CES Technical Report 113

Low cost biosorbents for dye removal

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LIST OF NOTATIONS AND ABBREVIATIONS

q	Amount of adsorbate adsorbed at equilibrium time t (mg of adsorbate / gram of adsorbent)
q_e	Amount of adsorbate adsorbed at equilibrium time (mg of adsorbate / gram of adsorbent)
qmax	Langmuir constant (adsorption capacity) (mg/g)
b	Langmuir constant (energy of adsorption) (L/mg)
R_L	Equilibrium parameter
k_f	Freundlich constant
n	Freundlich constant
C_{eq}	Adsorbate concentration in solution at equilibrium (mg/L)
k_{ad}	Lagergren adsorption rate constant (l/min)
LC_{50}	Lethal concentration for 50 percent mortality of the animal
BGH	Bengal gram husk
TDH	Tur dal husk
TH	Tamarind husk
CH	Coffee husk
AM	Amaranth
FG	Fast green
MB	Methylene blue
RB	Rhodamine B

Summary

Water resources are of critical importance to both natural ecosystem and human developments. Increasing environmental pollution from industrial wastewater particularly in developing countries is of major concern. Many industries like dye industries, textile, paper and plastics use dyes in order to colour their products and also consume substantial volumes of water. As a result they generate a considerable amount of coloured wastewater. The presence of small amount of dyes (less than 1 ppm) is highly visible and undesirable. Many of these dyes are also toxic and even carcinogenic and pose a serious threat to living organisms. Hence, there is a need to treat wastewaters containing toxic dyes and metals before they are discharged into the waterbodies.

Many physico-chemical methods like coagulation, flocculation, ion exchange, membrane separation, oxidation, etc are available for the treatment of dyes. Major drawbacks of these methods are high sludge production, handling and disposal problems, high cost, technical constraints, etc. This necessitates cost effective and environmentally sound techniques for treatment of watsewaters containing dyes.

The objective of the present study is to explore the feasibility of using four agricultural by-products namely channa dal (*Cicer arientinum*) husk, tur dal (*Cajanus cajan*) husk, tamarind pod (*Tamarindus indica*) shells and coffee (*Coffee arabica*) husk in the removal of four dyes namely methylene blue, fast green, amaranth and rhodamine B. Batch-mode kinetic and equilibrium studies have been carried out. Regeneration of dyes from the spent adsorbent to recover the adsorbent and adsorbate has been studied. The attractive features of the adsorbents used in the present study are that it is environmentally friendly and of low cost.

The results showed that coffee husk was not efficient in the biosorption of dyes. The maximum adsorption of methylene blue by the four husks was at pH 8.0; fast green 3.0; amaranth at pH 2.0 and rhodamine B at 7.0. The percentage of adsorption increased with increase in time till equilibrium was achieved. The equilibrium time varied with the initial dye concentration and the type of the adsorbent. The amount of adsorbent required to reach equilibrium differed with the type of the dye. In general, an increase in adsorption was seen with increase in adsorbent concentration. The adsorption capacity and intensity was calculated from Langmuir and Freundlich isotherm models and generally varied with the type

of the adsorbent and dye under investigation. The Langregren equation was used to calculate the disassociation constant, which varied with type of adsorbent, and dyes. The infrared spectra of the adsorbents before and after binding to the dye revealed the presence of carboxylic, amine and hydroxyl groups which facilitated the biosorption of dyes.

The agricultural byproducts used in the present investigation are attractive alternatives to the existing adsorbents. The adsorption capacity was comparable to activated carbon. The type of adsorption was mainly chemisorption showing that the adsorption was due to ion exchange or chemical bonding or both. The optimal conditions for adsorption varied on the basis of the charge carried by the individual dye; i.e., whether the dye under investigation was a cation or anion. Chemical reactions representing the adsorption mechanism have been worked out.

1. **Introduction**

Fresh water is already a limiting resource in many parts of the world. In the next century, it will become even more limiting due to increased population, urbanization, and climate change. This limitation is caused not just by increased demand for water, but also by pollution in freshwater ecosystems. Pollution decreases the supply of usable water and increases the cost of purifying it. Some pollutants, such as heavy metals or chlorinated organic compounds, contaminate aquatic resources and affect food supplies. This nutrient pollution, combined with human demand for water, affects biodiversity, ecosystem functioning, and the natural services of aquatic systems upon which society depends. Point sources are 'pipeline' discharges of pollutants to receiving waters, e.g. domestic sewage discharges or industrial waste effluents from factories or plants. They are relatively easy to identify and isolate. In contrast, non-point pollution results from storm runoff, which transports polluting materials diffusely and over land.

Major water pollutants include a variety of organic and inorganic chemicals such as heavy metals and industrial compounds. They can affect human health and/or interfere with industrial or agricultural water use. If the level of a pollutant in the water supply exceeds an acceptable level for a given water use (e.g., domestic or industrial water supply), the water is considered unsafe or too degraded for that use. Solutions to such pollution problems, therefore, usually focus on reduction of pollution at the source and/or treatment of the polluted water prior to use (Ahalya and Ramachandra, 2002).

Dyes are basically chemical compounds that can attach themselves to fabrics or surfaces to impart colour. Most dyes are complex organic molecules and are resistant to weather, action of detergents, etc. Synthetic dyes are extensively used in many fields of up-to-date technology, e.g., in various branches of the textile industry (Gupta *et al*., 1992; Shukla and Gupta, 1992 and Sokolowska-Gajda *et al*., 1996), of the leather tanning industry (Tünay *et al*., 1999 and Kabadasil *et al*., 1999) in paper production (Ivanov *et al*., 1996), in food technology (Bhat and Mathur, 1998 and Slampova *et al*., 2001), in agricultural research (Cook and Linden, 1997 and Kross *et al*., 1996), in light-harvesting arrays (Wagner and Lindsey, 1996), in photoelectrochemical cells (Wrobel *et al*., 2001), and in hair colourings (Scarpi *et al*., 1998). Moreover, synthetic dyes have been employed for the control of the efficacy of sewage (Morgan-Sagastume *et al*., 1997) and wastewater treatment (Hsu and

Chiang, 1997 and Orhon *et al*., 1999), for the determination of specific surface area of activated sludge (Sorensen and Wakeman, 1996) for ground water tracing (Field *et al*., 1995), etc. Dyes can be classified according to their chemical structure or according to their use. However, classifications vary from country to country though there are some fundamental categories that are common to all. According to the central pollution control board (CPCB), India there are approximately a million known dyes and dye intermediates out of which 5,000 are produced commercially. Based on their use based classification, the dyes are divided into 15 groups.

Table 1 Classification of dyes based on their use.

	Application	
Type of Dye	**According to CPCB[1]**	**According to World Bank[2]**
Acid dyes	Wool, silk, nylon	Animal fibres
Azo dyes	Cotton	Cotton
Basic dyes	Acrylic	Paper
Direct dyes	Cotton, leather, paper and synthetics	Cotton wool or cotton silk
Disperse dyes	Polyster	
Food dyes	Food, cosmetics	
Metal complexes	Cotton	
Mordant dyes	Wool	
Whitening agent	Plastics, paper, soap	
Pigment dyes	Paints and plastics	Paints and inks
Reactive dyes	Wool and cotton	
Solvent dyes	Synthetics	
Sulphur dyes	Cotton and Synthetics	
Vat dye	Cotton and Synthetics	

Source: [1] Anon 2002, Effluent toxicity status in water polluting industries, Part 1 – Dye and dye intermediate, bulk drugs and textile industries, Central Pollution Control Board, Ministry of Environment and Forests, Government of India, p7.

[2] Pollution prevention and abatement handbook, World Bank, p 298

Unfortunately, the exact amount of dyes produced in the world is not known. It is estimated to be over 10,000 tonnes per year. Exact data on the quantity of dyes discharged in the environment are also not available. It is assumed that a loss of 1–2% in production and 1–10% loss in use are a fair estimate. For reactive dyes, this figure can be about 4%. Due to large-scale production and extensive application, synthetic dyes can cause considerable environmental pollution and are serious health-risk factors. The growing concern of environmental protection has influenced industrial development promoting the development of ecofriendly technologies (Desphande, 2001), reduced consumption of freshwater and lowers output of wastewater (Knittel and Schollmeyer, 1996 and Petek and Glavic, 1996), etc. However, the release of important amounts of synthetic dyes to the environment has posed challenges to environmental scientists apart from increased public concern and legislation problems.

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to colour their products and also consume substantial volumes of water. As a result, they generate a considerable amount of coloured wastewater. It is recognized that public perception of water quality is greatly influenced by the colour. Colour is the first contaminant to be recognized in wastewater (Banat et al., 1996). The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable (Robinson et al., 2001 and Banat et al., 1996).

Dyeing industry effluents are one of the most problematic wastewaters to be treated not only for their high chemical oxygen demand, but also for high biological oxygen demand, suspended solids, turbidity, toxic constituents but also for colour, which is the first contaminant discernible by the human eye. Dyes may affect the photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, etc. in them (Clarke and Anliker 1980; Zollinger 1987; Mishra and Tripathy 1993; Banat *et al*1996; Fu and Viraraghvan 2001; Robinson *et al*2001).

Dyes usually have a synthetic origin and complex aromatic molecular structure, which make them more stable and more difficult to biodegrade. Dyes are classified as follows: anionic – direct, acid and reactive dyes; cationic – basic dyes; non-ionic – disperse dyes (Mishra and Tripathy 1993; Fu and Viraraghvan 2001). The chromophores in anionic and non-ionic dyes are mostly azo groups or anthroquinone types. The reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent. Anthraquinone based dyes are more resistant to degradation due to their fused aromatic structures and thus remain coloured in the wastewater. Reactive dyes are typically azo-based chromophore combined with different types of reactive groups e.g, vinyl sulphone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine. They differ from all other dyes in that they bind to textile fibers like cotton to form covalent bonds. They are used extensively in textile industries regarding favourable characteristics of bright colour, water fast, simple application techniques with low energy consumption.

Water soluble reactive and acid dyes are problematic; as they pass through the conventional treatment system unaffected, posing problems. Hence, their removal is also of great importance (Robinson *et al* 2001; Hu 1992; Juang *et al* 1997; Karcher *et al*1999; Sumathi and Manju 2000; Aksu and Tezer *et al*2000; O'Mahony *et al*2002; Moran *et al*1997).

Basic dyes have high brilliance and intensity of colours and are highly visible even in very low concentration (Clarke and Anliker, 1980; Banat *et al*., 1996; Fu and Viraraghavan, 2001; Mittal and Gupta, 1996; Chu and Chen, 2002; Fu and Viraraghavan, 2002). Metal complex dyes are mostly chromium based, which is carcinogenic (Clarke and Anliker, 1980; Banat *et al*., 1996; Mishra and Tripathy 1993; Gupta *et al*., 1990). Disperse dyes do not ionize in an aqueous medium and some disperse dyes have also been shown to have a tendency to bioaccumulate (Banat *et al*., 1996). Due to the chemical stability and low biodegradability of these, conventional biological wastewater treatment systems are inefficient in treating dye wastewater.

Dyes have generated much concern regarding its use, due to its toxic effects. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity and respiratory toxicity. McGeorge *et al*. (1985) reported the mutagenic activity of textile wastewater effluents, using the salmonella/microsome assay and contributed the highest percentage (67%) of mutagenic effluents. Costan *et al*. (1993) found that a textile effluent ranked second in toxicity, among eight industrial sectors represented, by using a series of bioassays assessing the acute, sublethal and chronic toxicity at various trophic levels.

Estimation of LC_{50} values of many commercial dyes at different time intervals on fish was done earlier by Clarke and Anliker 1980. Srivastava *et al.* (1995a) also observed changes in LC_{50} values of malachite green in a fresh water catfish. *Gambusia affinis* was used to find the LC_{50} value for acid red 73 and showed higher toxicity (Muthukumar *et al.,* 2005). Over 90% of some 4000 dyes tested in an ETAD (Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry) Survey had LD_{50} values greater than $2 \text{ X } 10^3$ mg/kg. The highest rates of toxicity were found amongst basic and diazo direct dyes (Shore, 1996).

Sub – chronic exposure (13 week) to benzidine – based dyes resulted in hepatocellular carcinomas and hepatic neoplastic nodules in rats (National Cancer Institute 1978) and carcinomas in very short duration (National Institute for Occupational Safety, 1980). Histopathological changes in the testes of textile wastewater exposed rats (sub – chronic) included a reduction in the number of germ and Leydig cells, resulting in impaired spermatogenesis (Mathur, *et al.* 2003).

Umbuzeiro *et al.* (2005) analysed the mutagenic activity of dyes in environmental samples of the Cristais River, Sao Paulo, Brazil. A low level mutagencity of textile/dye industries in the underground water of Sanganer, Jaipur (India) were also investigated (Mathur *et al*2005). A number of studies have demonstrated mutagenic activity in effluents from textile and dye-related industries (Mcgeorge, *et al.* 1985; Sanchez, *et al.*, 1988; Wells, *et al.* 1994).

Over 100,000 commercially available dyes exist and more than 7×10^5 tonnes per year are produced annually (Pearce et al., 2003 and McMullan et al., 2001). Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that two per cent of dyes that are produced are discharged directly in aqueous effluent (Pearce et al., 2003 and Robinson et al., 2001). Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms (O'Neill et al., 1999 and Vandevivere et al., 1998). However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents (Sun and Yang, 2003 and Ravi Kumar et al., 1998).

During the past three decades, several physical, chemical and biological decolorization methods have been reported; few, however, have been accepted by the paper and textile industries (Ghoreishi and Haghighi, 2003). Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials (Jain et al., 2003, Ho and McKay, 2003 and Derbyshire et al., 2001). If the adsorption system is designed correctly it will produce a high-quality treated effluent. Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies (Derbyshire et al., 2001). However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents.

Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from industry and agriculture, have been proposed by several workers. These materials could be used as sorbents for the removal of dyes from solution. Some of the reported sorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton).

In the Section below, we have reviewed the technical feasibility of various non-conventional low-cost adsorbents for dye removal from contaminated water. The Section provides a summary of recent information concerning the use of low-cost materials as sorbents. For this, an extensive list of sorbent literature has been compiled. The review (i) presents a critical analysis of these materials; (ii) describes their characteristics, advantages and limitations; and (iii) discusses various mechanisms involved. Recent reported adsorption capacities are also noted to give some idea of sorbent effectiveness. However, the reported adsorption capacities must be taken as an example of values that can be achieved under specific conditions since adsorption capacities of the sorbents presented vary, depending on the characteristics of the material, the experimental conditions, and also the extent of chemical modifications.

1.1 Technologies available for colour removal

1.1.1 General considerations

The methods for dye wastewater treatment have been reviewed by Pokhrel and Viraraghavan, 2004, Robinson et al., 2001, Slokar and Majcen Le Marechal, 1998, Delée et al., 1998 and Banat et al., 1996 and Cooper (1993). Fungal and bacterial decolorization methods have been reviewed by Aksu, 2005, Wesenberg et al., 2003, Pearce et al., 2003, McMullan et al., 2001 and Fu and Viraraghavan, 2001a and Stolz (2001).

The reported methods for the removal of pollutants from effluents are listed in Table 2. The technologies can be divided into three categories: biological, chemical and physical (Robinson et al., 2001). All of them have advantages and drawbacks. Due to the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries (Ghoreishi and Haghighi, 2003).

Table 2 Principal existing and emerging processes for dyes removal

	Technology	**Advantages**	**Disadvantages**
Conventional treatment processes	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery	Membrane separations	Removes all dye types, produce a high-quality	High pressures, expensive, incapable of treating large

	Technology	**Advantages**	**Disadvantages**
processes		treated effluent	volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

Presently, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents (Pereira et al., 2003 and Marco et al., 1997). In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way. A literature survey shows that research has been and continues to be conducted in the areas of combined adsorption-biological treatments in order to improve the biodegradation of dyestuffs and minimize the sludge production.

1.1.2. Biological treatments

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, 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 (McMullan et al., 2001, Fu and Viraraghavan, 2001a and Banat et al., 1996). However, their application is 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 (Bhattacharyya and Sarma, 2003). Biological treatment is incapable of obtaining satisfactory colour elimination with current conventional biodegradation processes (Robinson et al., 2001). Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin (Ravi Kumar et al., 1998). In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

1.1.3. Chemical methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with $Fe(II)/Ca(OH)_2$, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. 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 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.

1.2 Physical methods

Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis, etc.) and adsorption techniques. 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. In accordance with the very abundant 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 sorbent is inexpensive and does not require an additional pre-treatment step before its application.

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications (Dabrowski, 2001). Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

1.2 Colour removal using commercial activated carbons

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater (Babel and Kurniawan, 2003, Derbyshire et al., 2001 and Ramakrishna and Viraraghavan, 1997). In particular, the effectiveness of adsorption on commercial activated carbons (CAC) for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options (Ramakrishna and Viraraghavan, 1997). CAC are the most effective adsorbents due to of their great capacity to adsorb dyes and recent reported adsorption capacities for CAC are listed in Table 3. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages (Babel and Kurniawan, 2003). It is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications (Streat et al., 1995). This has led many workers to search for more economic adsorbents.

Table 3 Adsorption capacities q_m (mg/g) for commercial activated carbons

Supplier	**Dye**	q_m	**Sources**
Tapei Chemical Corp. (Taiwan)	Acid yellow	1179	Chern and Wu (2001)
Chemviron Carbon (UK)	Remazol yellow	1111	Al-Degs et al. (2000)
Chemviron Carbon (UK)	Basic yellow 21	860	Allen et al. (2003)
Chemviron Carbon (UK)	Basic red 22	720	Allen et al. (2003)
Filtrasorb Corporation (USA)	Reactive orange 107	714	Aksu and Tezer (2005)
Merck Co. (Taiwan)	Reactive red 2	712.3	Chiou et al. (2004)
Miloje Zakic (Macedonia)	Basic dye	309.2	Meshko et al. (2001)
E. Merck (India)	Basic blue 9	296.3	Kannan and Sundaram (2001)
Filtrasorb Corporation (USA)	Reactive red 5	278	Aksu and Tezer (2005)
Merck Co. (Taiwan)	Direct red 81	240.7	Chiou et al. (2004)
Filtrasorb Corporation (USA)	Acid yellow 117	155.8	Choy et al. (2000)
Chemviron Carbon (UK)	Acid blue 40	133.3	Özacar and Sengil (2002)
Filtrasorb Corporation (USA)	Acid blue 80	112.3	Choy et al. (2000)
Calgon Corporation (USA)	Acid red 88	109	Venkata Mohan et al. (1999)
Chemviron Carbon (UK)	Basic red 46	106	Martin et al. (2003)
Filtrasorb Corporation (USA)	Acid red 114	103.5	Choy et al. (2000)
Chemviron Carbon (UK)	Acid yellow 17	57.47	Özacar and Sengil (2002)
Calgon Corporation (USA)	Direct red 28	16.81	Fu and Viraraghavan (2002a)
Calgon Corporation (USA)	Direct brown 1	7.69	Venkata Mohan et al. (2002)

1.3. Non-conventional low-cost adsorbents and removal of dyes

Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. According to Bailey et al. (1999), a sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal.

1.3.1. Waste materials from agriculture and industry

The by-products from the agricultural and industries could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials.

a) Activated carbons from solid wastes: Commercially available activated carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents (Rozada et al., 2003, Rodriguez-Reinoso, 1997 and Pollard et al., 1992). Coal is the most commonly used precursor for AC production (Carrasco-Marin et al., 1996 and Illan Gomez et al., 1996) for its availability and cheapness. Coal is a mixture of carbonaceous materials and mineral matter, resulting from the degradation of plants. The sorption properties of each individual coal are determined by the nature of the original vegetation and the extent of the physical–chemical changes occurring after deposition (Karaca et al., 2004). Coal adsorption capacities are reported in Table 4. Coal based sorbents have been used by Karaca et al., 2004, Venkata Mohan et al., 1999 and Venkata Mohan et al., 2002 and McKay et al. (1999) with success for dye removal. However, since coal is not a pure material, it has a variety of surface properties and thus different sorption properties.

