpy change (ΔH, kJ/mol), apparent free energy change (ΔG, kJ/mol), and apparent entropy change (ΔS, kJ/mol.K) can be calculated for adsorption of dye LR on jute stick.

$$\ln K_c = - \Delta H / RT + \text{constant} \qquad (6.7)$$

$$\Delta G = - RT \ln K_c \qquad (6.8)$$

$$\Delta S = (\Delta H - \Delta G) / T \qquad (6.9)$$

Where R is the real gas constant and T is the absolute Temperature.The calculated values of thermodynamic parameters are given in the following table 6. 4

Table 6.4. Derived data for the thermodynamic parameters for adsorption of LR onto jute stick powder

Dye	**`Temperature (K)**	**ΔE(kJ/mol)**	**ΔG (kJ/mol)**	**ΔH (J/mol)**	**ΔS (J/mol.K)**
RR	303	-8.85	1.30	-8.18	-22.14
	313		5.95		
	323		6.52		

The value of apparent enthalpy change (ΔH) computed from the slope of linear dependence of $\ln K_c$ Vs 1/T ($R^2 = 0.92$) is negative, which indicates the fact that the process of adsorption is exothermic and favored lower than 40 kJ/moles, thus it can be presumed that the adsorption is physical in nature. It also indicates that the adsorption process is more favorable at lower temperature. The positive values of ΔG confirm that the reactive dye adsorption onto jute stick is not a spontaneous process and the spontaneity of the process increases with increase in temperature. The apparent entropy change (ΔS) values are almost constant over the temperature range. The negative, entropy characterizes a increased disorder of the system. It can be suggested that the driving force for adsorption process is due to both enthalpy and entropy effect[23]. This behavior was demonstrated by other experimental results concerning organic compounds adsorption mechanism.

6.3.11. Application of the Developed Treatment System to industrial waste water

The utility of the treated jute sticks was evaluated for the treatment of Levafix Red contaminated waste water samples. The concentration of total LR in the samples was 50 ppm. As the pH of the water samples were around 11.33, the pH of the solution is lowered to 3.0 by adding 0.001M HCl solution. The treatment results are presented in Table 6.5. 2.0 g of adsorbent was applied in the treatment. From the present results, it was evident that the Levafix Red was successfully removed from industrial waste water.

Table 6.5. Removal of Levafix red from the waste water by the developed method.

Sample No.	Adsorbent	Concentration (mg/L)	Removal efficiency,%
S1	Treated Jute stick	50	82.62
	Jute stick	50	70.12
S2	Treated Jute stick	50	83.47
	Jute stick	50	71.38
S3	Treated Jute stick	50	83.26
	Jute stick	50	71.80

6.4. Probable removal mechanism

The maximum removal percentages of Levafix Red (LR) dye was at acidic pH (3.0) and decreased gradually with increasing in pH. The protonated groups in jute stick powder were mainly carboxylic group (-COOH^{2+}), phenolic (-OH$^{2+)}$ and chromenic groups. Levafix red is an anionic dye (acid dye). It dissociated as anions into the solution. The de-protonated groups of LR dyes were probably the sulphonate groups (-SO$_3^-$). Generally, electrostatic interaction between positively charged groups of jute stick powder and negatively charged dye molecules was the main force controlling the adsorption process. In the pH range of >4.6, the surface of jute stick powder was negatively charged (pHpzc = 4.6) and Levafix dyes were positively charged because of the sulphonate groups of the dye were almost protonated (SO$_3$H). The low percentage of dye removal at highly basic solution could be due to the strong repulsion interaction between the negatively charged jute stick powder surfaces and the protonated LR dye molecules. At the same time, hydroxide ion concentration increased with the incremental solution pH, and it could be adsorbed preferentially on the surface of the jute stick powder. There was competition between OH− (at high pH) and dye ions for positively charged adsorption sites. These results could be decreased evidently the removal efficiency of Levafix Red dyes. The treatment of NaCl on jute stick facilitates the dye adsorption effectively. This can be attributed to an increase in dimerization of dyes in solution in contact with NaCl salt by the aggregation of dye molecules[26]. These forces include: vander Waals forces; ion-dipole forces; and dipole-dipole forces, which occur between the dyes in solution induced by the action of NaCl salt ions.

6.5. Conclusion

This study was performed using treated jute stick powder for the removal of Levafix Red dye solution at laboratory conditions. The optimized conditions were applied for real sample collected from Tongi industrial area, Dhaka, Bangladesh. However, the Levafix Red dye removal efficiency with the optimized conditions was low. The real samples are in fact complicated because textile industries use a mixture of various types of dyes for different applications. Research in this regard is being continued. Treated jute stick removed the Levafix Red significantly from waste water. Jute stick biosorbents are biodegradable, environmental friendly and nontoxic. Therefore, treated jute stick can be a low cost and effective way to reduce water pollution from industrial wastewater.

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Chapter - 7

Equilibrium and kinetic studies for the adsorption of reactive dyes from aqueous solution with Coir dust: A Comparative study

Abstract

Color removal from wastewater has been a matter of concern, both in the aesthetic sense and health point of view. In this research work, an extensive list of dyes has been compiled. The research evaluates different agricultural waste materials as low-cost adsorbents for the removal of dyes from waste water. These waste materials are sawdust, jute stick and coconut coir. The paper also outlines some of the fundamental principles of dye adsorption on to adsorbents. Removal of reactive dyes such as Remazol yellow (RY), Remazol red (RR) and Remazol blue (RB) from an aqueous solution by different adsorbents such as activated carbon from sawdust and coir dust, jute stick was investigated. It was found that a maximum uptake of Remazol blue was ~95% by activated charcoal prepared from coir dust. In this research work a comparative study has been carried out for the removal of textile dyes from waste water by using activated charcoal prepared from coir dust.