Table 4: Adsorption capacities q_m (mg/g) for carbon materials made from solid wastes and coal-based sorbents

Raw material	**Dye**	q_m	**Sources**
Pinewood	Acid blue 264	1176	Tseng et al. (2003)
Pinewood	Basic blue 69	1119	Tseng et al. (2003)
Corncob	Acid blue 25	1060	Juang et al. (2002a)
Bagasse	Basic red 22	942	Juang et al. (2002a)
Cane pith	Basic red 22	941.7	Juang et al. (2001)
Corncob	Basic red 22	790	Juang et al. (2002a)
Bagasse	Acid blue 25	674	Juang et al. (2002a)
Cane pith	Acid blue 25	673.6	Juang et al. (2001)
Pinewood	Basic blue 9	556	Tseng et al. (2003)
Rice husk	Basic green 4	511	Guo et al. (2003)
Bagasse	Acid blue 80	391	Valix et al. (2004)
Waste newspaper	Basic blue 9	390	Okada et al. (2003)
Coal	Basic blue 9	250	McKay et al. (1999)
Waste carbon slurries	Acid blue 113	219	Jain et al. (2003)
Waste carbon slurries	Acid yellow 36	211	Jain et al. (2003)
Waste carbon slurries	Ethyl orange	198	Jain et al. (2003)
Sewage sludge	Basic red 46	188	Martin et al. (2003)
Mahogany sawdust	Acid yellow 36	183.8	Malik (2003)
Coal	Basic red 2	120	McKay et al. (1999)
Sewage sludge	Basic blue 9	114.94	Otero et al. (2003a)
Charcoal	Acid red 114	101	Choy et al. (1999)

Raw material	**Dye**	***q_m***	**Sources**
Rice husk	Acid yellow 36	86.9	Malik (2003)
Rice husk	Acid blue	50	Mohamed (2004)
Charfines	Acid red 88	33.3	Venkata Mohan et al. (1999)
Lignite coal	Basic blue 9	32	Karaca et al. (2004)
Lignite coal	Acid red 88	30.8	Venkata Mohan et al. (1999)
Bituminous coal	Acid red 88	26.1	Venkata Mohan et al. (1999)
Rice husk	Basic blue 9	19.83	Kannan and Sundaram (2001)
Straw	Basic blue 9	19.82	Kannan and Sundaram (2001)
Date pits	Basic blue 9	17.3	Banat et al. (2003)
Hazelnut shell	Basic blue 9	8.82	Aygün et al. (2003)
Coir pith	Acid violet	8.06	Namasivayam et al. (2001a)
Charfines	Direct brown 1	6.4	Venkata Mohan et al. (1999)
Coir pith	Direct red 28	6.72	Namasivayam and Kavitha (2002)
Sugarcane bagasse	Acid orange 10	5.78	Tsai et al. (2001)
Coir pith	Basic violet 10	2.56	Namasivayam et al. (2001a)

Plentiful agricultural and wood by-products may also offer an inexpensive and renewable additional source of AC. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost by-products. So, their conversion into AC would add economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons.

A wide variety of carbons have been prepared from agricultural and wood wastes, such as bagasse (Valix et al., 2004, Juang et al., 2001, Juang et al., 2002a, Tsai et al., 2001 and Ahmedna et al., 2000), coir pith (Namasivayam and Kavitha, 2002 and Namasivayam et al., 2001a), banana pith (Kadirvelu et al., 2003), date pits (Banat et al., 2003), sago waste

(Kadirvelu et al., 2003), silk cotton hull (Kadirvelu et al., 2003), corn cob (Juang et al., 2002a), maize cob (Kadirvelu et al., 2003), straw (Kannan and Sundaram, 2001), rice husk (Mohamed, 2004, Malik, 2003, Guo et al., 2003 and Kannan and Sundaram, 2001), rice hulls (Ahmedna et al., 2000), fruit stones (Aygün et al., 2003), nutshells (Aygün et al., 2003 and Ahmedna et al., 2000), pinewood (Tseng et al., 2003), sawdust (Malik, 2003), coconut tree sawdust (Kadirvelu et al., 2000 and Kadirvelu et al., 2003), bamboo (Wu et al., 1999) and cassava peel (Rajeshwarisivaraj et al., 2001a). There are also several reports on the production of AC from various city wastes and industrial by-products such as waste PET bottles (Nakagawa et al., 2004), waste tires (Nakagawa et al., 2004), refuse derived fuel (Nakagawa et al., 2004), wastes generated during lactic acid fermentation from garbage (Nakagawa et al., 2004), sewage sludges (Rozada et al., 2003, Otero et al., 2003a, Otero et al., 2003b and Graham et al., 2001), waste newspaper (Okada et al., 2003), waste carbon slurries (Jain et al., 2003 and Gupta et al., 2003) and blast furnace slag (Jain et al., 2003 and Gupta et al., 2003).

The excellent ability and economic promise of the activated carbons prepared from by-products have been recently presented and described. Non-conventional activated carbons exhibited high sorption properties as shown in Table 4. Juang et al. (2002a) reported that the adsorption capacities of activated carbons made from corncob had very large values of 1060–790 mg of dye per g of carbon. However, the adsorption capacities of a carbon depend on the different sources of raw materials, the history of its preparation and treatment conditions such as pyrolysis temperature and activation time. Many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure. A suitable carbon should possess not only a porous texture, but also high surface area. Recently, Guo et al. (2003) showed that the adsorption does not always increase with surface area. Besides the physical structure, the adsorption capacity of a given carbon is strongly influenced by the chemical nature of the surface. The acid and base character of a carbon influences the nature of the dye isotherms. The adsorption capacity depends also on the accessibility of the pollutants to the inner surface of the adsorbent, which depends on their size. The specific sorption mechanisms by which the adsorption of dyes takes place on these adsorbents are still not clear. This is because adsorption is a complicated process depending on several interactions such as electrostatic and non-electrostatic (hydrophobic) interactions. Although much has been accomplished in terms of sorption properties and kinetics, much work is still necessary to identify the sorption mechanisms clearly.

b) Agricultural solid wastes: Raw agricultural solid wastes and waste materials from forest industries such as sawdust and bark have been used as adsorbents. These materials are available in large quantities and may have potential as sorbents due to their physico-chemical characteristics and low-cost. Sawdust is an abundant by-product of the wood industry that is either used as cooking fuel or as packing material. Sawdust is easily available in the countryside at zero or negligible price (Garg et al., 2004a). It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding dyes through different mechanisms. The role of sawdust materials in the removal of pollutants from aqueous solutions has been reviewed recently (Shukla et al., 2002). Some valuable guidelines can be drawn from the review. Sawdust has proven to be a promising effective material for the removal of dyes from wastewaters (Özacar and Sengil, 2005, Garg et al., 2004a, Garg et al., 2004b, Baouab et al., 2001 and Ho and McKay, 1998a). Sawdust adsorption capacities are reported in Table 5. The sorption mechanisms can be explained by the presence of several interactions, such as complexation, ion-exchange due to a surface ionisation, and hydrogen bonds. One problem with sawdust materials is that the sorption results are strongly pH-dependent (Garg et al., 2003, Garg et al., 2004b, Khattri and Singh, 2000 and Ho and McKay, 1998a). There is a neutral pH beyond which the sawdust will be either positively or negatively charged. Ho and McKay (1998a) showed that the sorption capacity of basic dye is much higher than that of acid dye because of the ionic charges on the dyes and the ionic character of sawdust. Khattri and Singh (2000) also noted that the adsorption capacity of Neem sawdust was highly concentration dependent. Chemical pretreatment of sawdust has been shown to improve the sorption capacity and to enhance the efficiency of sawdust adsorption (Garg et al., 2003, Garg et al., 2004a, Garg et al., 2004b and Batzias and Sidiras, 2004).

Table 5 Recent reported adsorption capacities q_m (mg/g) for waste materials from agriculture and industry

Adsorbent	**Dye**	q_m	**Sources**
Bark	Basic red 2	1119	McKay et al. (1999)
Bark	Basic blue 9	914	McKay et al. (1999)
Rice husk	Basic red 2	838	McKay et al. (1999)
Sugar-industry-mud	Basic red 22	519	Magdy and Daifullah (1998)
Tree fern	Basic red 13	408	Ho et al. (2005)
Pine sawdust	Acid yellow 132	398.8	Özacar and Sengil (2005)
Palm-fruit bunch	Basic yellow	327	Nassar and Magdy (1997)
Rice husk	Basic blue 9	312	McKay et al. (1999)
Pine sawdust	Acid blue 256	280.3	Özacar and Sengil (2005)
Vine	Basic red 22	210	Allen et al. (2003)
Rice hull ash	Direct red 28	171	Chou et al. (2001)
Egyptian bagasse pith	Basic blue 69	168	Ho and McKay (2003)
Vine	Basic yellow 21	160	Allen et al. (2003)
Egyptian bagasse pith	Basic blue 69	152	Chen et al. (2001)
Coir pith	Basic blue 9	120.43	Namasivayam et al. (2001b)
Coir pith	Basic violet 10	94.73	Namasivayam et al. (2001b)
Eucalyptus bark	Remazol BB	90	Morais et al. (1999)
Raw date pits	Basic blue 9	80.3	Banat et al. (2003)
Fly ash	Basic blue 9	75.52	Janos et al. (2003)
Egyptian bagasse pith	Basic red 22	75	Chen et al. (2001)
Treated sawdust	Basic green 4	74.5	Garg et al. (2003)
Wood sawdust	Basic blue 69	74.4	Ho and McKay (1998a)

Adsorbent	**Dye**	q_m	**Sources**
Metal hydroxide sludge	Reactive red 2	62.5	Netpradit et al. (2003)
Metal hydroxide sludge	Reactive red 141	56.18	Netpradit et al. (2003)
Metal hydroxide sludge	Reactive red 120	48.31	Netpradit et al. (2003)
Treated sawdust	Basic green 4	26.9	Garg et al. (2003)
Fe(III)/Cr(III) hydroxide	Basic blue 9	22.8	Namasivayam and Sumithra (2005)
Banana peel	Methyl orange	21	Annadurai et al. (2002)
Banana peel	Basic blue 9	20.8	Annadurai et al. (2002)
Banana peel	Basic violet 10	20.6	Annadurai et al. (2002)
Orange peel	Methyl orange	20.5	Annadurai et al. (2002)
Egyptian bagasse pith	Acid red 114	20	Chen et al. (2001)
Orange peel	Acid violet	19.88	Rajeshwarisivaraj et al. (2001b)
Orange peel	Basic blue 9	18.6	Annadurai et al. (2002)
Egyptian bagasse pith	Acid blue 25	17.5	Chen et al. (2001)
Egyptian bagasse pith	Acid blue 25	14.4	Ho and McKay (2003)
Orange peel	Basic violet 10	14.3	Annadurai et al. (2002)
Fly ash	Alizarin sulfonic	11.21	Woolard et al. (2002)
Coir pith	Acid violet	7.34	Namasivayam et al. (2001a)
Wood sawdust	Acid blue 25	5.99	Ho and McKay (1998a)
Sugar cane dust	Basic green 4	4.88	Khattri and Singh (1999)
Banana pith	Direct red	5.92	Namasivayam et al. (1998)
Red mud	Direct red 28	4.05	Namasivayam and Arasi (1997)
Neem sawdust	Basic violet 3	3.78	Khattri and Singh (2000)
Neem sawdust	Basic green 4	3.42	Khattri and Singh (2000)

Another waste product from the timber industry is bark, a polyphenol-rich material. Bark is an abundant forest residue which has been found to be effective in removing dyes from water solutions. Because of its low cost and high availability, bark is very attractive as an adsorbent. Like sawdust, the cost of forest wastes is only associated with the transport cost from the storage place to the site where they will be utilized (Palma et al., 2003). Bark is an effective adsorbent because of its high tannin content (Bailey et al., 1999 and Morais et al., 1999). The polyhydroxy polyphenol groups of tannin are thought to be the active species in the adsorption process. Morais et al. (1999) studied adsorption of Remazol BB onto eucalyptus bark from Eucalyptus globulus. The adsorption capacity at pH = 2.5 and 18 °C was found to be 90 mg of dye/g of dry bark. Parallel sorption tests, under similar conditions, carried out with a commercial activated carbon and with bark, showed for the latter an adsorption capacity about half that of the former. The authors concluded that there are promising perspectives for the utilization of eucalyptus bark as sorbent on an industrial scale. However, there are still several important aspects such as the sorption mechanism to clarify.

Tree fern, an agricultural by-product, has been recently investigated to remove pollutants from aqueous solutions (Ho et al., 2005 and Ho, 2003). Tree fern is a complex material containing lignin and cellulose as major constituents. Maximum adsorption capacity of tree fern for basic red 13 was 408 mg/g (Ho et al., 2005). The capacity increased as the sorbent particle size decreased. The sorption mechanism involves chemical bonding and ion-exchange.

Other agricultural solid wastes from cheap and readily available resources such as date piths (Banat et al., 2003), pith (Ho and McKay, 1999a, Ho and McKay, 2003, Chen et al., 2001, Namasivayam et al., 1993, Namasivayam et al., 1998, Namasivayam et al., 2001b, Namasivayam and Kadirvelu, 1994 and McKay et al., 1987), corncob (Robinson et al., 2002a), barley husk (Robinson et al., 2002a), wheat straw (Robinson et al., 2002b, Robinson et al., 2002c and Nigam et al., 2000), wood chips (Kun-She et al., 2000, Low et al., 2000 and Nigam et al., 2000) and orange peel (Rajeshwarisivaraj et al., 2001b and Namasivayam et al., 1996) have also been successfully employed for the removal of dyes from aqueous solution (Table 5).

c). Industrial by-products: Because of their low cost and local availability, industrial solid wastes such as metal hydroxide sludge, fly ash and red mud are classified as low-cost materials and can be used as adsorbents for dye removal (Namasivayam and Sumithra, 2005, Netpradit et al., 2003, Netpradit et al., 2004a, Netpradit et al., 2004b, Acemioglu, 2004, Janos et al., 2003, Mohan et al., 2002, Gupta et al., 2000, Ho and McKay, 1999b, Namasivayam and Arasi, 1997, Namasivayam et al., 1994 and Namasivayam and Chandrasekaran, 1991).

Recently, Netpradit et al., 2003, Netpradit et al., 2004a and Netpradit et al., 2004b studied the capacity and mechanisms of metal hydroxide sludge in removing azo reactive dyes. The sludge is a dried waste from the electroplating industry, which is produced by precipitation of metal ions in wastewater with calcium hydroxide. It contains insoluble metal hydroxides and other salts. The authors demonstrated that metal hydroxide sludge was an effective positively charged adsorbent with a high maximum adsorption capacity (48–62 mg dye/g material) for azo reactive (anionic) dyes. The charge of the dyes is an important factor for the adsorption due to the ion-exchange mechanism.

Another industrial by-product shown to adsorb dyes is fly ash (Wang et al., 2005, Acemioglu, 2004, Mohan et al., 2002, Gupta et al., 1990, Gupta et al., 2000, Ramakrishna and Viraraghavan, 1997 and Khare et al., 1987). 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 (Janos et al., 2003). However, bagasse fly ash generated in the sugar industry does not contain large amounts of toxic metals and has been widely used for adsorption of dyes (Mohan et al., 2002 and Gupta et al., 2000). Fly ash has a surface area of 15.6 m2/g (Wang et al., 2005). Its properties are extremely variable and depend strongly on its origin (Wang et al., 2005, Janos et al., 2003 and Ho and McKay, 1999b).

Another abundant industrial by-product is red mud (Wang et al., 2005, Namasivayam and Arasi, 1997 and Namasivayam and Chandrasekaran, 1991). Waste red mud is a bauxite processing residue discarded in alumina production. Namasivayam and Arasi (1997) proposed red mud as adsorbent for the removal of congo red. The maximum capacity was 4.05 mg/g. Wang et al. (2005) showed that physical and chemical treatment can significantly change the adsorption capacity.

1.3.2. Natural materials

a) Clays: Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion-exchange, clay materials are strong candidates as adsorbents. Clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite (Shichi and Takagi, 2000). The adsorption capabilities result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and high porosity (Alkan et al., 2004). Montmorillonite clay has the largest surface area and the highest cation exchange capacity. Its current market price (about US$ 0.04–0.12/kg) is considered to be 20 times cheaper than that of activated carbon (Babel and Kurniawan, 2003).

In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth for their capacity to adsorb not only inorganic but also organic molecules. In particular, interactions between dyes and clay particles have been extensively studied (Alkan et al., 2005, Alkan et al., 2004, Gürses et al., 2004, Wang et al., 2004, Al-Bastaki and Banat, 2004, Özcan et al., 2004, Ozdemir et al., 2004, Al-Ghouti et al., 2003, Atun et al., 2003, Espantaleon et al., 2003, Orthman et al., 2003, Lazaridis et al., 2003, Shawabkeh and Tutunji, 2003, Neumann et al., 2002, Ghosh and Bhattacharyya, 2002, Pala and Tokat, 2002, Harris et al., 2001, Ho et al., 2001, Bagane and Guiza, 2000, Ramakrishna and Viraraghavan, 1997, Kacha et al., 1997, El-Geundi, 1997, Kahr and Madsen, 1995 and Gupta et al., 1992). Clay minerals exhibit a strong affinity for both heteroatomic cationic and anionic dyes (Table 6). However, the sorption capacity for basic dye is much higher than for acid dye because of the ionic charges on the dyes and character of the clay. The adsorption of dyes on clay minerals is mainly dominated by ion-exchange processes. This means that the sorption capacity can vary strongly with pH. Al-Ghouti et al. (2003) showed that the mechanism of adsorption of dye onto diatomite is due to physical adsorption (depending on the particle size) and the presence of electrostatic interactions (depending on the pH used).

Table 6 Recent reported adsorption capacities q_m (mg/g) for natural materials

Adsorbent	S^a	**Dye**	q_m	**Sources**
Charred dolomite (Ireland)	36	Reactive dye E-4BA	950	Walker et al. (2003)
Activated bentonite (Turkey)	767	Acid blue 193	740.5	Özcan et al. (2004)
Activated bentonite (Spain)		Sella fast brown H	360.5	Espantaleon et al. (2003)
Clay (Tunisia)	71	Basic blue 9	300	Bagane and Guiza (2000)
Calcined alunite (Turkey)	66	Reactive yellow 64	236	Özacar and Sengil (2003)
Calcined alunite (Turkey)	42.8	Acid blue 40	212.8	Özacar and Sengil (2002)
Diatomite (Jordan)	27.8	Basic blue 9	198	Al-Ghouti et al. (2003)
Calcined alunite (Turkey)	66	Reactive blue 114	170.7	Özacar and Sengil (2003)
Sepiolite (Turkey)	50.5	Reactive yellow 176	169.1	Ozdemir et al. (2004)
Activated clay (Singapore)		Basic red 18	157	Ho et al. (2001)
Diatomite (Jordan)	33	Basic blue 9	156.6	Shawabkeh and Tutunji (2003)
Calcined alunite (Turkey)	66	Reactive red 124	153	Özacar and Sengil (2003)
Calcined alunite (Turkey)	42.8	Acid yellow 17	151.5	Özacar and Sengil (2002)
Sepiolite (Turkey)	50.5	Reactive black 5	120.5	Ozdemir et al. (2004)
Zeolite (Turkey)	11.8	Reactive red 239	111.1	Ozdemir et al. (2004)
Sepiolite (Turkey)	50.5	Reactive red 239	108.8	Ozdemir et al. (2004)
Zeolite (Turkey)	11.8	Reactive yellow 176	88.5	Ozdemir et al. (2004)
Clay/carbons mixture		Acid blue 9	64.7	Ho and Chiang (2001)
Zeolite (Turkey)	11.8	Reactive black 5	60.5	Ozdemir et al. (2004)
Activated clay (Singapore)		Acid blue 9	57.8	Ho et al. (2001)
Zeolite (Macedonia)		Basic dye	55.86	Meshko et al. (2001)
Hydrotalcite	100	Reactive yellow 208	47.8	Lazaridis et al. (2003)

Adsorbent	***S*[a]**	**Dye**	**q_m**	**Sources**
Modified silica	187	Acid blue 25	45.8	Phan et al. (2000)
Silica (Taiwan)		Basic blue 9	11.21	Woolard et al. (2002)
Clay (Turkey)	30	Basic blue 9	6.3	Gürses et al. (2004)
Alunite (Turkey)		Reactive yellow 64	5	Özacar and Sengil (2003)
Glass powder	2.37	Acid red 4	4.03	Atun and Hisarli (2003)
Alunite (Turkey)		Reactive blue 114	2.92	Özacar and Sengil (2003)
Alunite (Turkey)		Reactive red 124	2.85	Özacar and Sengil (2003)

[a] Surface area (in m^2/g).

Good removal capability of clay materials to take up dye has been demonstrated. Espantaleon et al. (2003) reported that an adsorption capacity of 360.5 mg of dye/g bentonite was achieved. Due to its high surface area, it was suggested that bentonite is a good adsorbent for (basic) dye removal. Similar results have been published by Bagane and Guiza (2000). It was found that 1 g bentonite could adsorb 300 mg of basic blue 9. The adsorption of dyes on kaolinite was also studied. The adsorption to kaolinite was about 20 times greater than to alumina (Harris et al., 2001). The removal performances of Fuller's earth and CAC for basic blue 9 were compared by Atun et al. (2003). They showed that the adsorption capacity is greater on Fuller's earth than on CAC. Moreover, Fuller's earth is an interesting sorbent since its average price is US$ 0.04/kg whereas CAC costs US$ 20/kg. Shawabkeh and Tutunji (2003) studied the adsorption of basic blue 9 onto diatomaceous earth (diatomite). They showed that this naturally occurring material could substitute for activated carbon as an adsorbent due to its availability and low cost, and its good sorption properties. The adsorption isotherms revealed that adsorption equilibrium was reached within 10 min. The feasibility of using diatomite for the removal of the problematic reactive dyes was also investigated by Al-Ghouti et al. (2003). The sorption of acid blue 9 onto mixed sorbent (activated clay and activated carbon 12:1) has been studied by Ho and Chiang (2001).

As with other materials, clay materials can be modified to improve their sorption capacity. Ozdemir et al. (2004) investigated modified sepiolite as an adsorbent for a variety of azo-reactive dyes. They showed that the adsorption capacities are substantially improved upon modifying their surfaces with quaternary amines. The adsorption capacity of kaolinite can be improved by purification and by treatment with NaOH solution (Ghosh and Bhattacharyya, 2002). The acid-treated bentonite showed a higher adsorption capacity than non-modified bentonite (Espantaleon et al., 2003). Similar results have been published by Özcan et al. (2004).

The results presented above show that clay materials may be promising adsorbents for environmental and purification purposes.

b) Siliceous materials: The use of natural siliceous sorbents such as silica beads, glasses, alunite, perlite and dolomite for wastewater is increasing because of their abundance, availability and low price. Among inorganic materials, silica beads deserve particular attention (Krysztafkiewicz et al., 2002, Crini and Morcellet, 2002, Woolard et al., 2002, Harris et al., 2001 and Phan et al., 2000), considering chemical reactivity of their hydrophilic surface, resulting from the presence of silanol groups. Their porous texture, high surface area and mechanical stability also make them attractive as sorbents for decontamination applications. However, due to their low resistance toward alkaline solutions their usage is limited to media of pH less than 8 (Ahmed and Ram, 1992). Moreover, the surface of siliceous materials contains acidic silanol (among other surface groups) which causes a strong and often irreversible non-specific adsorption. For that reason, it is necessary to eliminate the negative features of these sorbents. In order to promote their interaction with dyes, the silica surface can be modified using silane coupling agents with the amino functional group (Krysztafkiewicz et al., 2002). Phan et al. (2000) also showed that modified silica beads have a better potential for the removal of acid dyes from colored effluents.

Another sorbent from siliceous materials to adsorb dye is alunite (Özacar and Sengil, 2002, Özacar and Sengil, 2003 and Dill, 2001). Alunite is one of the minerals of the jarosite group and contains approximately 50% SiO2. Characteristics of alunite can be found in the review by Dill (2001). However, untreated alunite does not have good adsorbent properties (Özacar and Sengil, 2003). After a suitable process, alunite-type layered compounds are useful as adsorbents for removing color. An investigation on the use of modified alunite for removing acid dyes from wastewater was conducted by Özacar and Sengil, 2002 and Özacar and Sengil, 2003. It was observed that an adsorption capacity of 57.47 mg of acid blue 40 g−1 commercial activated carbon was achieved. Under the same experimental conditions, it was found that the adsorption capacity of acid blue 40 was greater on calcined alunite (212.8 mg/g) than on CAC. Alunite is so cheap that regeneration is not necessary. The surface charge on the sorbent and the pH play a significant role in influencing the capacity of alunite towards dyes.

Other siliceous materials such as dolomite, perlite and glass have been proposed for dye removal (Table 5). Dolomite is both a mineral and a rock. Outstanding removal capability of dolomite for dye uptake has been demonstrated (Walker et al., 2003). Charred dolomite has a higher equilibrium capacity for reactive dye removal than activated carbon, with a capacity of 950 mg/g of adsorbent for dolomite compared to 650 mg dye adsorbed per g of adsorbent for CAC. However, the mechanism was not clear (probably a combination of precipitation and adsorption). Perlite is a glassy volcanic rock and has a high silica content, usually greater than 70%. It is inexpensive and easily available in many countries. The use of perlite as a low-cost adsorbent for the removal of dyes has been investigated for the first time by Alkan and co-workers (Dogan et al., 2004, Dogan and Alkan, 2003a, Dogan and Alkan, 2003b and Demirbas et al., 2002). It was suggested that dyes are physically adsorbed onto the perlite. Perlite is a good adsorbent for decontamination purposes. However, perlites of different types (expanded and unexpanded) and of different origins have different properties because of the differences in composition.

c). Zeolites: Zeolites are highly porous aluminosilicates with different cavity structures. Their structures consist of a three dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations which are exchangeable with certain cations in solutions. Zeolites consist of a wide variety of species, more than 40 natural species. However, the most abundant and frequently studied zeolite is clinoptilolite, a mineral of the heulandite group. Its characteristic tabular morphology shows an open reticular structure of easy access, formed by open channels of 8–10 membered rings. Clinoptilolite applications of zeolites have been reviewed by Ghobarkar et al. (1999). High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites attractive adsorbents. Their price is about US$ 0.03–0.12/kg, depending on the quality of the mineral (Babel and Kurniawan, 2003). Another advantage of zeolites over resins is their ion selectivities generated by their rigid porous structures.

Zeolites are becoming widely used as alternative materials in areas where sorptive applications are required. They have been intensively studied recently because of their applicability in removing trace quantities of pollutants such as heavy metal ions and phenols thanks to their cage-like structures suitable for ion exchange. Zeolites also appear as suitable sorbents for dyes (Table 5). Several studies have been conducted on the sorbent behavior of natural zeolites (Ozdemir et al., 2004, Armagan et al., 2004, Meshko et al., 2001, Calzaferri et al., 2000, Ghobarkar et al., 1999 and El-Geundi, 1997). However, raw clinoptilolite was not suitable for the removal of reactive dyes due to extremely low sorption capacities (Armagan et al., 2004 and Karcher et al., 2001). Similar conclusions have been found by Ozdemir et al. (2004) and Benkli et al. (2005). These authors suggested chemical modification with quaternary amines as a means of increasing sorption. In spite of the promising results, the real applicability of these natural materials to purify dye waste waters is still quite unknown. Another problem of zeolites is their low permeability and this requires an artificial support when used in column operations. The sorption mechanism on zeolite particles is complex because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity and other imperfections on the surface (Calzaferri et al., 2000 and Altin et al., 1998). However, it is recognized that, like clay, the adsorption properties of zeolites result mainly from their ion-exchange capabilities. Although the removal efficiency of zeolites for dyes may not be as good as that of clay materials, their easy availability and low cost may compensate for the associated drawbacks.

1.3.3 Biosorbents

The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is termed biosorption. In this instance, biological materials, such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, are used as chelating and complexing sorbents in order to concentrate and to remove dyes from solutions. These biosorbents and their derivatives contain a variety of functional groups which can complex dyes. The biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce dye concentration to ppb levels. Biosorption is a novel approach, competitive, effective and cheap.

a) **Chitin and chitosan:** The sorption of dyes using biopolymers such as chitin and chitosan is one of the reported emerging biosorption methods for the removal of dyes, even at low concentration (ppm or ppb levels). Chitin and chitosan are abundant, renewable and biodegradable resources. Chitin, a naturally occurring mucopolysaccharide, has been found in a wide range of natural sources such as crustaceans, fungi, insects, annelids and molluscs. However, chitin and chitosan are only commercially extracted from crustaceans (crab, krill, crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a by-product of food processing. The annual worldwide crustacean shells production has been estimated to be 1.2 × 106 tonnes, and the recovery of chitin and protein from this waste is an additional source of revenue (Teng et al., 2001). Utilization of industrial solid wastes for the treatment of wastewater from another industry could be helpful not only to the environment in solving the solid waste disposal problem, but also to the economy.

Chitin contains 2-acetamido-2-deoxy-β-d-glucose through a β (1 → 4) linkage. This waste product is second only to cellulose in terms of abundance in nature. Chitosan contains 2-acetamido-2-deoxy-β-d-glucopyranose and 2-amino-2-deoxy-β-d-glucopyranose residues. Chitosan has drawn particular attention as a complexing agent due to its low cost compared to activated carbon and its high contents of amino and hydroxy functional groups showing high potential for adsorption of a wide range of molecules, including phenolic compounds, dyes and metal ions (Guibal, 2004, Varma et al., 2004 and Ravi Kumar, 2000). This biopolymer represents an attractive alternative to other biomaterials because of its physico-chemical characteristics, chemical stability, high reactivity, excellent chelation behavior and high selectivity toward pollutants (Guibal, 2004, Varma et al., 2004 and Ravi Kumar, 2000).

Various studies on chitin and chitosan have been conducted in recent years (Wong et al., 2004, Chao et al., 2004, Chiou et al., 2004, Chiou and Li, 2002, Chiou and Li, 2003, Juang et al., 1996, Juang et al., 1997, Juang et al., 2002b, Vachoud et al., 2001, Wu et al., 2000, Wu et al., 2001a, Wu et al., 2001b, Annadurai et al., 1999 and Annadurai and Krishnan, 1997). These studies demonstrated that chitosan-based biosorbents are efficient materials and have an extremely high affinity for many classes of dyes (Table 7). They are also versatile materials. This versatility allows the sorbent to be used in different forms, from flake-types to gels, bead-types or fibers.

Table 7 Recent reported adsorption capacities q_m (mg/g) for chitosan and chitosan-based biosorbents

Biosorbent	**Dye**	q_m	**Sources**
Crosslinked chitosan bead	Reactive blue 2	2498	Chiou et al. (2004)
Crosslinked chitosan bead	Reactive red 2	2422	Chiou et al. (2004)
Crosslinked chitosan bead	Direct red 81	2383	Chiou et al. (2004)
Crosslinked chitosan bead	Reactive red 189	1936	Chiou and Li (2002)
Crosslinked chitosan bead	Reactive yellow 86	1911	Chiou et al. (2004)
Chitosan bead	Reactive red 189	1189	Chiou and Li (2002)
Chitosan (bead, crab)	Reactive red 222	1106	Wu et al. (2000)
Chitosan (bead, lobster)	Reactive red 222	1037	Wu et al. (2000)
Chitosan	Acid orange 12	973.3	Wong et al. (2004)
Chitosan	Acid orange 10	922.9	Wong et al. (2004)
Chitosan	Acid red 73	728.2	Wong et al. (2004)
Chitosan	Acid red 18	693.2	Wong et al. (2004)
Chitosan	Acid green 25	645.1	Wong et al. (2004)
Chitosan (flake, lobster)	Reactive red 222	398	Wu et al. (2000)
Chitosan (flake, crab)	Reactive red 222	293	Wu et al. (2000)

The performance of chitosan as an adsorbent to remove acid dyes has been demonstrated by Wong et al. (2004). They found that the maximum adsorption capacities of chitosan for acid orange 12, acid orange 10, acid red 73 and acid red 18 were 973.3, 922.9, 728.2, and 693.2 mg/g, respectively. Wu et al. (2000) also reported the usefulness of chitosan for the removal of reactive dyes. However, the bead type of chitosan gives a higher capacity for dye than the flake type by a factor of 2–4 depending on the source of fishery wastes. For example, a comparison of the maximum adsorption capacity for reactive red 222 by chitosan flakes and beads showed 293 mg/g for flakes and 1103 mg/g for beads. This can be explained by the fact that the beads possessed a greater surface area than the flakes.

Both batch contacting and column processes are available for chitosan materials with solution containing dyestuffs (McKay et al., 1989). In sorption columns, chitin and chitosan are often used as powder or flake forms. This technique usually causes a significant pressure drop in the column. Moreover, another limitation of chitosan is that it is soluble in acidic media and therefore cannot be used as an insoluble sorbent under these conditions, except after physical and chemical modification. To avoid these problems, crosslinked beads have been developed. Chitosan-based biosorbents are easy to prepare with relatively inexpensive reagents. These materials are insoluble in acidic and alkaline media as well as in organic solvents and become more resistant to high temperature and low pH compared to their parent biopolymer. After crosslinking, they maintain their properties and original characteristics. Chemical modifications of chitosan have also been made to improve its removal performance and selectivity for dyes, to control its diffusion properties and to decrease the sensitivity of sorption to environmental conditions.

The interaction between crosslinked chitosan and dyes has been intensively investigated by Chiou et al. (Chiou et al., 2004, Chiou and Li, 2002 and Chiou and Li, 2003). Several crosslinked biomaterials were prepared by using a procedure described by Zeng and Ruckenstein (1996). Chitosan beads were crosslinked with glutaraldehyde (GLA), epichlorohydrin (EPI) or ethylene glycol diglycidyl ether (EGDE). Chiou and Li (2003) showed that the chitosan-EPI beads presented a higher adsorption capacity than GLA and EGDE resins. It was found that 1 g chitosan adsorbed 2498 mg of reactive blue 2. Chitosan-based biosorbents have also demonstrated outstanding removal capabilities for direct dyes. In comparison with commercial activated carbon, the beads exhibited excellent performance for adsorption of anionic dyes: the adsorption values were 3–15 times higher at the same pH (Chiou et al., 2004). Hence chitosan chelation is the procedure of choice for dye removal from aqueous solution. However, it is known that chitosan has a low affinity for cationic (basic) dyes. Chao et al. (2004) suggested enzymatic grafting of carboxyl groups onto chitosan as a means to confer the ability to adsorb basic dyes on beads. The presence of new functional groups on the surface of beads results in increases in surface polarity and the density of sorption sites, and this improves the sorption selectivity for the target dye.

There are, of course, disadvantages of using chitosan in wastewater treatment. Its adsorption properties depend on the different sources of chitin, the degree of N-acetylation, molecular weight and solution properties, and vary with crystallinity, affinity for water, percent deacetylation and amino group content (Guibal, 2004, Varma et al., 2004 and Ravi Kumar, 2000). These parameters, determined by the conditions selected during preparation, control swelling and diffusion properties of the biopolymer and influence its characteristics. Performance is dependent on the type of material used and the efficiency of adsorption depends on the accessibility of sorption sites. The uptake is strongly pH-dependent. Dye molecules have many different and complicated structures. This is one of the most important factors influencing adsorption (Wong et al., 2004). There is, as yet, little information in the literature on this topic. The traditional and commercial source of chitin is from shells of crab, shrimp and krill that are wastes from the processing of marine food products. However, this traditional method of extraction of chitin creates its own environmental problems as it generates large quantities of waste and the production of chitosan also involves a chemical deacetylation process. These problems can explain why it is difficult to develop chitosan-based materials as adsorbents at an industrial scale.

Despite the large number of papers dedicated to the removal of dyes by chitosan-based materials, most of them focus on the evaluation of sorption performances and only a few of them aim at gaining a better understanding of sorption mechanisms. This can perhaps be explained by the fact that different kinds of interactions, such as ion-exchange interactions, hydrophobic attraction, physical adsorption, etc., can be acting simultaneously. Wide ranges of chemical structures, pH, salt concentrations and presence of ligands often add to the complication. Wu et al. (2000) showed that intraparticle diffusion plays an important role in the sorption mechanism. The uptake of dyes on chitosan may also proceed through ion-exchange mechanisms. The major adsorption site of chitosan is a primary amine group which is easily protonated to form Click to view the MathML source in acidic solutions. The strong electrostatic interaction between the Click to view the MathML source groups and dye anions can be used to explain the sorption mechanism (Chiou et al., 2004). The difference in the degree of adsorption may also be attributed to the chemical structure of each dye (Wong et al., 2004).

The results presented above show that chitosan-based materials may be promising biosorbents for adsorption processes since they demonstrated outstanding removal capabilities for dyes.

b) Peat: Peat is a porous and rather complex soil material with organic matter in various stages of decomposition. Based on the nature of parent materials, peat is classified into four groups, namely moss peat, herbaceous peat, woody peat and sedimentary peat. This natural material is a plentiful, relatively inexpensive and widely available biosorbent, which has adsorption capabilities for a variety of pollutants. Raw peat contains lignin, cellulose, fulvic and humic acid as major constituents. These constituents, especially lignin and humic acid, bear polar functional groups, such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides and ethers that can be involved in chemical bonding.

Because of its polar character, peat can effectively remove dyes from solution (Allen et al., 2004, Ho and McKay, 1998b, Ho and McKay, 2003, Sun and Yang, 2003, Ramakrishna and Viraraghavan, 1997 and Poots et al., 1976). Peat adsorption capacities are reported in Table 8. The use of peat to remove dyes was investigated by Allen et al., 1988a, Allen et al., 1988b, Allen et al., 1994, Allen et al., 2004, Ho and McKay, 1998b and Ho and McKay, 2003 and Ramakrishna and Viraraghavan (1997). It was observed that peat tends to have a high cation exchange capacity, and is an effective sorbent for the removal of dyes. For acid and basic dyes, the removal performance was comparable with that of activated carbon, while for disperse dyes, the performance was much better.

Table 8 Recent reported adsorption capacities q_m (mg/g) for peat

Biosorbent	**Dye**	q_m	**Sources**
Treated peat	Basic violet 14	400	Sun and Yang (2003)
Treated peat	Basic green 4	350	Sun and Yang (2003)
Peat	Basic blue 69	195	Ho and McKay (1998b)
Peat	Acid blue 25	12.7	Ho and McKay (1998b)

However, when raw peat is used directly as an adsorbent, there are many limitations: Natural peat has a low mechanical strength, a high affinity for water, poor chemical stability, a tendency to shrink and/or swell, and to leach fulvic acid (Couillard, 1994 and Smith et al., 1977). Chemical pretreatment and the development of immobilized biomass beads can produce a more robust medium. As with other sorbents, chemical processes are also used for improving sorption properties and selectivity. For example, Sun and Yang (2003) prepared modified peat-resin by mixing oxidizing peat with polyvinylalcohol and formaldehyde. These materials possess a macroreticular porous structure with enhanced physical characteristics. Their studies demonstrated that modified peat can be used for the removal of a variety of basic dyes. The maximum adsorption capacities for basic violet 14 and basic green 4 were 400 and 350 mg/g treated peat, respectively.