7.1. Introduction

The discharge of dye-bearing wastewater into natural streams and rivers from the textile, paper, carpet, leather, distillery, and printing industries poses severe problems, as dyes impart toxicity to the aquatic life and are damaging to the aesthetic nature of the environment[1]. Many of the dyes used in these industries are stable to light and oxidation, as well as being resistant to aerobic digestion[2]. The industrial effluents are characterized by complex compositions that make impossible a general available method for removing textile dyes. Several technologies have been developed to remove dyes from industrial wastewater; these include chemical precipitation, coagulation/flocculation process, membrane filtration, oxidation process, adsorption, reverse osmosis, ion exchange, solvent extraction [3, 4, 5].

Sorption has been found to be an efficient and economic method for dyes removal. One of the advantages is the possibility to use a large variety of solid materials: synthetic to natural low-cost materials (natural as well as wasted materials from different industries and agriculture) as suitable sorbents for decolourization of industrial effluents [6]. Sorption onto activated charcoal is a very useful technique, but the high cost implied to obtain this sorbent stimulated the search of cheaper alternatives. In this context, the overall attention was moved to the non-conventional and low-cost materials which include industrial and agricultural by-products and wastes [3, 7, 8].

With an attempt to develop a low cost method for the removal of Remazol Red (RR), Remazol Yellow (RY), Remazol Blue(RB) by using waste materials coir dust that has practically no use or very little significant use, even in some case recycling or reuse is not essential, for that it has been chosen as adsorbent. Natural coir dust shows very poor removal efficiency (30-40%). For this adsorbent was used with chemical pretreatment. It is sulfuric acid activated carbon of coir dust (C.D). It is chemically stable and insoluble in water. 1.0 g of adsorbent was taken in a bottle in a batch mode. Then 50 mL of 50.0 ppm dyes standard solution were taken. Removal efficiency of the adsorbent was found 92- 96% for T.C.D. On the basis of given data it can be said that dye removal efficiency for Remazol Red and Remazol Blue was excellent.

7.2. Materials and methods

Materials and methods used are already described in Chapter 3, Section 3.2; Chapter 4, Section 4.2; Chapter 5, Section 5.2.

Fig.7.1. Coconut husk

Fig. 7.2. Coconut coir

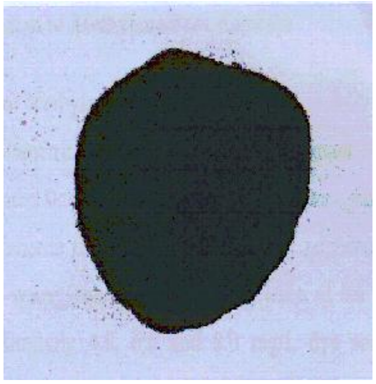

Fig. 7.3. Activated charcoal from coir

7.3. Results and Discussion

For comparative study to develop a low cost method for the removal of dyes, some factors were chosen. The adsorption can be influenced by a number of factors, such as particle size, adsorbent amount, dye concentration, volume of dye, effect of pH, contact time and temperature. Hence, there is a need to optimize these factors to maximize the removal efficiency of adsorbent and minimize the treatment cost for textile wastewater.

7.3.1. Effect of Particle Size

About 92.36-96.00 % dye were removed by 1.0 g of coir with the particle size of <140µm as shown in Fig. 7.4. From the Fig. 7.4, it is clear that lower the particle size higher the adsorption efficiency. The size of the coir particles increased the adsorption of dye solution decreased. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites. Therefore, particle size <140µm was chosen for the next experiment.

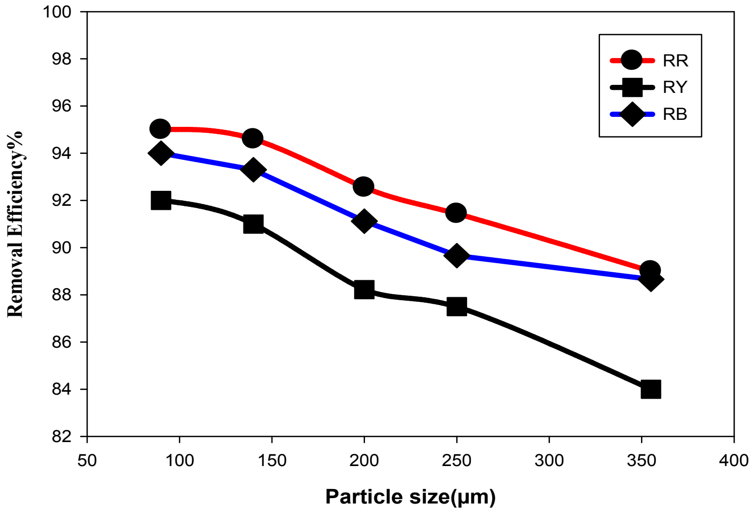

Fig. 7.4. Comparison of the removal efficiency of RR, RY, RB with particle size. Contact time: 6 hours; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

7.3.2. *Effect of Adsorbent Amount*

The effects of the amount of coir on the removal of dyes were investigated. Fig. 7.5 shows that about 96.90-98.33% of dye were removed with 3.0 g saw dust respectively. The removal efficiencies of dye increased gradually with increasing amount of adsorbent. With increasing the amount of adsorbents (from 1.0 g to 3.0 g) removal efficiency also increased due to the availability of free binding sites. However, 1, 2 and 2.5 g of adsorbent also showed almost the similar removal efficiency with same particle size of <140µm. This was due to the agglomeration of the particles themselves so that the removal efficiency was not increased with amount of adsorbents. Therefore 1.0 g of adsorbent was chosen for the next experiment.