The mechanism by which dyes are adsorbed onto peat has been a matter of considerable debate. Different studies have reached different conclusions. Various pollutant-binding mechanisms are thought to be involved in the biosorption process, including physical adsorption, ion-exchange, complexation, adsorption–complexation and chemisorption (Brown et al., 2000). Variations in peat type and sorbent preparation also make the comparison of results difficult. However, it is now recognized that ion-exchange is the most prevalent mechanism.

c). Biomass: Decolorization and/or bioadsorption of dye wastewater by (dead or living) biomass, white-rot fungi and other microbial cultures was the subject of many studies reviewed in several recent papers (Aksu, 2005, Pearce et al., 2003, McMullan et al., 2001, Fu and Viraraghavan, 2001a, Stolz, 2001 and Robinson et al., 2001). In particular, these studies demonstrated that biosorbents derived from suitable microbial biomass can be used for the effective removal of dyes from solutions since certain dyes have a particular affinity for binding with microbial species (Robinson et al., 2001, Fu and Viraraghavan, 2001a, Bustard et al., 1998 and Nigam et al., 1996). The use of biomass for wastewater is increasing because of its availability in large quantities and at low price. Microbial biomass is produced in fermentation processes to synthesize valuable products such as antibiotics and enzymes. In such processes, a large amount of by-products is generated, which can be used in biosorption of pollutants. Biomass has a high potential as a sorbent due to its physico-chemical characteristics. A wide variety of microorganisms including algae, yeasts, bacteria and fungi are capable of decolorizing a wide range of dyes with a high efficiency (Swamy and Ramsay, 1999, Nigam et al., 1996, Jinqi and Houtian, 1992 and Mou et al., 1991).

In fungal decolorization, fungi can be classified into two kinds according to their life state: living cells to biodegrade and biosorb dyes, and dead cells (fungal biomass) to adsorb dye (Fu and Viraraghavan, 2001a). Most of the studies concentrated on living fungi for biosorption of the dyes. There are few studies on dye removal using dead fungal biomass, except in recent years. Table 9 shows some of the adsorption capacities reported in the literature. Removal of dyes has recently been studied with strains of Aspergillus niger (Fu and Viraraghavan, 2002a and Fu and Viraraghavan, 2002b) and Rhizopus arrhizus (O'Mahony et al., 2002 and Aksu and Tezer, 2000). Fu and Viraraghavan, 2000, Fu and Viraraghavan, 2001b, Fu and Viraraghavan, 2002a and Fu and Viraraghavan, 2002b demonstrated that, compared with commercial activated carbon, dead fungal biomass of Aspergillus niger is a promising biosorbent for dye removal. Aksu and Tezer (2000) demonstrated uptake of 588.2 mg of reactive black 5 per g using Rhizopus arrhizus biomass. Waranusantigul et al. (2003) and Chu and Chen, 2002a and Chu and Chen, 2002b also reported the usefulness of biomass for the removal of basic dyes. The biosorption capacity of fungal biomass could be increased by some pretreatment (by autoclaving or by reacting with chemicals) (Fu and Viraraghavan, 2001a). Other types of biomass such as yeasts have been studied for their dye uptake capacities. Yeasts are extensively used in a variety of large-scale industrial fermentation processes and waste biomass from these processes is a potential source of cheap adsorbent material. The performance of yeasts as a low-cost adsorbent to remove dyes has been demonstrated by Aksu and coworkers (Aksu and Dönmez, 2003 and Aksu, 2003). They found that the maximum adsorption capacities of yeasts for remazol blue and reactive black 5 were 173.1 and 88.5 mg/g, respectively.

Table 9. Recent reported adsorption capacities q_m (mg/g) for biomass

Adsorbent	**Dye**	**q_m**	**Sources**
Rhizopus arrhizus biomass	Reactive black 5	588.2	Aksu and Tezer (2000)
Chlorella vulgaris biomass	Reactive red 5	555.6	Aksu and Tezer (2005)
Activated sludge biomass	Reactive yellow 2	333.3	Aksu (2001)
Activated sludge biomass	Basic red 18	285.71	Gulnaz et al. (2004)
Activated sludge biomass	Basic blue 9	256.41	Gulnaz et al. (2004)
Activated sludge biomass	Reactive blue 2	250	Aksu (2001)
Rhizopus arrhizus biomass	Reactive orange 16	190	O'Mahony et al. (2002)

Adsorbent	**Dye**	q_m	**Sources**
Yeasts	Remazol blue	173.1	Aksu and Dönmez (2003)
Activated sludge biomass	Basic blue 47	157.5	Chu and Chen (2002a)
Rhizopus arrhizus biomass	Reactive red 4	150	O'Mahony et al. (2002)
Spirodela polyrrhiza biomass	Basic blue 9	144.93	Waranusantigul et al. (2003)
Activated sludge biomass	Basic red 18	133.9	Chu and Chen (2002a)
Activated sludge biomass	Basic red 29	113.2	Chu and Chen (2002a)
Activated sludge biomass	Direct yellow 12	98	Kargi and Ozmihci (2004)
Rhizopus arrhizus biomass	Reactive blue 19	90	O'Mahony et al. (2002)
Yeasts	Reactive black 5	88.5	Aksu (2003)
Activated sludge biomass	Basic yellow 24	56.98	Chu and Chen (2002b)
Dead fungus *Aspergillus niger*	Basic blue 9	18.54	Fu and Viraraghavan (2000)
Dead fungus *Aspergillus niger*	Direct red 28	14.72	Fu and Viraraghavan (2002a)
Dead fungus *Aspergillus niger*	Acid blue 29	13.82	Fu and Viraraghavan (2001b)
Living biomass	Acid blue 29	6.63	Fu and Viraraghavan (2001b)
Modified fungal biomass	Disperse red 1	5.59	Fu and Viraraghavan (2002b)
Living biomass	Basic blue 9	1.17	Fu and Viraraghavan (2000)

The major advantages of biosorption technology are its effectiveness in reducing the concentration of dyes to very low levels and the use of inexpensive biosorbent material. Fungal biomass can be produced cheaply using relatively simple fermentation techniques and inexpensive growth media (Fu and Viraraghavan, 2002a and Mittal and Gupta, 1996). The use of biomass is especially interesting when the dye-containing effluent is very toxic. Biosorption is also an emerging technology that attempts to overcome the selectivity disadvantage of conventional adsorption processes. The use of dead rather than live biomass eliminates the problems of waste toxicity and nutrient requirements. Biomass adsorption is effective when conditions are not always favorable for the growth and maintenance of the microbial population.

In spite of good sorption properties and high selectivity, some problems can occur. The sorption process is slow: in the case of biomass of Aspergillus niger equilibrium was reached in 42 h. Another problem is that the initial pH of the dye solution strongly influenced the biosorption (Aksu and Dönmez, 2003). Biosorption was also influenced by the functional groups in the fungal biomass and its specific surface properties (Kargi and Ozmihci, 2004). Biosorption performance depends on some external factors such as salts and ions in solution which may be in competition. Other limitations of the technology include the fact that the method has only been tested for limited practical applications since biomass is not appropriate for the treatment of effluents using column systems, due to the clogging effect. Because of major limitations regarding its efficient utilization in a column reactor, there is a need for it to be immobilized. This step forms a major cost factor of the process.

Dyes vary greatly in their chemistries and their interactions with microorganisms depend on the chemistry of a particular dye. There is also limited information available on the interactions between biomass and dyes (Chu and Chen, 2002b and Banks and Parinson, 1992). This can be explained by the fact that decolorization by living and dead cells involves several complex mechanisms such as surface adsorption, ion-exchange, complexation (coordination), complexation–chelation and micro-precipitation. Cell walls consisting mainly of polysaccharides, proteins and lipids offer many functional groups. The dyes can interact with these active groups on the cell surface in a different manner. The accumulation of dyes by biomass may involve a combination of active, metabolism-dependent and passive transport mechanisms starting with the diffusion of the adsorbed solute to the surface of the microbial cell (O'Mahony et al., 2002, Aksu and Tezer, 2000 and Veglio and Beolchini, 1997). Once the dye has diffused to the surface, it will bind to sites on the cell surface. The precise binding mechanisms may range from physical (i.e. electrostatic or Van der Waal forces) to chemical binding (i.e. ionic and covalent). However, it is now recognized that the efficiency and the selectivity of adsorption by biomass are due to ion-exchange mechanisms.

Biosorption processes are particularly suitable for the treatment of solutions containing dilute (toxic) dye concentration. Biosorption is a promising potential alternative to conventional processes for the removal of dyes (Aksu, 2005, Aksu and Tezer, 2005, Fu and Viraraghavan, 2002a, Fu and Viraraghavan, 2001a and Robinson et al., 2001). However, these technologies are still being developed and much more work is required.

4.4. **Miscellaneous sorbents**

Other materials have been studied as low-cost sorbents, such as starch (Delval et al., 2001, Delval et al., 2002 and Delval et al., 2003) and cyclodextrins (Crini, 2003, Crini and Morcellet, 2002, Crini et al., 1999, Crini et al., 2002a, Crini et al., 2002b, Martel et al., 2001 and Shao et al., 1996). Adsorption capacities are reported in Table 10. Next to cellulose, starch is the most abundant carbohydrate in the world and is present in living plants as an energy storage material. Starches are mixtures of two polyglucans, amylopectin and amylose, but they contain only a single type of carbohydrate, glucose. They are composed of α-d-glucose units linked together in 1,4-position. Amylose is nearly unbranched, while amylopectin is highly branched with the branches connected via the α-1,6-position of the anhydroglucose unit. Starch is used mostly in food applications, but there is a growing interest in its utilization as a renewable raw material for non-food industrial applications. Starches are unique raw materials in that they are very abundant natural polymers, inexpensive and widely available in many countries. They possess several other advantages that make them excellent materials for industrial use. They have biological and chemical properties such as hydrophilicity, biodegradability, polyfunctionality, high chemical reactivity and adsorption capacities. However, the hydrophilic nature of starch is a major constraint that seriously limits the development of starch based-materials. Chemical derivatisation has been proposed as a way to solve this problem and to produce water resistant sorbents.

Table10 Recent reported adsorption capacities q_m (mg/g) for other sorbents

Adsorbent	**Dye**	q_m	**Sources**
Cotton waste	Basic red 2	875	McKay et al. (1999)
Treated cotton	Acid blue 25	589	Bouzaida and Rammah (2002)
Treated cotton	Acid yellow 99	448	Bouzaida and Rammah (2002)
Treated cotton	Reactive yellow 23	302	Bouzaida and Rammah (2002)
Cotton waste	Basic blue 9	277	McKay et al. (1999)
Starch-based material	Acid blue 25	249	Delval et al. (2002)
Crosslinked cyclodextrin	Acid blue 25	88	Crini (2003)
Chitosan/cyclodextrin material	Acid blue 25	77.4	Martel et al. (2001)

More important than starch is its cyclic derivative, cyclodextrin. Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The CD molecules are natural macrocyclic polymers, formed by the action of an enzyme on starch (Szejtli, 1998). Beta-cyclodextrins containing seven glucose units are available commercially at a low cost. The most characteristic feature of CDs is the ability to form inclusion compounds with various aromatic molecules, including dyes. CDs possess a hydrophobic cavity in which a pollutant can be trapped. A review of cyclodextrin-based materials can be found in a recent review by Crini and Morcellet (2002).

Like other polysaccharides, starches and cyclodextrins can be crosslinked by a reaction between the hydroxyl groups of the chains with a coupling agent to form water-insoluble crosslinked networks. Due to the hydrophilic nature of their crosslinking units, crosslinked starches also possess a remarkably high swelling capacity in water, and consequently their networks are sufficiently expanded to allow a fast diffusion process for the pollutants. Crosslinked cyclodextrin polymers also have interesting diffusion properties and possess an amphiphilic character. It is precisely this character of these sorbents what makes them so appealing, since they are hydrophilic enough to swell considerably in water allowing fast diffusion processes for the dyes, while at the same time they possess highly hydrophobic sites which trap non-polar dyes efficiently. It is well known that synthetic resins have a poor contact with aqueous solutions and their modification is necessary for enhanced water wettability. Activated carbons adsorb some hydrophilic substances poorly.

In spite of varied characteristics and properties, a limited number of dye adsorption studies have been carried out on starch-based derivatives. Crini et al. (Crini, 2003, Crini and Morcellet, 2002, Crini et al., 1999, Crini et al., 2002a and Crini et al., 2002b) demonstrated that efficient extraction of dyes is achieved using crosslinked cyclodextrin gels. The presence of CD molecules in the polymer network permits an increase in its sorption properties. Delval et al., 2001, Delval et al., 2002 and Delval et al., 2003 proposed crosslinked starch polymers containing amine groups. The polymers were prepared by crosslinking an agroalimentary by-product. The sorption results showed that the adsorption rate was high and the sorption capacities were significant. Several hundred ppm of dyes could be removed from water effectively in a few minutes using column experiments. The control of the crosslinking reaction allows control of the sorption properties of the material. However, due to the protonation of the amine groups on the surface of the sorbent, its adsorption behavior is strongly influenced by the pH values. Another interesting idea is to combine the properties of two biopolymers. Attempts were made to prepare adsorbents by coupling chitosan and cyclodextrin (CD) via several spacer arms without affecting the selectivity of the two polymers. The novel biosorbents containing both cyclodextrin and chitosan are in general more hydrophilic than commercial synthetic resins. Decontamination of water containing textile dyes was carried out with these sorbents (Martel et al., 2001). The results showed excellent sorption properties toward different classes of dyes. The chitosan beads containing CD are also characterized by a rate of sorption and an efficiency superior to that of the parent chitosan bead without CD and of the crosslinking cyclodextrin-epichlorohydrin gels. The maximum adsorption capacities of starch-based material, crosslinked cyclodextrin and chitosan/cyclodextrin mixed sorbents for acid blue 25 were 249, 88 and 77.4 mg/g, respectively. There are several disadvantages of using starch-based materials for dye removal. The efficiency of adsorption depends strongly on the control or particle size and the expansion of the polymer network (Crini, 2003). Performance is also dependent on the type of material used. Another problem with these materials is that they are non-porous and possess low surface area. Adsorption by starch-based materials occurs by physical adsorption, complexation and ion-exchange interactions (Delval et al., 2003 and Crini, 2003).

Other materials used to adsorb dyes are cotton waste (Sawada and Ueda, 2003, Bouzaida and Rammah, 2002 and McKay et al., 1999) and alumina (Harris et al., 2001 and Desai et al., 1997). Adsorption capacities are reported in Table 10. Cotton is the most abundant of all naturally occurring organic substrates and is widely used. This material characteristically exhibits excellent physical and chemical properties in terms of stability, water absorbency and dye removal ability. The performance of treated cotton in a continuous system has been demonstrated by Bouzaida and Rammah (2002). They found that the adsorption capacities of cotton for acid blue 25, acid yellow 99 and reactive yellow 23 were 589, 448 and 302 mg/g, respectively. McKay et al. (1999) also evaluated the performance of cotton waste for dye removal. It was found that this waste had the potential to adsorb 875 and 277 mg of basic red 2 and basic blue 9/g, respectively.

1.3.4 Comparison of sorption performance

Generally, a suitable non-conventional low-cost adsorbent for dye adsorption should meet several requirements: (i) efficient for removal of a wide variety of dyes; (ii) high capacity and rate of adsorption; (iii) high selectivity for different concentrations; and (iv) tolerant of a wide range of wastewater parameters.

Certain waste products, natural materials and biosorbents have been tested and proposed for dye removal. Which low-cost adsorbent is better? There is no direct answer to this question because each low-cost adsorbent has its specific physical and chemical characteristics such as porosity, surface area and physical strength, as well as inherent advantages and disadvantages in wastewater treatment. In addition, adsorption capacities of sorbents also vary, depending on the experimental conditions. Therefore, comparison of sorption performance is difficult to make. However, it is clear from the present literature survey that non-conventional adsorbents may have potential as readily available, inexpensive and effective sorbents. They also possess several other advantages that make them excellent materials for environmental purposes, such as high capacity and rate of adsorption (Table 11), high selectivity for different concentrations, and also rapid kinetics (Table 12).

Table 11 Compared maximum adsorption capacities (q_m in mg/g) for commercial activated carbon (CAC) and other low-cost sorbents

Dye	**Adsorbent/q_m**		**Sources**
Reactive blue 2	Chitosan/2498	CAC/217.2	Chiou et al. (2004)
Reactive red 2	Chitosan/2422	CAC/712.3	Chiou et al. (2004)
Direct red 81	Chitosan/2383	CAC/240.7	Chiou et al. (2004)
Reactive yellow 86	Chitosan/1911	CAC/127.4	Chiou et al. (2004)
Reactive red	Dolomite/950	CAC/650	Walker et al. (2003)
Reactive red 5	Alga/555.6	CAC/278	Aksu and Tezer (2005)
Acid blue 80	Bagasse/391	CAC/121	Valix et al. (2004)
Acid blue 40	Alunite/212.8	CAC/133.3	Özacar and Sengil (2002)

Dye	**Adsorbent/q_m**		**Sources**
Basic red 46	Sewage sludge/188	CAC/106	Martin et al. (2003)
Acid yellow 17	Alunite/151.5	CAC/57.47	Özacar and Sengil (2002)
Reactive orange 107	Alga/71.9	CAC/714	Aksu and Tezer (2005)
Basic dye	Zeolite/55.86	CAC/309.2	Meshko et al. (2001)
Direct red 28	Dead fungus/14.72	CAC/16.81	Fu and Viraraghavan (2002a)
Direct brown 1	Charfines/6.4	CAC/7.69	Venkata Mohan et al. (2002)

Table 12 Contact time (in min) for different adsorption materials

Adsorbent	**Contact time**	**Dye**	**Sources**
Lignite	5	Basic blue 9	Karaca et al. (2004)
Diatomite	10	Basic blue 9	Shawabkeh and Tutunji (2003)
Perlite	30	Methyl violet	Dogan and Alkan (2003a)
Perlite	30	Basic blue 9	Dogan et al. (2004)
Sawdust	30	Basic blue 9	Garg et al. (2004a)
Rice husk based carbons	35	Basic blue 9	Kannan and Sundaram (2001)
Activated sludge	45	Basic blue 9	Gulnaz et al. (2004)
Metal hydroxide sludge	50	Reactive red 141	Netpradit et al. (2003)
Clay	60	Basic blue 9	Gürses et al. (2004)
Hydrotalcite	60	Acid blue 29	Orthman et al. (2003)
Orange peel	80	Acid violet 17	Rajeshwarisivaraj et al. (2001b)
Rice husk based carbons	90	Basic green 4	Guo et al. (2003)
Calcined alunite	90	Acid blue 40	Özacar and Sengil (2002)
Kaolinite	120	Basic blue 9	Ghosh and Bhattacharyya (2002)
Zeolite	120	Reactive red 239	Ozdemir et al. (2004)

Adsorbent	**Contact time**	**Dye**	**Sources**
Pine sawdust	120	Acid blue 256	Özacar and Sengil (2005)
Calcined alunite	120	Reactive yellow 64	Özacar and Sengil (2003)
Perlite	210	Basic blue 9	Acemioglu (2005)
Fuller's earth	240	Basic blue 9	Atun et al. (2003)
Bark	720	Remazol BB	Morais et al. (1999)
Dead fungus	2520	Direct red 28	Fu and Viraraghavan (2002a)
Diatomite	2880	Basic blue 9	Al-Ghouti et al. (2003)

Table 11 presents a summary of some of the highest adsorption capacities reported. From the recent literature reviewed, adsorbents that stand out for high adsorption capacities are chitosan (2498, 2422, 2383, 1911 mg/g of reactive blue 2, reactive red 2, direct red 81, and reactive yellow 86, respectively), pinewood (1176 and 1119 mg/g of acid blue 264 and basic blue 25, respectively), bark (1119 mg/g of basic red 2) and corncob (1060 mg/g of acid blue 25). These adsorbents are efficient and can be used effectively for the removal of dye from aqueous solutions. In particular, chitosan has received considerable interest for dye removal due to its excellent dye-binding capacities. Since fishery wastes are abundantly available, chitosan may be produced at a low cost and it was competitive against CAC. Chitosan has demonstrated outstanding removal capabilities for certain dyes compared to activated carbon (Table 11). For example, the adsorption capacity for reactive blue 2 is much greater on chitosan (2498 mg/g) than on CAC (217.2 mg/g). Several significant sorption results have been published by Chiou et al. (Chiou et al., 2004, Chiou and Li, 2002 and Chiou and Li, 2003). They demonstrated that chitosan can be used for the decontamination of effluents. It offers both a procedure of choice for extraction processes and a lot of promising benefits for commercial purposes. Another interesting low-cost adsorbent shown to adsorb pollutants is peat. Adsorption using peat is well established. Its use in water treatment systems has received attention over the past 30 years and peat filters and biofilters currently offer an attractive method of wastewater treatment (Allen et al., 1994, Allen et al., 2004 and Brown et al., 2000).