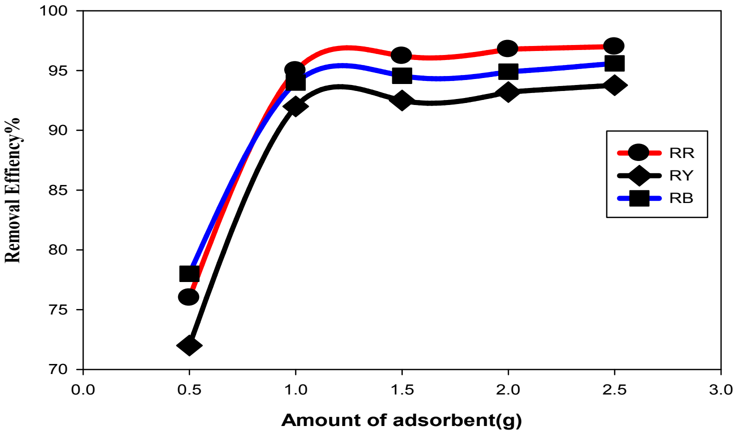

Fig. 7. 5. Comparison of the removal efficiency of RR, RY, RB with Adsorbent amount Particle size: 140µm; Initial concentration: 50 mg/L; Initial volume: 50mL; pH: 7.0; Contact time: 6 hours; Temp.: 25 ^{0}C.

7.3.3. *Effect of Initial Concentration*

The initial dye concentration also play an important role, as a given mass of adsorbent can adsorb only a certain amount of dye. For this investigation, the adsorption experiments were carried out with initial dye concentration range of 50-200 mg/L and the results were illustrated in Fig. 7.6. The removal efficiency decreased with increasing of initial concentration of sample solution. The higher adsorption rate at the initial stage may be due to availability of more number of vacant sites, as a result, there exists increased dye concentration gradient in solution on the adsorbent surface. After a certain period of time, this gradient is reduced due to accumulation of dye in the vacant sites, leading to a decrease in adsorption rate.The higher removal efficiency was achieved using 50 mg/L of dye solution. Therefore, 50mg/L dye solution was chosen for the next experiment.

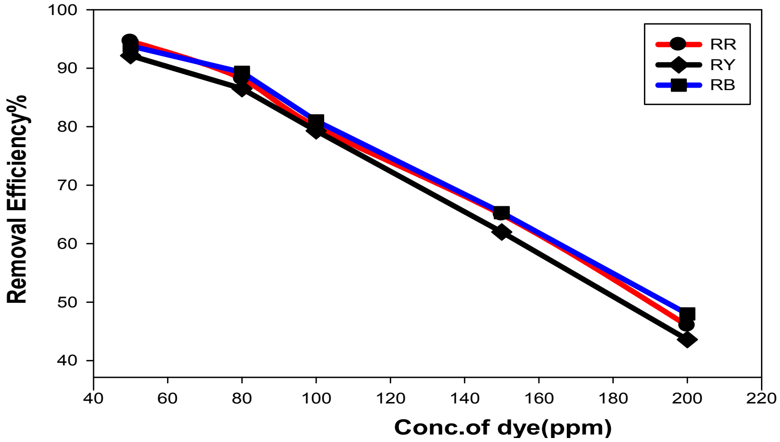

Fig. 7.6. Comparison of the removal efficiency of RR, RY, RB with initial concentration. Contact time: 6 hours; Adsorbent amount: 1.0 g; Particle size: 140µm; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

7.3.4. *Effect of the initial volume of dye solution*

To investigate the effect of initial volume on the adsorption of dyes, a series of adsorption experiments were carried out with different initial volumes (25-100 mL). Different initial volumes with optimized concentration 50 mg/ L of dye solution were treated onto treated coir dust and results were summarized in Fig.7.7.

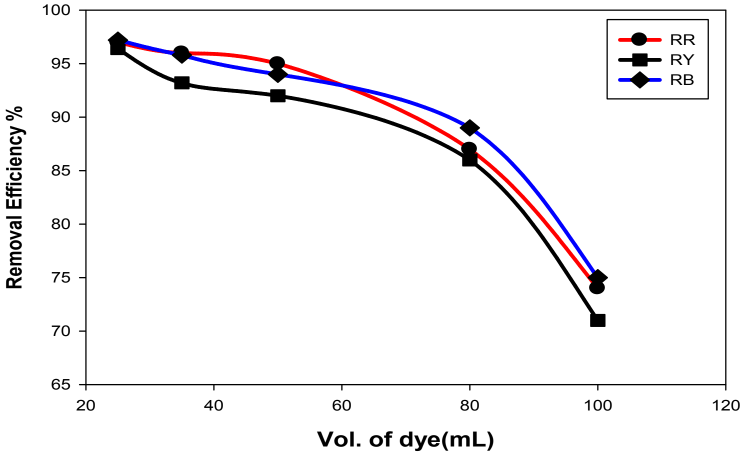

Fig. 7.7. Comparison of the removal efficiency of RR, RY, RB with initial volume. Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Contact time: 6 h; Temp.: 25^{0}C.; pH: 7.0.

It shows clearly that removal efficiency decreases with increase of initial volume. The removal efficiency varied from 97 to 75 % (C.D.) with initial volume 25 mL to 100 mL. Decrease of the removal efficiency suggests that it happened due to the decrease of contact of dye with active sites on coir dust. At lower volume of dye solution, most of the dye might get available adsorbent sites. Moreover, increasing volume of the dye solution, active adsorbent sites were unavailable due to fill by the previous dye solution.

7.3.5. *Effect of pH on removal of dye*

The initial pH value of the solution is an important factor which can determine the degree of ionization of adsorbate. Different species may present divergent ranges of suitable pH depending on which adsorbent is used. The effect of pH on the uptake of dyes (RR, RY, RB) on treated coir dust was analyzed over the pH range from 2 to 12 by using 0.01 M. HCl and 0.01M NaOH aqueous solution. In this investigation, 1.0 g of adsorbent was treated with 50 mL of dye solution (50 mg L-1) for 3 h at room temperature. But here coconut-based carbon coir dust was unaffected by pH changes in the range of 2-12. This behavior explains the high adsorption capacity of treated coir dust for dyes at pH 2-12. In order to continue the adsorption studies, the initial pH was fixed at 7.

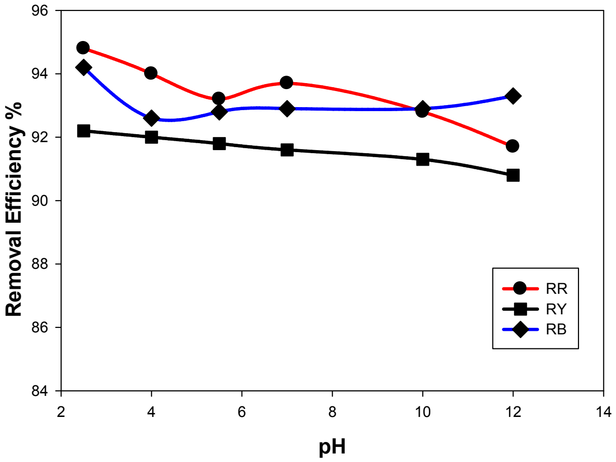

Fig. 7.8. Comparison of the removal efficiency of RR, RY, RB with pH. Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL Contact time: 6 h; Temp.: 25 ^{0}C.

7.3.6. *Effect of Contact Time*

To determine the equilibrium time for the maximum uptake of dye solutions, the adsorption onto treated coir dust (C.D.) was studied for the above optimized condition as a function of time (1,2,3,4,6 and 8 hours). Generally the rate of removal of dye increases with an increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material.

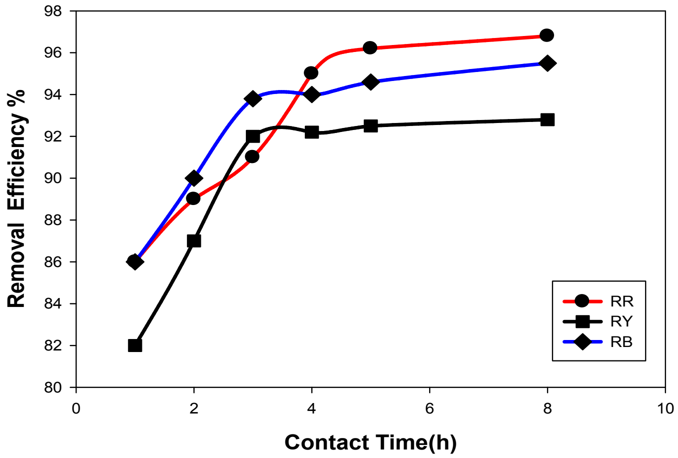

Fig. 7.9. Comparison of the removal efficiency of RR, RY, RB with contact Time. Particle size: 140µm; Adsorbent amount: 1.0 g; Initial conc.: 50 mg/L; Initial volume: 50 mL; pH: 7.0; Temp.: 25 ^{0}C.

Fig.7.9. depict the time courses for adsorption of dye at pH 6-7 on the bioadsorbent. Adsorption of dye proceeds rapidly on most materials and reaches an adsorption ratio of over 97% after 4 hour, after which equilibrium is established in about 8 hour (97%). Removal efficiency is maximum (97%) at 4 hour and remain almost unchanged after 4 hour. So the contact time is fixed about 3-4 hour for the adsorbent coir dust.

7.3.7. *Effect of Temperature*

To determine the equilibrium temperature for the maximum uptake of dye solutions (RR, RY, RB), the adsorption onto treated coir dust (C.D.) was studied for the above optimized condition as a function of temperature (25, 30, 40 &50 ^{0}C). A study of the temperature dependence of adsorption process gives valuable information about the enthalpy change during adsorption.

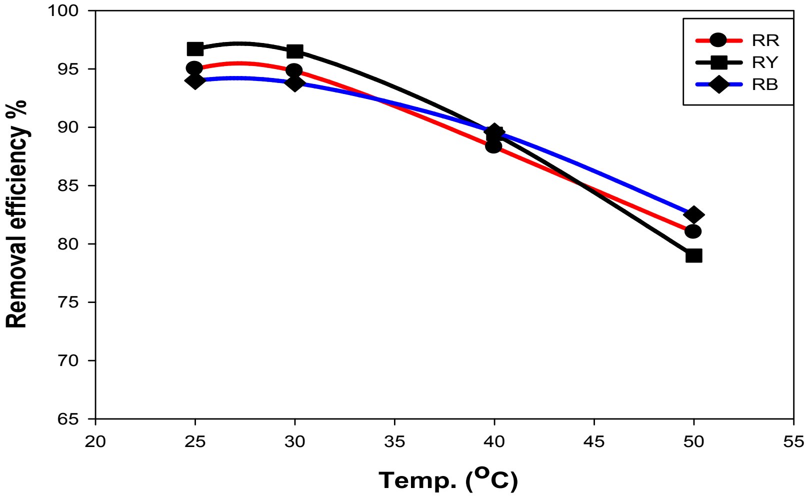

Fig. 7. 10. Comparison of the removal efficiency of RR, RY, RB with temperature. Particle size: 140µm; Adsorbent amount: 1.0g; Initial conc.: 50 mg/L; Initial volume: 50 mL; Contact time: 6 h; pH: 6.

Fig.7.10. indicates that removal efficiency increases slightly with increasing temperature from 25 ^{0}C to 30 ^{0}C. The fact that, adsorption increases with temperature indicates the increase in the mobility of the large dye ions with increasing temperature. The adsorption capacity does not change as much, when temperature increases from 40 ^{0}C to 50 ^{0}C. This observation reveals that the adsorption process is slightly endothermic or unaffected by temperature.

7.3. 8. Optimized Conditions

For the financial circumstances of Bangladesh, the removal of dye by adsorption onto low-cost waste materials has recently become the subject of considerable interest. Due to their low cost, they can be disposed of without further expensive regeneration. To find out suitable conditions, different parameters have been optimized. The parameters are particle size variation, adsorbent amount, initial concentration of dye solution, initial volume of dye, pH variation, contact time variation and temperature variation.