Several recent reports have been published on the comparison of sorption performance. For example, Atun et al. (2003) demonstrated that basic blue 9 adsorption on Fuller's earth was very fast compared to that on CAC and Fuller's earth particles have higher adsorption capacity. Furthermore, Fuller's earth is approximately 500 times cheaper than CAC. Espantaleon et al. (2003) reported that the capacity of sepiolite and acid-treated bentonite to adsorb anionic dyes was much greater than that of conventional adsorbents. Bagane and Guiza (2000) showed that the adsorption capacity was 20 times greater on kaolinite than on alumina. Wang et al. (2005) showed that fly ash exhibited higher capacity than red mud. Peat has excellent ion-exchange properties similar to those of natural zeolites (Allen et al., 2004). Kargi and Ozmihci (2004) reported that powdered activated sludge can be used for removal of different dyestuffs as an alternative to powdered activated carbon.

It is evident that natural materials, waste materials from industry and agriculture and biosorbents are an interesting alternative to replace activated carbons. Some promising results could be noted in the case of clays, peat and chitosan-based materials (Alkan et al., 2005, Alkan et al., 2004, Allen et al., 2004, Guibal, 2004, Varma et al., 2004, Ho and McKay, 2003 and Ravi Kumar, 2000). Several biosorption processes have also been developed, patented and introduced for application in removing contaminants from waters (Aksu, 2005, Aksu and Tezer, 2005, Pokhrel and Viraraghavan, 2004, Fu and Viraraghavan, 2002a, Fu and Viraraghavan, 2001a and Robinson et al., 2001). A comprehensive study of the application of biosorption for the removal of organic pollutants can be found in a recent review by Aksu (2005). However, despite the number of published laboratory data, non-conventional low-cost adsorbents have not been applied at an industrial scale. There are several reasons for this difficulty in transferring the process to industrial applications. They can be summarized as follows:

- The variability in the material characteristics and the availability of the resource that is controlled by the demand at the commercial level can discourage industrial users (Guibal, 2004).
- The applicability of low-cost adsorbents such as chitosan, peat, zeolites, biomass, fly ashes and red mud for water treatment depends strongly on their origin (Wang et al., 2005, Kargi and Ozmihci, 2004, Varma et al., 2004, Guibal, 2004, Ravi Kumar, 2000, Calzaferri et al., 2000 and Altin et al., 1998). For example, the sorption capacity of chitosan materials depends on the origin of the polysaccharide and the degree of deacetylation. These parameters influence its adsorption properties (Guibal, 2004, Varma et al., 2004 and Ravi Kumar, 2000). The characteristics of the particles can

also introduce hydrodynamic limitations and column fouling, which limits the use of these materials for large-scale columns. These problems can explain why it is difficult to develop chitosan-based materials as adsorbents at an industrial-scale.

- The adsorption process will provide an attractive technology if the low-cost sorbent is ready for use. However, physical and chemical processes such as drying, autoclaving, crosslinking reactions or contacting with organic or inorganic chemicals are proposed for improving the sorption capacity and the selectivity. For example, for the industrial application of biosorption, immobilization of biomass is necessary (Aksu, 2005). These pre-treatment methods are not cost effective at large scale. The production of chitosan also involves a chemical deacetylation process. Commercial production of chitosan by deacetylation of crustacean chitin with strong alkali appears to have limited potential for industrial acceptance because of difficulties in processing, particularly with the large amount of waste concentrated alkaline solution causing environmental pollution. However, several yeasts and filamentous fungi have been recently reported as containing chitin and chitosan in their cell wall and septa. They can be readily cultured in simple nutrients and used as a source of chitosan. With advances in fermentation technology chitosan preparation from fungal cell walls could become an alternative route for the production of this biopolymer via an ecofriendly pathway.
- Performance is dependent on the type of material used. Each low-cost sorbent has its specific advantage in wastewater treatment. For example, clay minerals exhibit a strong affinity for basic dye (Bagane and Guiza, 2000) and alunite has high affinities for acid dyes (Özacar and Sengil, 2002 and Özacar and Sengil, 2003). Chitosan has a low affinity for cationic dyes while peat is shown to be a particularly effective adsorbent for cationic dyes. However, peat has a lower capacity for acid dyes (Allen et al., 1994 and Allen et al., 2004).
- The effectiveness of treatment depends not only on the properties of the adsorbent and adsorbate, but also on the following environmental conditions and variables used for the adsorption process: pH, ionic strength, temperature, existence of competing organic or inorganic ligands in solution, contact time and adsorbent concentration. Despite the fact that industrial effluents contain several pollutants simultaneously, little attention has been given to adsorption of pollutants from mixtures (Aksu, 2005).

The development of the adsorption process requires further investigation in the direction of testing low-cost sorbents with real industrial effluents.

- There is as yet little literature containing a full study of comparisons between sorbents. The comparison of sorption performance depends not only the parameters related to the experimental conditions and the effluent, but also on the analytical method used for decontamination tests (batch method, column, reactors, etc.). Thus, a direct comparison of data obtained using different low-cost sorbents is difficult because of inconsistencies in the data presentation (Babel and Kurniawan, 2003 and Bailey et al., 1999).
- There is a lack of data concerning the reproducibility of the adsorption properties and the equilibrium data, commonly known as adsorption isotherms. In view of industrial developments of the various kinds of sorbents described in the literature, the physical and chemical stability of the materials and the reproducibility of the sorption properties is of utmost importance. Unfortunately, there is little information on this subject. The design and efficient operation of adsorption processes also requires equilibrium adsorption data for use in kinetic and mass transfer models (Allen et al., 2004). These models play an important role in predictive modeling for analysis and design of adsorption systems. Additional work on this subject is needed.

In this review, a wide range of non-conventional low-cost adsorbents has been presented. Inexpensive, locally available and effective materials could be used in place of commercial activated carbon for the removal of dyes from aqueous solution. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purposes in the future. In particular, from the recent literature reviewed, chitosan-based sorbents have demonstrated outstanding removal capabilities for certain dyes in comparison to activated carbon. However, despite a number of papers published on low-cost adsorbents, there is as yet little information containing a full study of comparison between sorbents. Although much has been accomplished in the area of low-cost sorbents, much work is necessary (i) to predict the performance of the adsorption processes for dye removal from real industrial effluents under a range of operating conditions, (ii) to better understand adsorption mechanisms and (iii) to demonstrate the use of inexpensive adsorbents at an industrial scale.

2.0 Objectives

The effluent treatment in developing countries is expensive and major cost is associated with the dependence on imported technologies and chemicals. The indigenous production of treatment techniques and chemicals locally, or use locally available non-conventional materials to treat pollutants seems to be the solution to the increasing problem of treatment of effluents. In this regard, there has been a focus on the use of appropriate low cost technology for the treatment of wastewater in developing countries in recent years. Technically feasible and economically viable pretreatment procedures with suitable biomaterials based on better understanding of the metal biosorbent mechanism(s) are gaining importance. Activated carbons of agricultural waste products as low cost adsorbents have been reported till now. However, there is an additional cost involved in the processing of the agricultural wastes to convet the same to activated carbon, which is posing economic difficulties necessitating research on alternate adsorbents with equivalent potential of activated carbon.

The objective of the present study was to find out the adsorption capacity of the four husks namely Tur dal (*Cajanus cajan*) husk (TDH); bengal gram husk (BGH), seed coat of *Cicer arientinum*; coffee (*Coffee arabica*) husk (CH) and tamarind (*Tamarindus indica*) pod shells (TH) for the removal of dyes from aqueous solutions so as to facilitate comparison with other adsorbents and provide a sound basis for further modification of the adsorbent to improve its efficiency.

The four adsorbents chosen for the present study is available in plenty in tropical regions. Adsorption properties of these adsorbents have not yet been reported in literature. The four dyes chosen are methylene blue, rhodamine B, fast green and amaranth.

The dyes like Trisodium 2-hydroxy-1-(4-sulphonato-1-naphthylazo) naphthalene-3,6-disulphonate (Amaranth) are widely used for colouring textiles, paper, phenol-formaldehye resins, wood and leather. These dyes were also employed as food additives in jams, jellies, ketchup and cake decoration before its legal prohibition to use as colouring agent for food and beverages. It has now been well proved that higher concentration of these dyes can adversely affect human/animal health and can cause tumour, allergic and respiratory problems. There are also some evidences, which suggest that it may also cause birth defects. They are all water-soluble dyes with high solubility and thus difficult to remove by common chemical treatments.

Keeping these environmental, ecological and societal health issues in view, it is considered necessary to attempt and provide an easy, feasible, economical and reliable method for the removal of dyes. Hence, adsorption by locally available, environmentally-friendly and cost effective adsorbents have been explored and exploited.

The objective is achieved through:

1) Characterisation of the adsorbents for their carbon, nitrogen and sulphur content
2) Characterisation of functional groups on the surface of the adsorbent that contributes to the biosorption of dyes used in the present study through infrared spectroscopy.
3) Determination of the agitation/equilibrium time, pH and effect of adsorbent at different initial dye concentrations.
4) Calculation of the adsorption capacity and intensity using Langmuir and Freundlich isotherm models,
5) Desorption of dyes from dye loaded adsorbents to determine the mechanism of adsorption.
6) Comparison between the adsorbents for their adsorption capacity with those found in literature.

3.0 Materials and methods

In this chapter, methods for using viable non-conventional low-cost adsorbents like tur dal husk (TDH); bengal gram husk (BGH), coffee husk (CH) and tamarind husk (TH) for removal of dyes fast green (FG) , methylene blue (MB) , amaranth (AM) and rhodamine B (RB).

3.1 Materials

Tur dal (*Cajanus cajan*) husk (TDH) and bengal gram (*Cicer arientinu*) husk (BGH), was collected from a legume seed-splitting mill. The coffee husk (CH) was collected from coffee processing unit and tamarind pod shells (TH) were obtained from a de-hulling unit. The four husks were washed extensively in running tap water to remove dirt and other particulate matter. This was later subjected to colour removal through washing and boiling in distilled water repeatedly. Subsequently the husks were oven dried at 105°C for 24 hours, stored in a desiccator and used for biosorption studies in the original piece size.

3.2 Preparation of adsorbate solutions

Dye solutions: Individual stock solutions of 1000 mg/L of Fast green FCF, Methylene Blue, Rhodamine B and Amaranth were prepared by dissolving dyes in water. Solutions of various concentrations were prepared by using the above stock solution.

3.3 Determination of carbon, nitrogen and sulphur in the four husks

Total carbon, nitrogen and sulphur were determined, in order to understand the dye binding mechanisms of four agricultural byproducts. Elemental analysis was carried out with a C.H.N. 1106 Carlo Erba MicroAnalysing device equipped with inductive furnace analyzer. Samples of the four husks were put in an oven at 1000°C under oxygen in order to obtain a quick and complete combustion. N_2, H_2O and CO_2 were released and conducted in a copper oven at 650°C, then passed through a 2 m column with helium vector gas, and analyzed by a catharometer detector.

3.4 Infrared spectroscopic analysis

FT-IR spectra of the four adsorbents namely BGH, TDH, CH and TH were obtained using shimadzu, Model FTIR – 8201PC. The infrared spectral analysis was done to determine the functional groups responsible for the adsorption of dyes. As chemical bonds absorb infrared energy at specific frequencies (or wavelengths), the basic structure of compounds can be determined by the spectral locations of their IR absorptions. The plot of a compound's IR transmission vs. frequency is its "fingerprint", which when compared to reference spectra identifies the material.

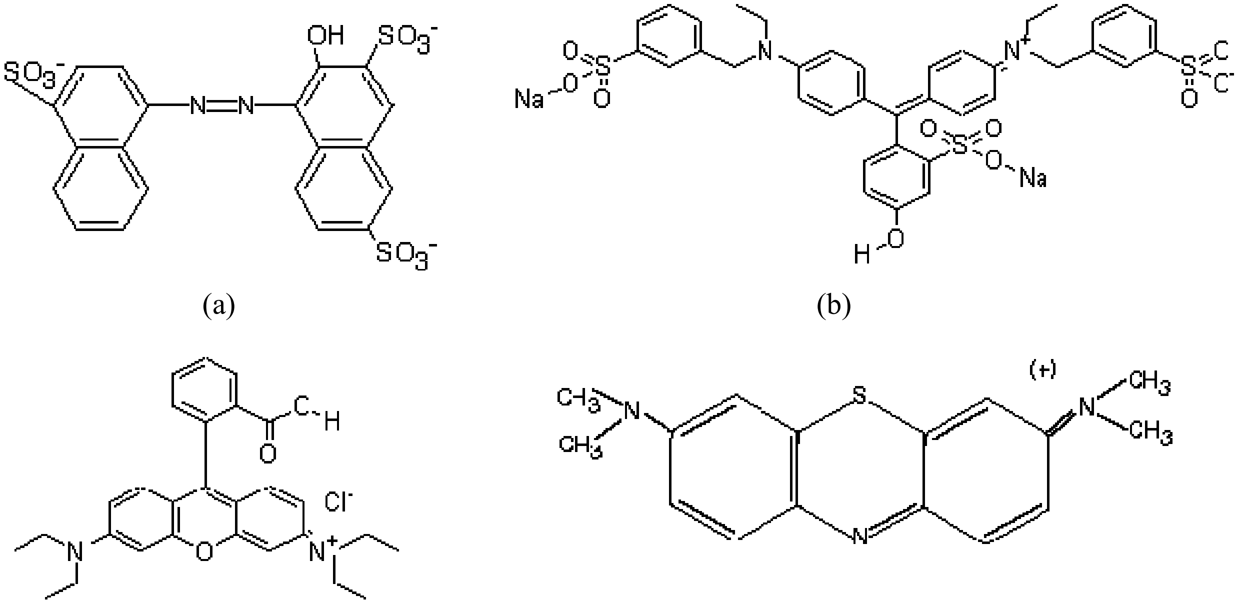
3.5 Analysis of adsorbates

Estimation of dyes

Absorbance measurements were carried out using Visible Spectrophotometer. Absorption maxima of dyes were used as the monitoring wavelengths for the estimation of dye adsorption. Absorption maxima for the dyes, Fast green, Methylene Blue, Rhodamine B and Amaranth were found to be 620, 665, 555 and 520 nm respectively.

Table 13 The general data of four dyes used in this study

Commercial name	Classification	λ_{max} (nm)
Amaranth	Anionic Monoazo	520
Methylene Blue	Cationic Thiazine	665
Fast green FCF	Anionic Triphenylmethane	620
Rhodamine B	Cationic Xanthine	555



(a) (b)

(c) (d)

Figure 1: Structure of the four dyes used in present study (a) Amaranth; (b) Fast green; (c) Rhodamine B; (d) Methylene blue.

3.6 Batch mode adsorption studies

Batch mode adsorption studies for individual dyes were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, agitation time and pH. Solution containing adsorbate and adsorbent was taken in 250 mL capacity beakers and agitated at 150 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using Whatman No.1 filter paper. To avoid the adsorption of adsorbate on the container walls, the containers were pretreated with the respective adsorbate for 24 hours.

3.6.1 Effect of agitation time

For the determination of rate of dye biosorption by BGH, TDH and TH from 100 ml (at 10, 20, 50, 100 mgL^{-1}), the supernatant was analysed for residual dye at different time intervals. The pH and the adsorbent dosage was kept constant, which varied according to the adsorbent and adsorbate under consideration.

3.6.2 Effect of adsorbent dosage

The effect of adsorbent dosage i.e., the amount of the four husks on the adsorption of dyes was studied at different dosages ranging from 1 to 40 g/l with varied dye concentrations of 10, 20, 50 and 100 mg/L. The equilibrium time and the pH were kept constant depending on the dye under consideration.

3.6.3 pH effect

To determine the effect of pH on the adsorption of dyes solutions (100 mL) of different concentration ranges (0-100 mgL^{-}1) were adjusted to desired pH values and mixed with known weight of adsorbent and agitated at preset equilibrium time. The equilibrium time and adsorbent dosage varied with the dye and adsorbent under consideration.

3.6.4 Desorption studies

After adsorption, the adsorbates – loaded adsorbent were separated from the solution by centrifugation and the supernatant was drained out. The adsorbent was gently washed with water to remove any unadsorbed adsorbate. Regeneration of adsorbate from the adsorbate – laden adsorbent was carried out using the desorbing media – distilled water at pH ranges 4.0 to 12.0 using dilute solutions of NaOH and HCl. Then they were agitated for the equilibrium time of respective adsorbate. The desorbed adsorbate in the solution was separated and analyzed for the residual dyes.

This Section presents the results obtained from the batch studies of biosorption of dyes by the four agricultural by products namely bengal gram husk, coffee husk, tur dal husk and tamarind husk. The four dyes include amaranth, methylene blue, fast green and rhodamine B. Preliminary results showed that coffee husk was not efficient in the biosorption of dyes. Hence the results of biosorption of dyes by coffee husk are not presented here.

4.0 Results

4.1 Characteristics of the adsorbent

The approximate percentages of total carbon, nitrogen and hydrogen in the four husks are shown in Table 14. The greater percentage of carbon content in all the four husks reveal that carbon compounds might be responsible for adsorption of dyes [methylene blue, amaranth, rhodamine B and fast green]. The protein content is less in all the four husks, as revealed by low nitrogen values. The approximate percentages of total carbon, nitrogen and hydrogen in the four husks are listed in Table 14.

Table 14 Percentage content of carbon, hydrogen and nitrogen in the four husks

Adsorbent	Carbon	Hydrogen	Nitrogen
Bengal gram husk	38.57	6.31	0.86
Tur dal husk	40.66	6.35	1.13
Coffee husk	45.33	6.21	0.63
Tamarind husk	46.01	6.14	0.94

The preliminary results showed that coffee husk was not efficient in the biosorption of dyes. Hence the results of biosorption of dyes by coffee husk are not presented here.

4.2 Infrared spectroscopic studies

Unreacted samples of BGH, TDH, TH and CH were subjected to Fourier transform infrared spectroscopy and the percentage transmissions for various wavenumbers are presented in Figures 2 to 5 respectively. The absorption bands identified in the spectra and their assignment to the corresponding functional groups are discussed in detail in the discussion section.