The optimized conditions are summarized in the Table 7.1.

Table 7.1. Optimized conditions for removal of dyes onto biomaterials; treated coir dust

Name of the parameter	**Optimized value**
Particle size	<140µm
Adsorbent amount	1.0 g
Initial concentration	50mg/L
Initial volume	50mL
pH	6-7
Contact time	3-4hour
Temperature	25 ^{0}C

7.3.9. Adsorption Isotherm

The equilibrium removal of dye was mathematically expressed in terms of adsorption isotherm. The adsorption isotherm is a function of expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature. Freundlich and Langmuir models are the most frequently employed isotherm. In the present work both models were used.The dye sorption isotherm followed the linearized Freundlich model as shown in Fig. 7.11.The relation between the dye uptake capacity of the adsorbent q_e(mg/g) and the residual dye concentration at equilibrium C_e (ppm) is given by eqn[9].

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(K_F) \tag{7.1}$$

Which will have a straight line with a slope of 1/n and an intercept of $\log(K_F)$ when $\log(q_e)$ is plotted against $\log(C_e)$, where K_F and 1/n are empirical constants dependent on several environmental factors.

Here the intercept $\log K_F$ is a measure of adsorbent capacity and the slope 1/n, is the sorption intensity. The fact that value of 1/n is less than 1, indicates a favourable adsorption.

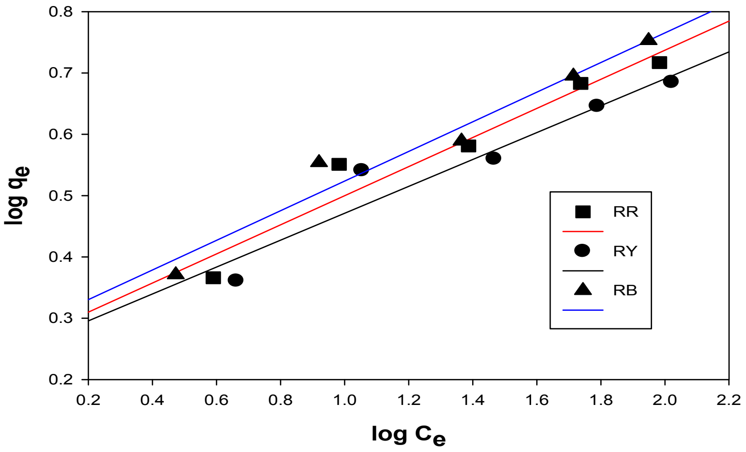

Fig. 7.11. Freundlich isotherm of RR, RY, RB by adsorption onto coir dust.

Langmuir isotherm is given by eqn[10].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \tag{7.2}$$

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(K_L q_m)$. Alternatively

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{7.3}$$

which will have a straight line with a slope of $1/(K_L q_m)$ and an intercept of $1/q_m$ when $1/q_e$ is plotted against $1/C_e$, where C_e is the equilibrium concentration (mg/dm^3), q_e the amount of metal sorbed (mg/g), q_m is q_e for a complete monolayer (mg/g), and K_L is the sorption equilibrium constant (dm^3/mg).

The essential characteristics of Langmuir eqn. can be expressed in terms of separation factor R_L[11],

Where $R_L = 1/(1+K_L.Co)$.

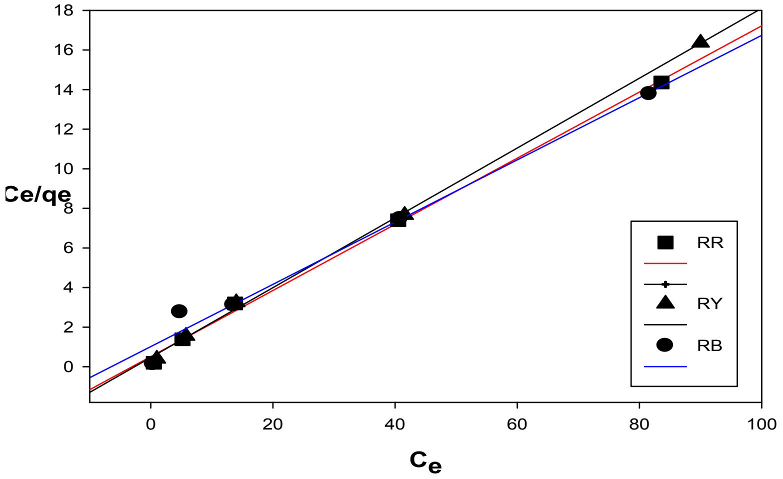

Fig. 7.12. Langmuir isotherm of RR, RY, RB by adsorption onto the coir dust.

Table 7.2. Freundlich and Langmuir Parameters and Separation factor R_L for Adsorption of dyes on treated coir dust.

Dye	Freundlich isotherm			Langmuir isotherm			
	K_F	1/n	R^2	q_m	K_L	R^2	R_L
RR	2.793	0.171	0.995	5.984	0.327	0.997	0.015
RY	2.660	0.175	0.979	5.681	0.371	0.998	0.013
RB	2.916	0.161	0.996	6.064	0.325	0.996	0.015

Analysis of adsorption isotherm

The simplest method to determine isotherm constants for two-parameter isotherms is to transform the isotherm variables, so that the equation is converted to a linear form and then to apply the linear regression. The linear isotherm constants, q_m, K_L and R^2 are also listed in Table 7.2. The individual constants, K_L and R^2 significantly differ, although the ratios give values for the monolayer saturation capacity, q_m which are very close to those obtained using Eq^n. (7.1) and (7.2). In Table 7.2, a comparison of values of the Langmuir monolayer saturation capacity, q_m is made for the sorption of dye onto coir dust. The 1/n is an indication of the affinity between adsorbent and adsorbate. Its value is 0.1-0.5, indicating that the adsorbents employed have a high adsorptive capability. The value of K_F is large, and $1/n$ is 0-1, indicating that the adsorbents employed have a high adsorptive capability.

7.3.10. Adsorption Kinetics

Adsorption kinetics depends on the adsorbate–adsorbent interaction and system condition and has been investigated for their suitability for application in water pollution control.

Pseudo first order rate expression[12] is given by Eq^n .-- 7.4

$$dq_1/dt = k_1(q_e-q_t) \tag{7.4}$$

Which on integration give Eq^n. -- 7.5

$$\log(q_e-q_t) = \log qe - k_1t/2.303 \tag{7.5}$$

Where qe and qt are the amount of adsorbed (mg/g) at equilibrium and at any time t & k_1 is rate constant.

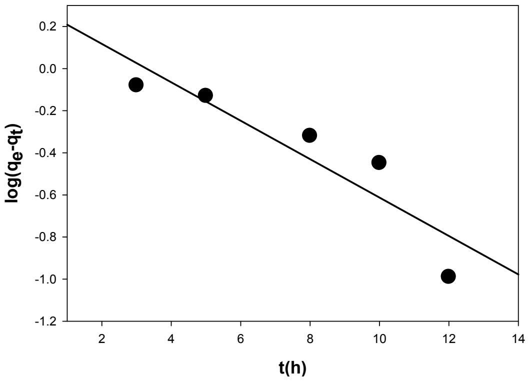

Fig. 7.13. Pseudo first order Kinetics

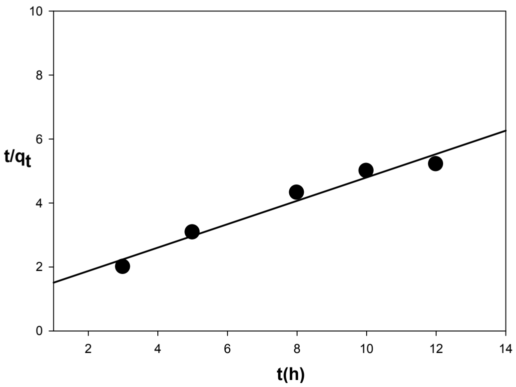

Fig. 7.14. Pseudo second order Kinetics

Pseudo second order rate expression[13] is given by Eq^n .

$$\frac{t}{q_1} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e} t \tag{7.6}$$

A plot of $\frac{t}{q_t}$ vs. t given a slope = $\frac{1}{q_e}$, intercept $\frac{1}{K_2(q_e)2}$

Table 7.3. Pseudo first order & second order rate constants, calculated & experimental q_e values for adsorption of RR, RY, RB on treated coir dust at 298K

Pseudo first order Kinetic model				**q_e exp. mg/g**	**Pseudo second order Kinetic model**			**Intra-Particle diff. coefficient**
Dye	q_e(mg/g)	$k_1(h^{-1})$	R^2		q_e(mg/g)	k_2(h , g/mg)	R^2	k_{id}. $mg/min^{-o.5}g$
RR	1.40	0.515	0.92	2.47	2.73	0.550	0.97	0.72
RY	1.66	0.531	0.83	2.46	2.80	0.415	0.95	0.88
RB	1.57	0.856	0.97	2.48	2.85	0.641	0.99	0.73

7.3.11. Intra-Particle diffusion model

The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and adsorbent. Rate of adsorption is usually measured by determining the change in concentrations of adsorbate with the adsorbent as a function of time. The effect of intra-particle diffusion resistance on adsorption can be determined by the following relationship[14].

$$q_t = k_{id}\, t^{1/2} + C$$

Where k_{id} is the intra-particle rate constant (g mg−1 min−1/2), and the intra-particle rate constant k_{id} is a function of equilibrium concentration in solid phase *q*e and intra-particle diffusivity. Adsorption mechanism follows the intra-particle diffusion model, a plot of q_t against $t^{1/2}$ should give a linear line with slope k_{id} and intercept *C*. Values of *C give* information about the thickness of the boundary layer, i.e. the larger intercept the greater is the boundary layer effect. It can be seen from above eq. that if pore-diffusion is the rate limiting step, then a plot of q_t against $t^{1/2}$ must give a straight line with a slope that equals k_{id} and an intercept equal to zero.

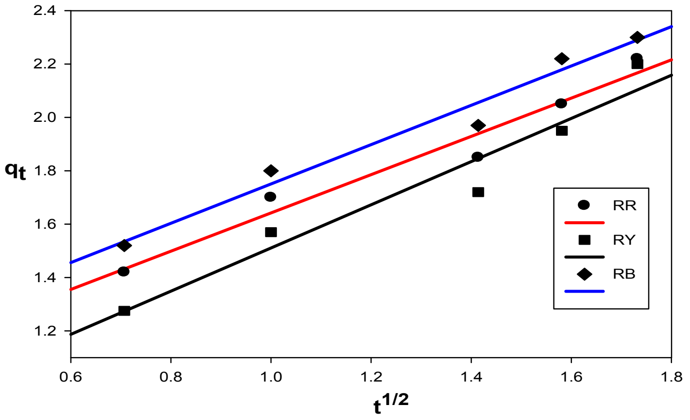

Fig. 7.15. Intra-Particle Diffusion Model of RR, RY, RB.

Kinetic Analysis

The results of adsorption kinetics were processed based on the three kinetic models: pseudo-first order, pseudo-second and intra-particle diffusion models. The kinetic parameters related to each kinetic model were calculated from the intercepts and slopes of the corresponding linear plots and the estimated parameters are summarized in table 7.10. The correlation coefficients (R^2) obtained for pseudo-second-order model (0.96) are higher than those obtained -first-order model (0.83). The calculated adsorption capacity value obtained from pseudo-second-order model (q_e) agrees well with the related experimental value (qe, exp). It could be concluded that the adsorption systems are fitted well to the pseudo-second-order model. The intra-particle diffusion plots for adsorption of dyes were linear but did not pass through the origin, indicated that the pore diffusion is not the rate limiting step of the studied adsorption process.