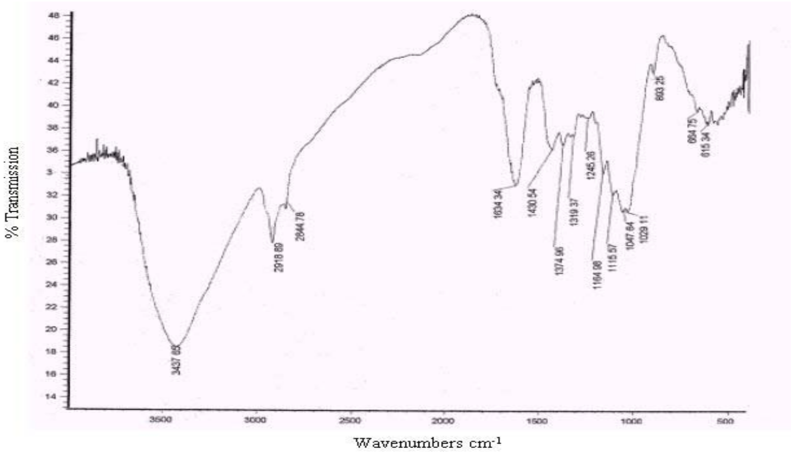


Figure 2 Infrared spectra of BGH

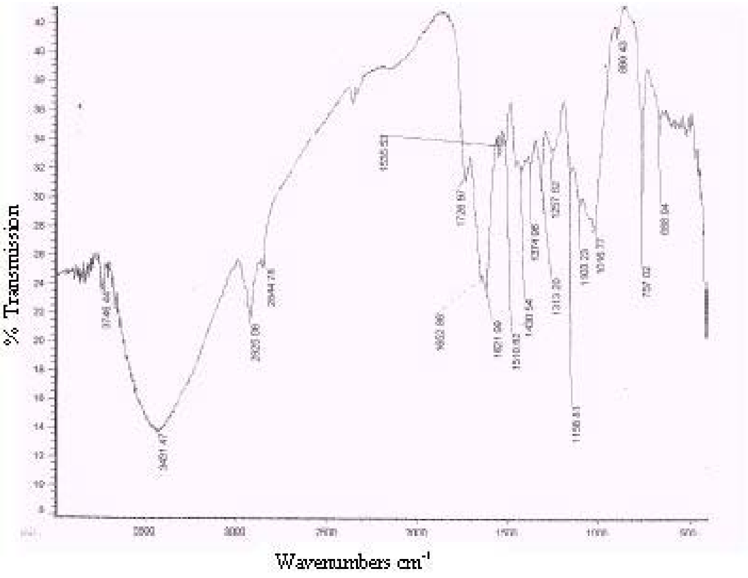


Figure 3 Infrared spectra of TDH

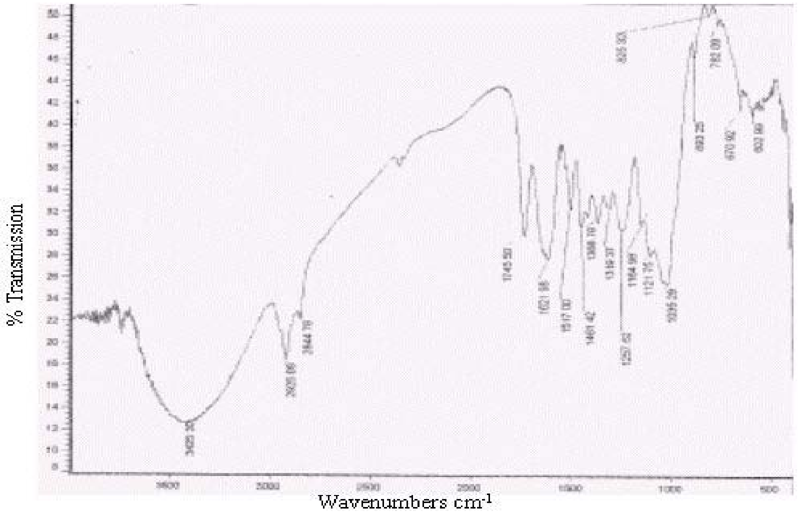


Figure 4 Infrared spectra of CH

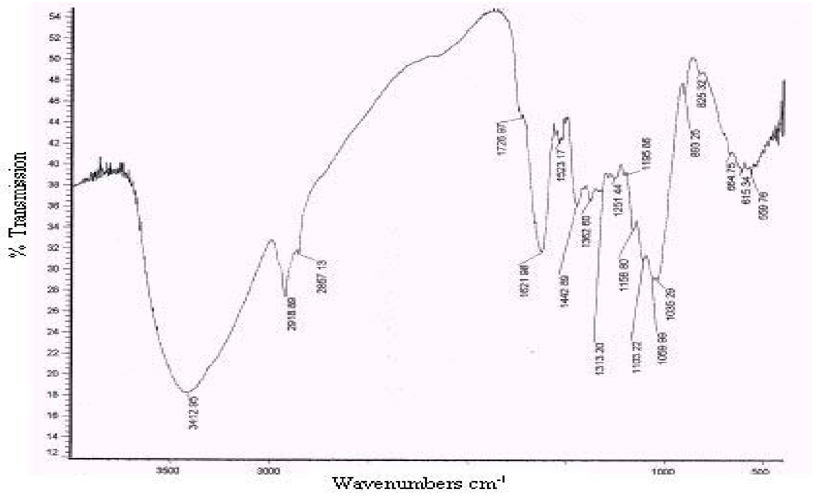


Figure 5 Infrared spectra of TH

4.3 Batch mode adsorption studies

4.3.1 Effect of agitation time

The results on the effect of agitation time at various dye concentrations are presented in Tables and Figures. Adsorption of amaranth by bengal gram husk; tur dal husk and tamarind husk are presented in Tables 15 to 17 and Figures 6-8. Tables 18 to 20 and Figures 9 -11 present the results of agitation time of Methylene blue by bengal gram husk; tur dal husk and tamarind husk. Similarly, Figures 12 - 14 and Tables 21 to 23 represent the agitation time of adsorption of Fast green by bengal gram husk; tur dal husk and coffee husk. Adsorption of rhodamine B by the various husks is given in Figures 15 - 17 and Tables 24 to 26.

Amaranth was maximally adsorbed within 50 minutes of contact between the adsorbent and dye molecules. The agitation time was dependent on initial dye concentration for biosorption of methylene blue by BGH and TH. The adsorption of fast green by BGH and TH was independent of time. An equilibrium time of 60 minutes was required for the bioremoval of Fast green by TDH. The amount of rhodamine B biosorbed was least in TH and maximum by Tur dal husk. Generally, among all the dyes, the equilibrium time for Rhodamine B was higher than for all the other dyes Tur dal husk exhibited maximum uptake of the dyes followed by BGH and TDH.

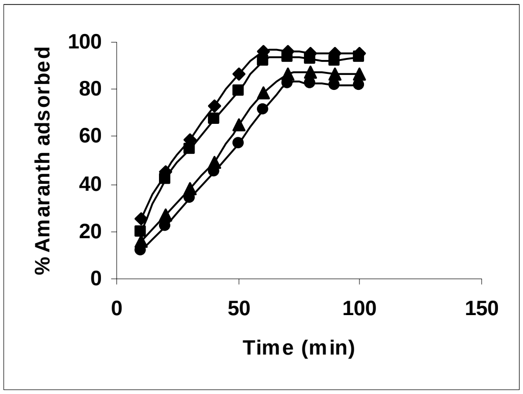
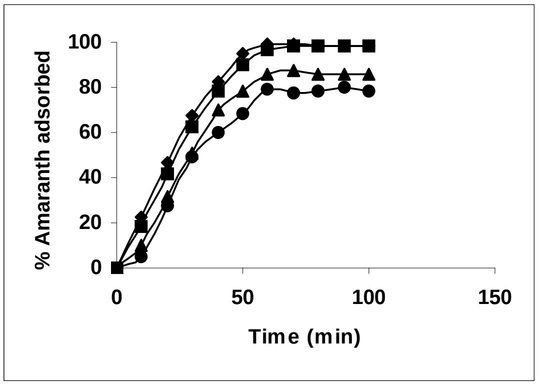


Figure: 6



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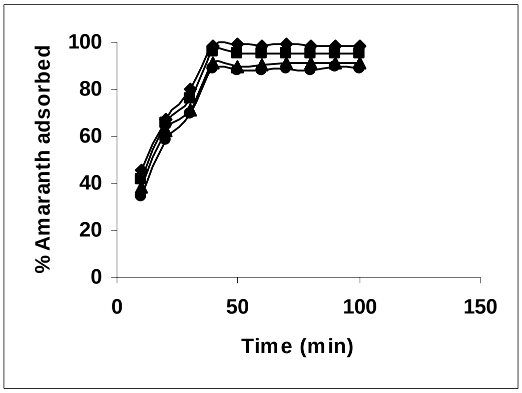
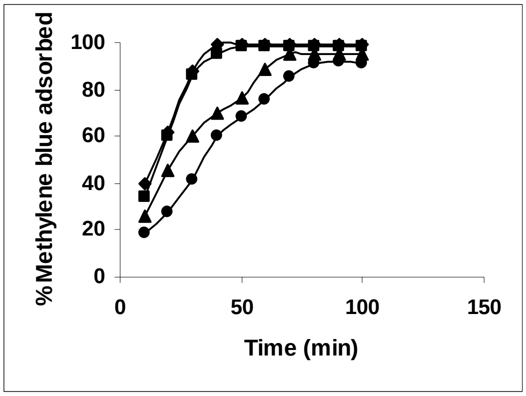


Figure 8

Figure 6-8 Effect of agitation time on the amaranth biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)



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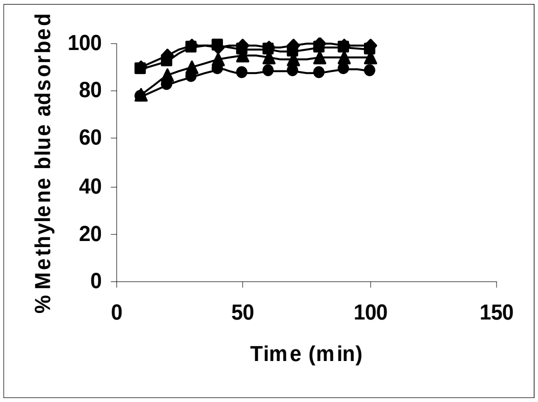

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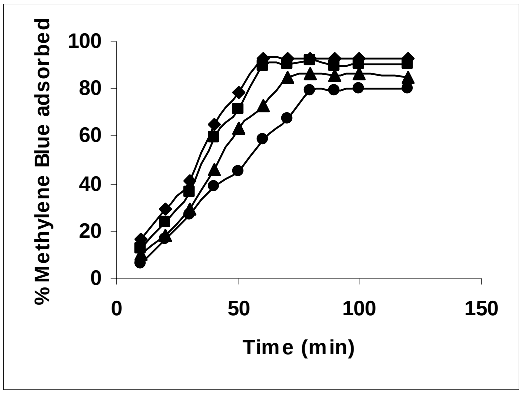


Figure: 11

Figure 9-11 Effect of agitation time on the Methylene blue biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

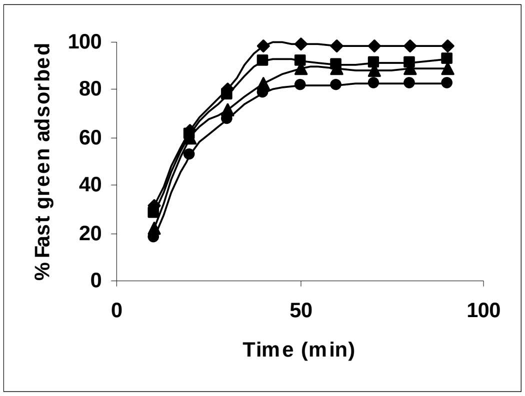


Figure: 12

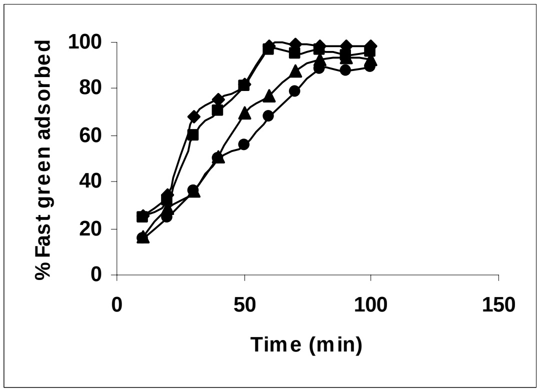


Figure: 13

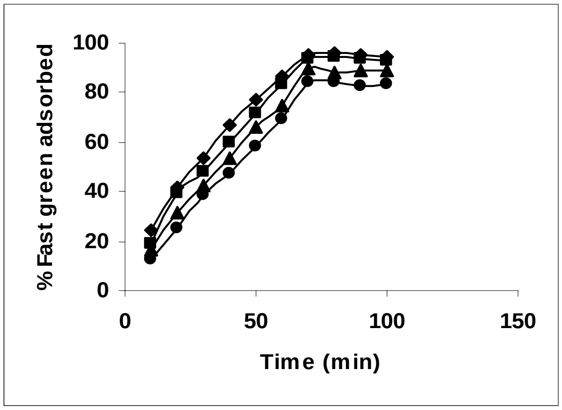


Figure: 15

Figure 12-15 Effect of agitation time on the Fast green biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

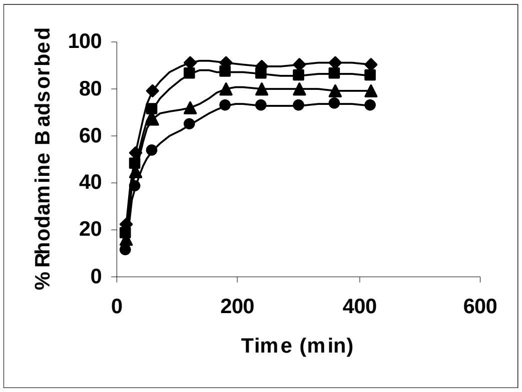


Figure: 16

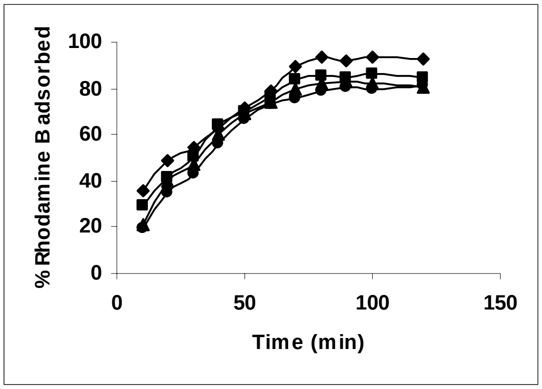


Figure: 17

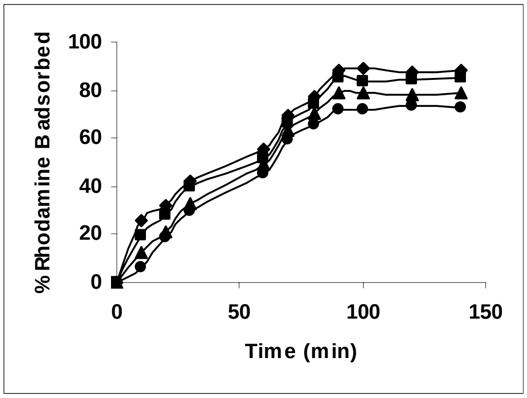


Figure: 18

Figure 16-18 Effect of agitation time on the Rhodamine B biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

Table 15 Effect of agitation time and initial dye concentration on Amaranth adsorption by bengal gram husk (Adsorbent dose = 0. 25 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	AM adsorbed (mg/g)	qe-q		% adsorbed	AM adsorbed (mg/g)	qe-q
10	25.65	1.03	2.82	10	19.57	1.57	5.8
20	45.23	1.81	2.04	20	41.89	3.35	4.02
30	58.65	2.35	1.5	30	54.75	4.38	2.99
40	72.64	2.91	0.94	40	67.48	5.40	1.97
50	86.49	3.46	0.39	50	79.41	6.35	1.02
60	95.68	3.83		60	92.16	7.37	
70	96.19	3.85		70	93.54	7.48	
80	95.53	3.82		80	92.89	7.43	
90	94.89	3.80		90	92.16	7.37	
100	95.18	3.81		100	93.32	7.47	
		Qe= 3.85				Qe = 7.37	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	AM adsorbed (mg/g)	qe-q		% adsorbed	AM adsorbed (mg/g)	qe-q
10	15.64	3.13	14.17	10	11.85	4.74	28.13
20	27.33	5.47	11.83	20	22.16	8.86	24.01
30	38.48	7.70	9.6	30	34.21	13.68	19.19
40	48.98	9.80	7.5	40	45.59	18.24	14.63
50	64.98	13.00	4.3	50	57.49	23.00	9.87
60	78.27	15.65		60	71.29	28.52	4.35
70	86.49	17.30		70	82.56	33.02	
80	87.08	17.42		80	82.18	32.87	
90	86.74	17.35		90	81.97	32.79	
100	86.18	17.24		100	81.77	32.71	
		Qe=17.30				Qe=32.87	

Table 16 Effect of agitation time and initial dye concentration on Amaranth adsorption by Tur dal husk (Adsorbent dose = 0.3 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	AM adsorbed (mg/g)	qe-q		% adsorbed	AM adsorbed (mg/g)	qe-q
10	22.12	0.74	2.55	10	18.56	1.24	5.33
20	46.32	1.54	1.75	20	41.28	2.75	3.82
30	67.49	2.25	1.04	30	62.56	4.17	2.4
40	82.56	2.75	0.54	40	78.45	5.23	1.34
50	94.65	3.16	0.13	50	89.65	5.98	0.59
60	99.23	3.31		60	96.58	6.44	0.13
70	98.95	3.30		70	98.56	6.57	
80	98.64	3.29		80	98.14	6.54	
90	98.15	3.27		90	98.56	6.57	
100	98.75	3.29		100	98.56	6.57	
		Qe=3.30				Qe=6.57	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	AM adsorbed (mg/g)	qe-q		% adsorbed	AM adsorbed (mg/g)	qe-q
10	10.23	1.71	12.67	10	5.23	1.74	24.71
20	31.45	5.24	9.14	20	27.56	9.19	17.26
30	51.23	8.54	5.84	30	48.98	16.33	10.12
40	69.82	11.64	2.74	40	59.87	19.96	6.49
50	78.45	13.08	1.3	50	67.95	22.65	3.8
60	86.25	14.38		60	79.36	26.45	
70	87.56	14.59		70	77.56	25.85	
80	85.54	14.26		80	78.35	26.12	
90	86.12	14.35		90	79.87	26.62	
100	85.45	14.24		100	78.45	26.15	
		Qe=14.38				Qe=26.45	

Table 17 Effect of agitation time and initial dye concentration on Amaranth adsorption by Tamarind husk. (Adsorbent dose = 0.25 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	AM adsorbed (mg/g)	qe-q		% adsorbed	AM adsorbed (mg/g)	qe-q
10	45.68	1.83	2.12	10	41.69	3.34	4.33
20	67.25	2.69	1.26	20	65.87	5.27	2.4
30	79.67	3.19	0.76	30	76.23	6.10	1.57
40	98.5	3.94		40	95.89	7.67	
50	99.12	3.96		50	94.87	7.59	
60	98.65	3.95		60	95.12	7.61	
70	99.52	3.98		70	95.34	7.63	
80	98.29	3.93		80	95.28	7.62	
90	98.37	3.93		90	95.44	7.64	
100	98.66	3.95		100	95.36	7.63	
		Qe=3.95				Qe=7.67	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	AM adsorbed (mg/g)	qe-q		% adsorbed	AM adsorbed (mg/g)	qe-q
10	38.59	7.72	10.48	10	34.12	13.65	21.78
20	62.36	12.47	5.73	20	58.23	23.29	12.14
30	71.5	14.30	3.9	30	69.77	27.91	7.52
40	91.23	18.25		40	88.57	35.43	
50	89.52	17.90		50	87.93	35.17	
60	90.03	18.01		60	88.23	35.29	
70	91.11	18.22		70	88.57	35.43	
80	90.89	18.18		80	87.98	35.19	
90	90.89	18.18		90	89.95	35.98	
100	91.11	18.22		100	88.59	35.44	
		Qe=18.20				Qe=35.43	

Table 18 Effect of agitation time and initial dye concentration on Methylene Blue adsorption by bengal gram husk (Adsorbent dose = 0.15 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	MB adsorbed (mg/g)	qe-q		% adsorbed	MB adsorbed (mg/g)	qe-q
10	39.56	2.64	3.96	10	34.21	4.56	8.52
20	61.65	4.11	2.49	20	59.86	7.98	5.1
30	87.54	5.84	0.76	30	86.35	11.51	1.57
40	99.55	6.64		40	95.23	12.70	0.38
50	99.2	6.61		50	98.12	13.08	
60	98.99	6.60		60	98.45	13.13	
70	99.2	6.61		70	98.56	13.14	
80	99.55	6.64		80	98.21	13.09	
90	99.2	6.61		90	98.25	13.10	
100	99.5	6.63		100	98.56	13.14	
		Qe=6.60				Qe=13.08	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	MB adsorbed (mg/g)	qe-q		% adsorbed	MB adsorbed (mg/g)	qe-q
10	25.66	8.55	23.25	10	18.99	12.66	48.15
20	45.45	15.15	16.65	20	27.82	18.55	42.26
30	59.88	19.96	11.84	30	41.23	27.49	33.32
40	69.89	23.30	8.5	40	59.89	39.93	20.88
50	76.21	25.40	6.4	50	68.23	45.49	15.32
60	88.89	29.63	2.17	60	75.44	50.29	10.52
70	95.41	31.80		70	85.69	57.13	3.68
80	95.12	31.71		80	91.22	60.81	
90	94.99	31.66		90	91.68	61.12	
100	95.23	31.74		100	91.45	60.97	
		Qe=31.80				Qe=60.81	

Table 19 Effect of agitation time and initial dye concentration on Methylene Blue adsorption by Tur dal husk (Adsorbent dose = 0.1 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	MB adsorbed (mg/g)	qe-q		% adsorbed	MB adsorbed (mg/g)	qe-q
10	90.12	9.01	0.9	10	89.56	17.91	1.8
20	95.23	9.52	0.39	20	92.45	18.49	1.22
30	99.26	9.93		30	98.56	19.71	
40	98.65	9.87		40	98.95	19.79	
50	99.26	9.93		50	97.68	19.54	
60	98.75	9.88		60	97.88	19.58	
70	98.78	9.88		70	97	19.40	
80	99.65	9.97		80	98.45	19.69	
90	98.78	9.88		90	98.45	19.69	
100	99.56	9.96		100	97.68	19.54	
		Qe=9.93				Qe=19.7	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	MB adsorbed (mg/g)	qe-q		% adsorbed	MB adsorbed (mg/g)	qe-q
10	78.65	39.33	7.4	10	77.85	77.85	11.13
20	86.56	43.28	3.45	20	82.55	82.55	6.43
30	89.96	44.98	1.75	30	85.65	85.65	3.33
40	93.45	46.73		40	88.98	88.98	
50	94.87	47.44		50	87.28	87.28	
60	93.88	46.94		60	88.53	88.53	
70	93.45	46.73		70	88.14	88.14	
80	94.12	47.06		80	87.68	87.68	
90	93.88	46.94		90	88.98	88.98	
100	94.23	47.12		100	88.14	88.14	
		Qe=46.73				Qe=88.98	

Table 20 Effect of agitation time and initial dye concentration on Methylene Blue adsorption by Tamarind husk (Adsorbent dose = 0.2 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	MB adsorbed (mg/g)	qe-q		% adsorbed	MB adsorbed (mg/g)	qe-q
10	16.38	0.82	3.81	10	12.89	1.29	7.72
20	29.56	1.48	3.15	20	23.45	2.35	6.66
30	41.23	2.06	2.57	30	36.77	3.68	5.33
40	65.19	3.26	1.37	40	59.41	5.94	3.07
50	78.96	3.95	0.68	50	71.36	7.14	1.87
60	92.56	4.63		60	89.35	8.94	0.07
70	93.12	4.66		70	90.12	9.01	
80	92.51	4.63		80	91.69	9.17	
90	93.24	4.66		90	89.46	8.95	
100	93.12	4.66		100	90.12	9.01	
120	92.56	4.63		120	90.34	9.03	
		Qe=4.63				Qe=9.01	
Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	MB adsorbed (mg/g)	qe-q		% adsorbed	MB adsorbed (mg/g)	qe-q
10	10.24	2.6	18.7	10	6.59	3.30	36.48
20	18.23	4.6	16.7	20	17	8.50	31.28
30	29.27	7.3	14	30	26.81	13.41	26.37
40	45.66	11.4	9.9	40	39.22	19.61	20.17
50	63.45	15.9	5.4	50	45.49	22.75	17.03
60	72.98	18.2	3.1	60	58.64	29.32	10.46
70	85.28	21.3		70	67.11	33.56	6.22
80	86.19	21.5		80	79.56	39.78	
90	85.51	21.4		90	79.12	39.56	
100	86.38	21.6		100	80.24	40.12	
120	85.28	21.32		120	80.11	40.06	
		Qe=21.3				Qe=39.78	

Table 21 Effect of agitation time and initial dye concentration on Fast green (FCF) adsorption by bengal gram husk (Adsorbent dose = 0. 3 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	FG adsorbed (mg/g)	qe-q		% adsorbed	FG adsorbed (mg/g)	qe-q
10	31.48	1.05	2.24	10	28.55	1.90	4.22
20	62.89	2.10	1.19	20	61.64	4.11	2.01
30	80.48	2.68	0.61	30	78.11	5.21	0.91
40	98.58	3.29		40	91.77	6.12	
50	99.12	3.30		50	92.45	6.16	
60	98.36	3.28		60	90.88	6.06	
70	98.57	3.29		70	91.59	6.11	
80	98.78	3.29		80	91.45	6.10	
90	98.59	3.29		90	92.67	6.18	
		Qe=3.29				Qe=6.12	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	FG adsorbed (mg/g)	qe-q		% adsorbed	FG adsorbed (mg/g)	qe-q
10	22.33	3.72	11.08	10	18.42	6.14	21.25
20	59.77	9.96	4.84	20	52.57	17.52	9.87
30	71.48	11.91	2.89	30	67.89	22.63	4.76
40	82.39	13.73	1.07	40	78.68	26.23	1.16
50	88.78	14.80		50	82.18	27.39	
60	89.18	14.86		60	81.75	27.25	
70	88.54	14.76		70	82.49	27.50	
80	88.78	14.80		80	82.89	27.63	
90	89.08	14.85		90	82.57	27.52	
		Qe=14.8				Qe=27.39	

Table 22 Effect of agitation time and initial dye concentration on Fast green adsorption by Tur dal husk (Adsorbent dose = 0.15g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	FG adsorbed (mg/g)	qe-q		% adsorbed	FG adsorbed (mg/g)	qe-q
10	25.65	1.71	4.87	10	24.88	3.32	9.53
20	34.58	2.31	4.27	20	32.12	4.28	8.57
30	67.89	4.53	2.05	30	59.87	7.98	4.87
40	75.38	5.03	1.55	40	70.21	9.36	3.49
50	82.31	5.49		50	81.23	10.83	2.02
60	98.7	6.58		60	96.35	12.85	
70	99.23	6.62		70	95.21	12.69	
80	98.44	6.56		80	96.45	12.86	
90	98.19	6.55		90	94.58	12.61	
100	98.7	6.58		100	96.21	12.83	
		Qe=6.58				Qe=12.85	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	FG adsorbed (mg/g)	qe-q		% adsorbed	FG adsorbed (mg/g)	qe-q
10	16.56	5.52	23.65	10	15.89	10.59	48.6
20	28.96	9.65	19.52	20	24.69	16.46	42.73
30	36.45	12.15	17.02	30	35.85	23.90	35.29
40	51	17.00	12.17	40	49.68	33.12	26.07
50	69.27	23.09	6.08	50	56.05	37.37	21.82
60	76.85	25.62	3.55	60	68.22	45.48	13.71
70	87.52	29.17		70	78.29	52.19	7
80	92.87	30.96		80	88.78	59.19	
90	93.21	31.07		90	87.59	58.39	
100	92.56	30.85		100	89.21	59.47	
		Qe=29.17				Qe=59.19	

Table 23 Effect of agitation time and initial dye concentration on Fast green (FCF) adsorption by Tamarind husk (Adsorbent dose = 0. 3 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	FG adsorbed (mg/g)	qe-q		% adsorbed	FG adsorbed (mg/g)	qe-q
10	24.65	0.82	2.37	10	19.28	1.29	4.93
20	41.56	1.39	1.8	20	39.57	2.64	3.58
30	53.84	1.79	1.4	30	48.32	3.22	3
40	67.25	2.24	0.95	40	59.95	4.00	2.22
50	76.98	2.57	0.62	50	71.29	4.75	1.47
60	86.37	2.88	0.31	60	83.56	5.57	0.65
70	95.56	3.19		70	93.35	6.22	
80	96.21	3.21		80	94.19	6.28	
90	94.89	3.16		90	93.87	6.26	
100	94.58	3.15		100	93.15	6.21	
		Qe=3.19				Qe=6.22	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	FG adsorbed (mg/g)	qe-q		% adsorbed	FG adsorbed (mg/g)	qe-q
10	16.49	2.75	12.21	10	12.98	4.33	23.66
20	31.28	5.21	9.75	20	25.14	8.38	19.61
30	42.54	7.09	7.87	30	38.41	12.80	15.19
40	53.89	8.98	5.98	40	47.29	15.76	12.23
50	66.22	11.04	3.92	50	58.64	19.55	8.44
60	74.51	12.42	2.54	60	69.49	23.16	4.83
70	89.78	14.96		70	84.56	28.19	
80	87.89	14.65		80	83.98	27.99	
90	88.95	14.83		90	82.58	27.53	
100	88.84	14.81		100	83.41	27.80	
		Qe=14.96				Qe=27.99	

Table 24 Effect of agitation time and initial dye concentration on Rhodamine B by bengal gram husk (Adsorbent dose = 0. 35 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	RB adsorbed (mg/g)	qe-q		% adsorbed	RB adsorbed (mg/g)	qe-q
15	22.59	0.645	1.97	15	18.54	1.06	3.89
30	53.09	1.517	1.09	30	48.38	2.76	2.19
60	79.24	2.264	0.35	60	71.52	4.09	0.86
120	91.56	2.616		120	86.57	4.95	
180	90.85	2.596		180	87.19	4.98	
240	89.67	2.562		240	86.67	4.95	
300	90.27	2.579		300	85.99	4.91	
360	91.58	2.617		360	86.17	4.92	
420	90.37	2.582		420	85.79	4.90	
		Qe=2.61				Qe=4.95	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	RB adsorbed (mg/g)	qe-q		% adsorbed	RB adsorbed (mg/g)	qe-q
15	15.89	2.27	9.14	15	10.85	3.10	17.65
30	44.78	6.40	5.01	30	38.56	11.02	9.73
60	67.45	9.64	1.77	60	53.78	15.37	5.38
120	72.12	10.30	1.11	120	65.19	18.63	2.12
180	79.85	11.41		180	72.63	20.75	
240	80.17	11.45		240	73.09	20.88	
300	79.68	11.38		300	72.98	20.85	
360	78.93	11.28		360	73.49	21.00	
420	79.54	11.36		420	72.63	20.75	
		Qe=11.41				Qe=20.75	

Table 25 Effect of agitation time and initial dye concentration on Rhodamine B adsorption by Tur dal husk (Adsorbent dose = 0.5 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	RB adsorbed (mg/g)	qe-q		% adsorbed	RB adsorbed (mg/g)	qe-q
10	25.65	1.71	4.87	10	24.88	3.32	9.53
20	34.58	2.31	4.27	20	32.12	4.28	8.57
30	67.89	4.53	2.05	30	59.87	7.98	4.87
40	75.38	5.03	1.55	40	70.21	9.36	3.49
50	82.31	5.49	1.09	50	81.23	10.83	2.02
60	98.7	6.58		60	96.35	12.85	
70	99.23	6.62		70	95.21	12.69	
80	98.44	6.56		80	96.45	12.86	
90	98.19	6.55		90	94.58	12.61	
100	98.7	6.58		100	96.21	12.83	
		Qe=6.58				Qe=12.85	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	RB adsorbed (mg/g)	qe-q		% adsorbed	RB adsorbed (mg/g)	qe-q
10	16.56	5.52	25.44	10	15.89	10.59	48.6
20	28.96	9.65	21.31	20	24.69	16.46	42.73
30	36.45	12.15	18.81	30	35.85	23.90	35.29
40	51	17.00	13.96	40	49.68	33.12	26.07
50	69.27	23.09	7.87	50	56.05	37.37	21.82
60	76.85	25.62	5.34	60	68.22	45.48	13.71
70	87.52	29.17	1.79	70	78.29	52.19	7
80	92.87	30.96		80	88.78	59.19	
90	93.21	31.07		90	87.59	58.39	
100	92.56	30.85		100	89.21	59.47	
		Qe=30.96				Qe=59.19	

Table 26 Effect of agitation time and initial dye concentration on Rhodamine B adsorption by Tamarind husk (Adsorbent dose = 0. 4 g/100mL)

Agitation time (min)	**10 mg/L**			**Agitation time (min)**	**20 mg/L**		
	% adsorbed	RB adsorbed (mg/g)	qe-q		% adsorbed	RB adsorbed (mg/g)	qe-q
10	25.76	0.64	1.57	10	19.87	0.99	3.21
20	31.87	0.80	1.41	20	28.33	1.42	2.78
30	42.18	1.05	1.16	30	39.65	1.98	2.22
60	55.23	1.38	0.83	60	51.89	2.59	1.61
70	69.45	1.74	0.47	70	66.74	3.34	0.86
80	77.21	1.93	0.28	80	74.52	3.73	0.47
90	88.26	2.21		90	84.89	4.24	
100	89.25	2.23		100	83.95	4.20	
120	87.48	2.19		120	84.56	4.23	
140	88.56	2.21		140	85.01	4.25	
		Qe=2.21				Qe=4.20	
Agitation time (min)	**50 mg/L**			**Agitation time (min)**	**100 mg/L**		
	% adsorbed	RB adsorbed (mg/g)	qe-q		% adsorbed	RB adsorbed (mg/g)	qe-q
10	12.46	1.56	8.26	10	6.57	1.64	16.41
20	21.19	2.65	7.17	20	18.49	4.62	13.43
30	32.78	4.10	5.72	30	29.88	7.47	10.58
60	49.6	6.20	3.62	60	45.68	11.42	6.63
70	63.49	7.94	1.88	70	59.29	14.82	3.23
80	70.27	8.78	1.04	80	65.84	16.46	1.59
90	78.59	9.82		90	72.21	18.05	
100	79.12	9.89		100	71.58	17.90	
120	78.21	9.78		120	73.12	18.28	
140	78.65	9.83		140	72.89	18.22	
		Qe=9.82				Qe=18.05	

4.3.2 Effect of adsorbent dosage

Results on the effect of adsorbent dosage at various initial dye concentrations are presented in this section. The effect of adsorbent dosage on biosorption of dyes at different husks is given in Figures 19 to 29 Figures 19 to 21 show the effect of adsorbent dosage on the bioremoval of amaranth by bengal gram husk; amaranth removal by tur dal husk and tamarind husk. Similarly Figures 22 to 24 represent removal of methylene blue by the three husks followed by fast green (Figures 25 to 27) and rhodamine B by BGH, TDH and TH (Figures 28 to 30).

It was seen from the results that maximum percentage of dye removal occurred with Tur dal husk at a given adsorbent dosage. Most of the dyes were removed at an adsorbent dosage of 0.5 to 2 g/L for all the husks at initial dye concentrations of 10, 20 and 50 mg/L.

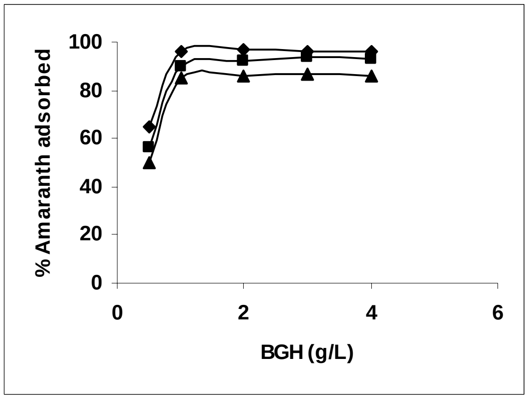


Figure: 19

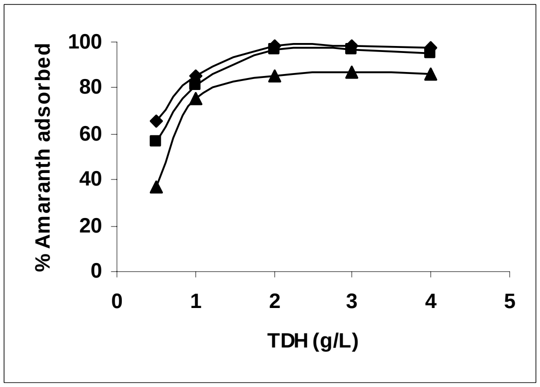


Figure: 20

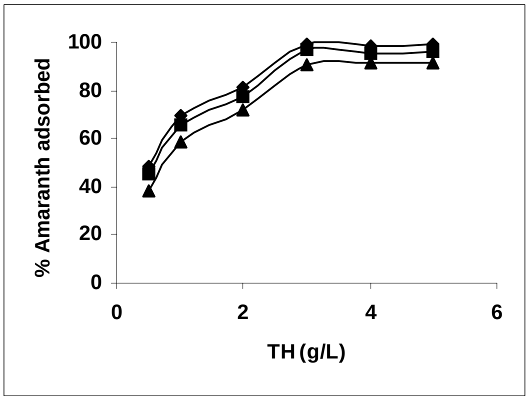


Figure: 21

Figure 19-21 Effect of adsorbent dose on the Amaranth biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

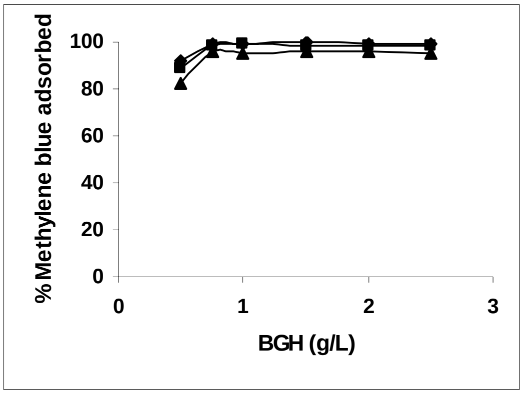
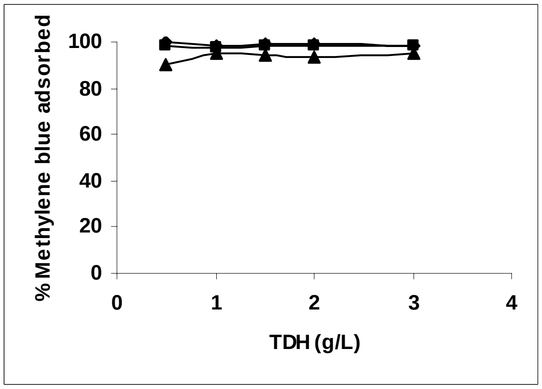


Figure: 22



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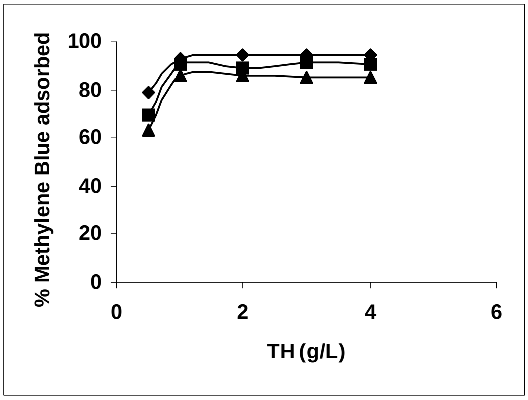


Figure: 24

Figure 22-24 Effect of adsorbent dose on the Methylene blue biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

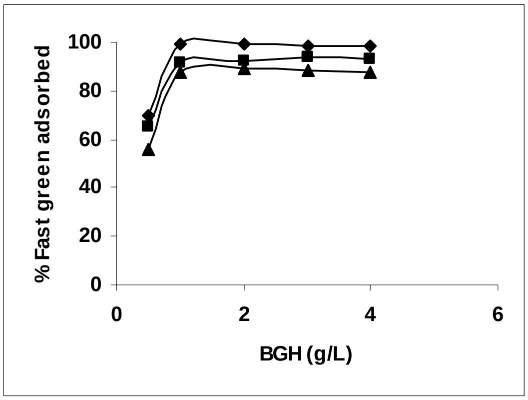


Figure: 25

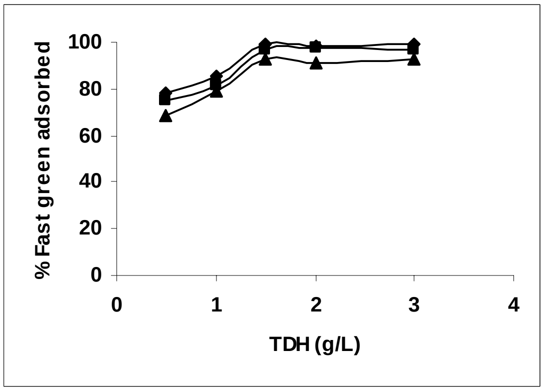


Figure: 26

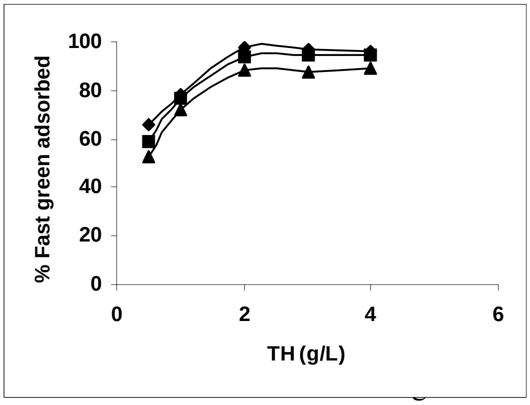


Figure: 27

Figure 25-27 Effect of adsorbent dose on the Fast green biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