7.3.12. Desorption kinetic

After completing the adsorption the residue was dried in air and then used to investigate the desorption. The results obtained are shown in fig-7.16, which shows that the amount of desorption increases with time. This also indicates that the adsorption is physical in nature.

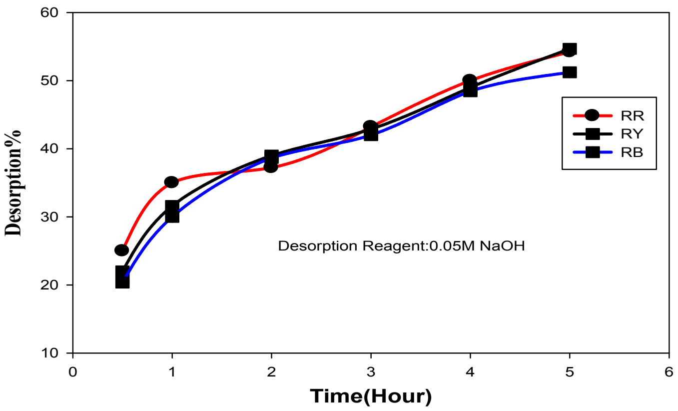

Fig. 7.16. Plot of desorption vs time

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dyes[15]. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. If sulphuric acid or alkaline water desorp the dyes, then the adsorption is by ion exchange. If organic acids, like acetic acid desorp the dyes, then the dye is attached to the adsorbent through chemisorption. The effect of various reagents used for desorption studies shows that sodium hydroxide is a better reagent for desorption, because we could get more than 53% removal of adsorbed dyes. The reversibility of adsorbed dyes in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of dyes by mineral acids and alkaline medium indicates that the dyes are adsorbed onto the activated carbon by physisorption.

7.3.13. Thermodynamic study of adsorption of RR, RY and RB on charcoal

In this work the thermodynamic parameter including activation energy (Δ E), change in free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) for the adsorption of each dye sample on coir dust could not be determined. Previously it was mentioned that the adsorption of dyes on coir dust was not significantly affected with temperatues.

7.4. Proposed Mechanism

There are many factors that may influence the adsorption behavior. Adsorption occurs due to the interactions between ions, molecules and the adsorbent surface. Remazol Red (RR), Remazol Yellow (RY), Remazol Blue (RB), are an anionic type dye having a sulfonic acid, hydroxyl group in its structure. In aqueous sol^{n}. it dissociates as a negative anion:

$$\text{Dye-SO}_3\text{H} + \text{H}_2\text{O} \longrightarrow \text{Dye-SO}_3^-$$

The presence of positive charges on the surface on the coir dust has the tendency to attract anionic dye as follow:

$$\text{Dye-SO}_3^- + (\text{C.D})^+ \longrightarrow \text{Dye-CD}$$

7.5. Application of developed method to textile effluent for removal of dyes.

Textile effluents were collected from some renowned textile industries situated in Dhaka city and around Dhaka city. The samples were collected from respective sites. The color, temperature and pH of the sample were recorded on the site and samples were transported to the laboratory for storage at 5 ^oC. Adsorbents used in the research work were treated sawdust, jute stick powder and treated coir dust. All the prepared adsorbents show good removal efficiency, around 85-97%. As the pH of the water samples was around 9-11.5, the pH of the solution is lowered by adding 0.01M HCl solution. The treatment results are presented in Table 7.5. 1.0 g of adsorbent was applied for 50mL effluent in the treatment. From the given results, It is evident that the prepared adsorbents is suitable not for only synthetic dye but also for textile effluent containing dye**.**

Table 7.4. Characteristics of samples collected from different textile mill, Bangladesh.

SL No.	Organizations	Nature of Sample	Color	pH	Temperature(^0C)
1	Esquire composite mill	Liquid	Dark Green to Blue	9.84	25
2	Thermex group	Liquid	Dark Blue	11.2	25
3	Beximco composite mill	Liquid	Light Redish	9.2	25
4	Padma Polycotton	Liquid	RedishYellow	9.64	25

Table 7.5. Removal efficiency of various textile effluents

Organizations	Adsorbents	Removal Efficiency%
Esquire composite mill Narayanganj	Treated Coir dust	96.3
	Jute stick powder	85
	Treated saw dust	89
Thermex group Narsinghdi	Treated Coir dust	98.9
	Jute stick powder	96.5
	Treated saw dust	97
Beximco composite mill Saver, Dhaka.	Treated Coir dust	96.8
	Jute stick powder	93
	Treated saw dust	92.3
Padma Polycotton Tejgaon, Dhaka	Treated Coir dust	97.8
	Jute stick powder	93
	Treated saw dust	95.3

Fig. 7.17. Textile Effluent (a) before treatment (b) after treatment

Table 7.6. Removal efficiency of mixed textile dyes

Mixed Dye	Adsorbents	Removal Efficiency%
RR+RY+RB	Treated Coir dust	91
RR+RY+RB	Jute stick powder	82.5
RR+RY+RB	Treated saw dust	85.3

7.6. Summary of removal efficiency of Dyestuffs used in the research work

In this research work, various types of dye were used such as-Reactive dye, Direct dye and Disperse dye, supplied by Dye star Ltd, Colourtex Ltd Dhaka, Bangladesh. Reactive dyes form a covalent bond with the fiber, usually cotton, although they are used to small extent on wool and nylon. Disperse dyes are insoluble in water, but are capable of dissolving certain synthetic fibres. These are used for acetate, rayons, Dacron, Nylon and other synthetic fibres. Direct dyes contain acidic or basic groups and combine with polar groups in the fibre. These are used to dye wool and silk. All the prepared adsorbents used in this research work were very suitable for mentioned dyes type. Among all types of dye, reactive dye show more removal efficiency and disperse dye show less removal efficiency. The analysis results are presented in Table 7.7.

Table 7.7. Dyestuffs used in the experiments and their removal efficiency**.**

Name of dye	Type	Chemical Class	Abbreviations	λ_{max}	Removal %
Remazol Red	Reactive	Azo	RR	520	95
Remazol Yellow	Reactive	Azo	RY	416	92
Remazol Blue	Reactive	Anthraquinone	RB	607	96
Levafix Red	Reactive	Anthraquinone	LR	513	91
Coralene Scarlet XF	Disperse	Azo	CS XF	517	88
Coralene Blue MD	Disperse	Anthraquinone	CB MD	612	85
Congo Red	Direct	Azo	CR	497	96

7.7. Conclusion

Dye removal has been an important but challenging area of the waste water treatment.The removal of Remazol Red, Remazol Blue and Remazol Yellow from aqueous solution using activated charcoal prepared from coir dust has been investigated under different experimental conditions in batch mode. Adsorption of dye almost remain unchanged with the variation in pH and slightly increases with increasing temperature. Freundlich and Langmuir models were found to be linear, indicating the applicability of classical adsorption isotherm to this particular adsorption system. The kinetic study of all dyes followed pseudo second order model better than first order model .Comparatively Remazol Red, Remazol Blue show better removal efficiency then Remazol Yellow. Lower removal efficiency of Remazol Yellow is due to its larger size and different functional group. This developed method using an inexpensive and readily available bio-adsorbent (activated charcoal) provide an attractive alternative treatment for dye removal. Such type of prepared activated charcoal will be as effective as commercial activated charcoal in the adsorption of textile dyes.

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Chapter - 8

Concluding Remarks and Perspectives

8.1 Concluding Remarks and Perspectives

In this study, the adsorption of various dyestuffs (reactive, direct and disperse dye) onto natural low cost adsorbents such as saw dust, coconut coir and jute stick powder were investigated. In order to increase the adsorption capacities of adsorbents for various dyestuffs, surface treatment (modified) with H_2SO_4 and $ZnCl_2$ or NaCl was applied to the adsorbents. With the surface modification the change in the surface charges of adsorbent materials was aimed. Finally, the adsorptive capacities of various adsorbents were compared for the same dyes and under the same experimental conditions.

The conclusions drawn from the results of this study are listed as follows:

- The adsorption capacities of saw dust, coconut coir and jute stick powder in their natural form for the adsorption of reactive, direct and disperse dye (anionic dyes) are not good enough(40-50%). Surface treatment of these adsorbents need to be done with H_2SO_4 and $ZnCl_2$ or NaCl.
- The adsorption capacities of a treated adsorbents for various dyes were increased several times based on the type of the dye used. Modified coconut coir has higher adsorption capacity for reactive, direct and disperse dye than other adsorbents.
- From this experiment, it is clear that highest removal efficiency could be achieved with lower particle size (>140μm)
- Adsorption of dye on treated saw dust, jute stick powder decreases with the increase of pH. Adsorption is highest for pH 2.5- 3.5. Adsorption of dye on coconut coir remains almost unchanged with variation of pH.
- Removal efficiency increases slightly with increasing temperature in case of saw dust and coir dust. Adsorption of dye was highest with 35^0 C. But removal efficiency decreases with increasing temperature in case of jute stick. However, at room temperature (25 ^{0}C) removal efficiency (%) is satisfactory for all the above adsorbents. So, as a low cost method the experiment was carried out at room temperature.
- The value of K_F is large and 1/n is 0.657-0.896, indicating that the adsorbents employed have a high adsorptive capacity. $R_L > 0$ but < 1 also indicates a favourable adsorption.

- Pseudo-second order equation was found to be in good agreement with those of experimental values.
- BET surface studied showed that coconut coir has higher BET surface area.
- Thermodynamic data indicates the exothermic and endothermic nature of adsorption systems.

Overall, a new low cost dye removal method was developed by using local adsorbents. This can be applied for the removal of dyes (Remazol Blue, Levafix Red, and Coralene Scarlet etc.) before discharge in the water. At present, large international retailers of the textile sector, with 'social and environmental' agendas, insist that effluent treatment should be carried out. However, many of the small to medium sized industries state that they cannot afford the capital expenditure to install ETP, which is a negative impact of the textile industries**.** Therefore, this developed method would be helpful to minimize the negative impacts of the textile industries in Bangladesh through establishment of low cost Effluent Treatment Plants (ETP).

List of Publications

1. Nargish Jahan Ara, Md. Abu Hasan, Mohammad Arifur Rahman, Md. Abdus Salam, Abdus Salam and A. M. Shafiqul Alam**.** Removal of Remazol Red from Textile Waste Water Using Treated Sawdust. *Bangladesh Pharmaceutical Journal,* **2013,** 16(1): 93-98.

2. Nargish Jahan Ara, Mohammad Afrifur Rahman and A. M. Shafiqul Alam, Study of Removal Efficiency of Reactive Dyes from Textile Effluent, *35th Annual Conference of Bangladesh Chemical Society,* **2012***,* PP-109.

3. Nargish Jahan Ara, Mohammad Afrifur Rahman and A. M. Shafiqul Alam
Removal of Remazol Blue from Waste Water by Adsorption on activated carbon developed from Coir dust. *Dhaka University Journal of Science,* Submitted.

4. Nargish Jahan Ara, Mohammad Afrifur Rahman and A. M. Shafiqul Alam, Removal of Remazol Yellow, Textile dye from aqueous solution with chemical treated Sawdust. *Journal of the Bangladesh Chemical Society,* Submitted.

5. Nargish Jahan Ara, Rayhan Hossain, Mohammad Arifur Rahman, A. M. Shafiqul Alam. Removal of Levafix Red from aqueous solution with treated Jute Stick. *Bangladesh Pharmaceutical Journal,* Submitted.