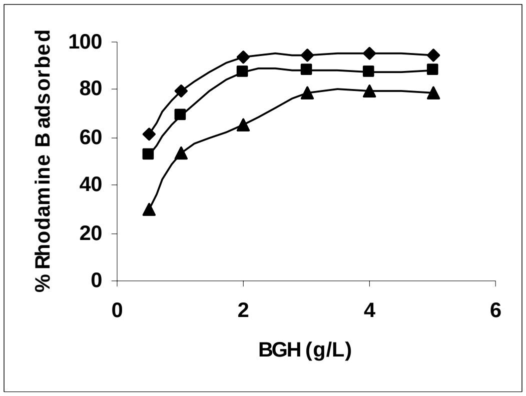
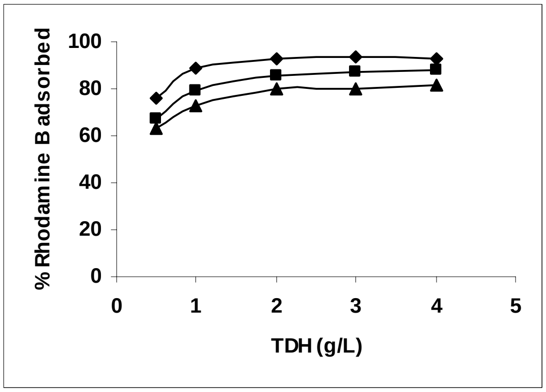


Figure: 28



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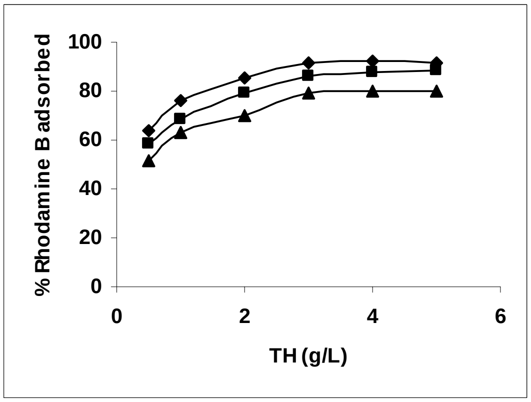


Figure: 30

Figure 28-30 Effect of adsorbent dose on the Rhodamine B biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

4.3.3 Effect of pH

The effect of pH on adsorption of various dyes at different initial dye concentrations is given in Tables and Figures. The adsorption of amaranth by bengal gram husk; tur dal husk and tamarind husk is given in Figures 31 to 33 and Tables 27 to 29. pH effects on Methylene blue by bengal gram husk, tur dal husk and tamarind husk are given in Tables 30-32 and Figures 34 to 36 respectively. Fast green adsorption by the three husks is given in Tables 33 to 35 and Figures 37 to 39. pH effects on Rhodamine B by bengal gram husk, tur dal husk and tamarind husk are given in Tables 36-38 and Figures 40 to 42 respectively.

The maximum percentage of anionic dyes namely amaranth and fast green was biosorbed at pH 2.0. Methylene blue exhibited an optimum range of 6-11 and rhodamine B was adsorbed at pH 7-11.

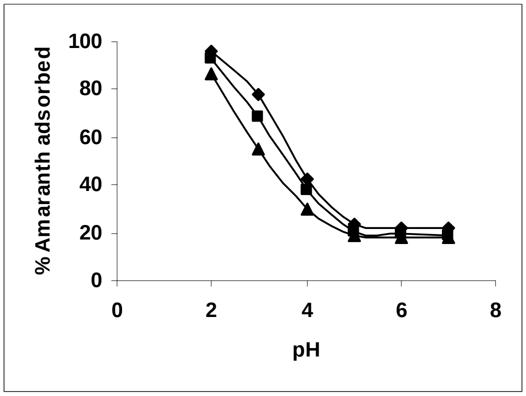


Figure: 31

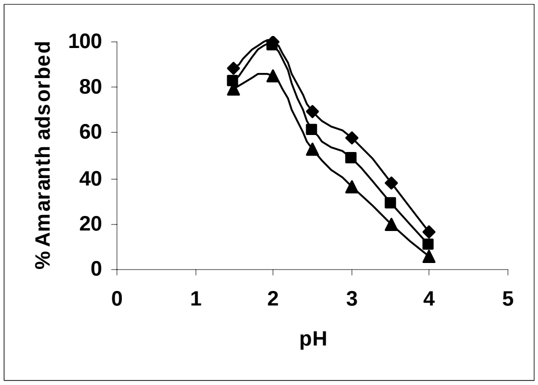


Figure: 32

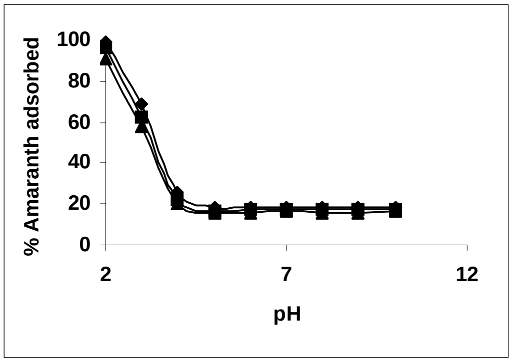


Figure: 33

Figure 31-33 Effect of pH on the Amaranth biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

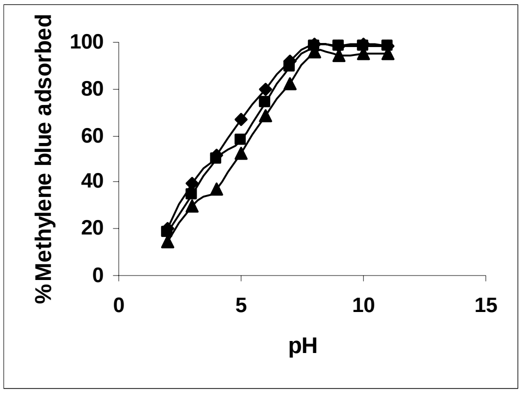


Figure: 34

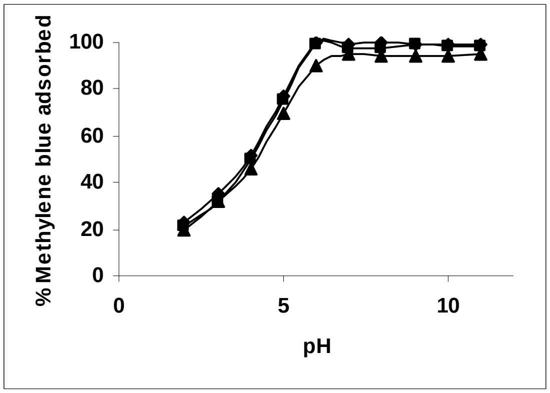


Figure: 35

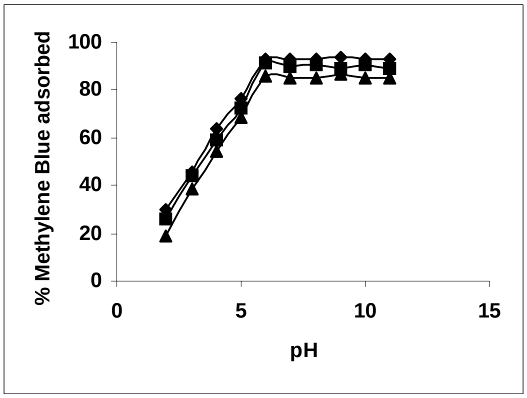


Figure: 36

Figure 34-36 Effect of pH on the Methylene blue biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

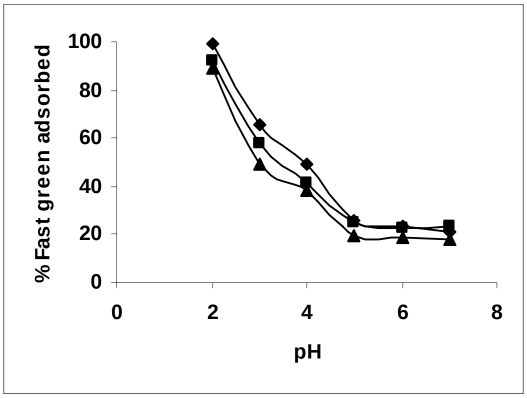


Figure: 37

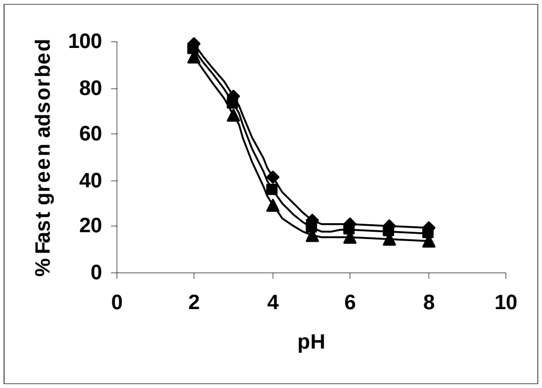


Figure: 38

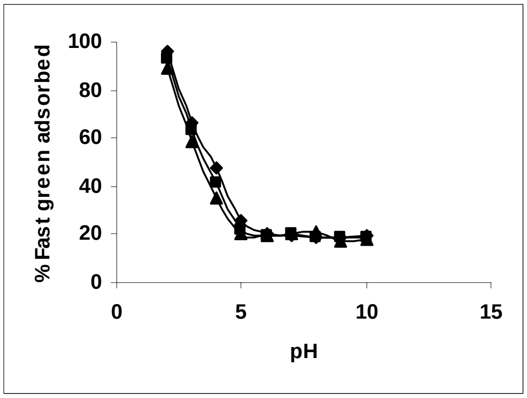
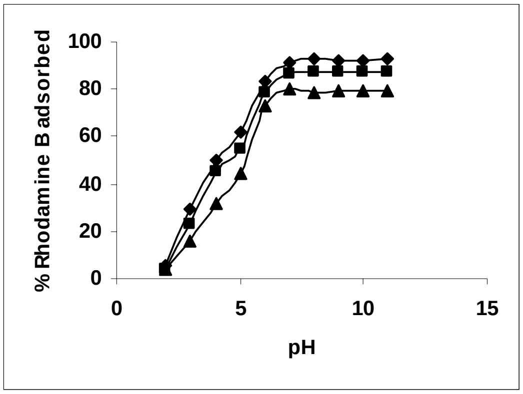
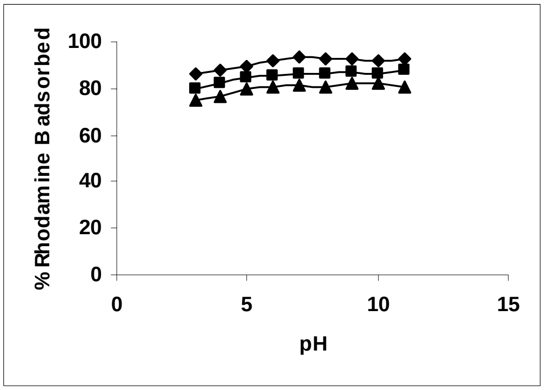


Figure: 39

Figure 37-39 Effect of pH on the Fast green biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)



Figue: 40



Figue: 41

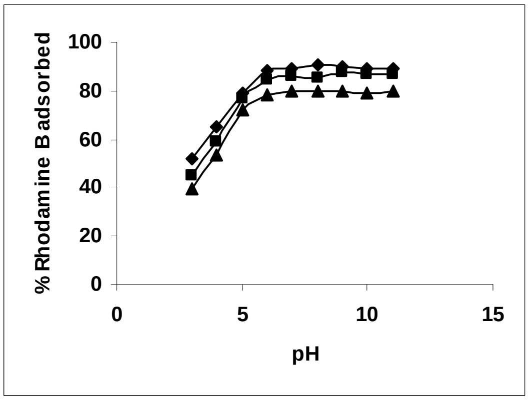


Figure: 42

Figure 40-42 Effect of pH on the Rhodamine B biosorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

Table 27 Effect of pH and initial dye ion concentration on Amaranth adsorption by Bengal gram husk (Adsorbent dose = 0.25g/100ml)

	10 mg/L		**20 mg/L**		**50 mg/L**	
pH	**% adsorbed**	**AM adsorbed (mg/g)**	**% adsorbed**	**AM adsorbed (mg/g)**	**% adsorbed**	**AM adsorbed (mg/g)**
2	96.28	3.85	92.57	7.41	86.34	17.27
3	78.29	3.13	68.19	5.46	55.49	11.10
4	42.24	1.69	37.54	3.00	30.14	6.03
5	23.75	0.95	20.17	1.61	18.79	3.76
6	22.38	0.90	19.85	1.59	17.85	3.57
7	21.86	0.87	18.82	1.51	18.12	3.62

Table 28 Effect of pH and initial dye ion concentration on Amaranth adsorption by Tur dal husk (Adsorbent dose = 0.3g/100ml)

	10 mg/L		**20 mg/L**		**50 mg/L**	
pH	**% adsorbed**	**AM adsorbed (mg/g)**	**% adsorbed**	**AM adsorbed (mg/g)**	**% adsorbed**	**AM adsorbed (mg/g)**
1.5	88.23	2.94	82.36	5.49	79.65	13.28
2	99.64	3.32	98.64	6.58	85.24	14.21
2.5	69.49	2.32	61.36	4.09	53.23	8.87
3	57.56	1.92	48.92	3.26	36.45	6.08
3.5	38.12	1.27	29.12	1.94	19.56	3.26
4	16.52	0.55	10.53	0.70	5.63	0.94

Table 29 Effect of pH and initial dye ion concentration on Amaranth adsorption by tamarind husk (Adsorbent dose = 0.25g/100ml)

	10 mg/L		**20 mg/L**		**50 mg/L**	
pH	**% adsorbed**	**AM adsorbed (mg/g)**	**% adsorbed**	**AM adsorbed (mg/g)**	**% adsorbed**	**AM adsorbed (mg/g)**
2	99.25	3.97	96.56	7.72	90.88	18.18
3	68.56	2.74	62.35	4.99	58.24	11.65
4	25.34	1.01	22.14	1.77	19.85	3.97
5	18.21	0.73	16.89	1.35	15.69	3.14
6	17.98	0.72	17.26	1.38	15.88	3.18
7	18.54	0.74	16.99	1.36	16.21	3.24
8	18.21	0.73	17.35	1.39	15.55	3.11
9	18.21	0.73	17.88	1.43	16.04	3.21
10	17.98	0.72	17.26	1.38	16.21	3.24

Table 30 Effect of pH and initial dye ion concentration on Methylene Blue adsorption by bengal gram husk (Adsorbent dose = 0.15g/100ml)

	10 mg/L		**20 mg/L**		**50 mg/L**	
pH	**% adsorbed**	**MB adsorbed (mg/g)**	**% adsorbed**	**MB adsorbed (mg/g)**	**% adsorbed**	**MB adsorbed (mg/g)**
2	20.52	1.37	18.65	2.49	14.56	4.85
3	39.37	2.62	34.35	4.58	29.89	9.96
4	51.55	3.44	49.89	6.65	36.75	12.25
5	66.92	4.46	58.12	7.75	52.34	17.45
6	79.89	5.33	74.23	9.90	68.77	22.92
7	91.98	6.13	89.12	11.88	82.21	27.40
8	99.23	6.62	98.45	13.13	95.66	31.89
9	98.59	6.57	98.32	13.11	94.58	31.53
10	99.12	6.61	98.41	13.12	95.37	31.79
11	98.52	6.57	98.34	13.11	95.27	31.76

Table 31 Effect of pH and initial metal ion concentration on Methylene Blue adsorption by Tur dal husk (Adsorbent dose = 0.1g/100ml)

pH	10 mg/L % adsorbed	MB adsorbed (mg/g)	20 mg/L % adsorbed	MB adsorbed (mg/g)	50 mg/L % adsorbed	MB adsorbed (mg/g)
2	23.11	2.31	21.25	4.25	19.78	9.89
3	35.65	3.57	32.14	6.43	31.79	15.90
4	51.88	5.19	49.87	9.97	45.69	22.85
5	76.78	7.68	75.78	15.16	69.97	34.99
6	99.75	9.98	98.95	19.79	89.89	44.95
7	98.78	9.88	97.68	19.54	95.45	47.73
8	99.65	9.97	97.88	19.58	94.12	47.06
9	98.78	9.88	99.23	19.85	93.88	46.94
10	99.56	9.96	98.66	19.73	94.23	47.12
11	99.48	9.95	98.45	19.69	94.88	47.44

Table 32 Effect of pH and initial dye ion concentration on Methylene blue adsorption by tamarind husk (Adsorbent dose = 0.2 g/100ml)

pH	10 mg/L % adsorbed	MB adsorbed (mg/g)	20 mg/L % adsorbed	MB adsorbed (mg/g)	50 mg/L % adsorbed	MB adsorbed (mg/g)
2	29.56	1.48	26.21	2.62	19.12	4.78
3	45.68	2.28	43.71	4.37	38.94	9.74
4	63.92	3.20	59.14	5.91	54.19	13.55
5	76.19	3.81	72.22	7.22	68.45	17.11
6	93.12	4.66	91.69	9.17	85.51	21.38
7	92.65	4.63	90.12	9.01	85.28	21.32
8	92.56	4.63	90.56	9.06	84.78	21.20
9	93.45	4.67	89.21	8.92	86.72	21.68
10	92.57	4.63	90.34	9.03	85.21	21.30
11	93.12	4.66	89.35	8.94	85.28	21.32

Table 33 Effect of pH and initial metal ion concentration on Fast green adsorption by bengal gram husk (Adsorbent dose = 0.3g/100ml)

	10 mg/L		**20 mg/L**		**50 mg/L**	
pH	**% adsorbed**	**FG adsorbed (mg/g)**	**% adsorbed**	**FG adsorbed (mg/g)**	**% adsorbed**	**FG adsorbed (mg/g)**
2	99.12	3.30	92.45	6.16	88.78	14.80
3	65.48	2.18	57.95	3.86	49.57	8.26
4	49.51	1.65	41.26	2.75	38.55	6.43
5	25.67	0.86	24.78	1.65	19.38	3.23
6	23.12	0.77	22.91	1.53	18.44	3.07
7	21.38	0.71	23.66	1.58	17.89	2.98

Table 34 Effect of pH and initial dye ion concentration on Fast green adsorption by Tur dal husk (Adsorbent dose = 0.15g/100ml)

	10 mg/L		**20 mg/L**		**50 mg/L**	
pH	**% adsorbed**	**FG adsorbed (mg/g)**	**% adsorbed**	**FG adsorbed (mg/g)**	**% adsorbed**	**FG adsorbed (mg/g)**
2	99.17	6.61	97.15	12.95	93.56	31.19
3	76.23	5.08	73.25	9.77	68.57	22.86
4	41.21	2.75	35.86	4.78	28.94	9.65
5	23.14	1.54	19.84	2.65	16.32	5.44
6	21.45	1.43	18.56	2.47	15.21	5.07
7	20.12	1.34	17.99	2.40	14.98	4.99
8	19.58	1.31	16.87	2.25	13.85	4.62

Table 35 Effect of pH and initial dye ion concentration on Fast green adsorption by Tamarind husk (Adsorbent dose = 0.3g/100ml)

	10 mg/L		**20 mg/L**		**50 mg/L**	
pH	**% adsorbed**	**FG adsorbed (mg/g)**	**% adsorbed**	**FG adsorbed (mg/g)**	**% adsorbed**	**FG adsorbed (mg/g)**
2	96.21	3.21	93.25	6.22	88.84	14.81
3	66.75	2.23	63.58	4.24	58.69	9.78
4	47.68	1.59	41.23	2.75	35.24	5.87
5	25.89	0.86	21.59	1.44	20.54	3.42
6	20.15	0.67	19.24	1.28	19.47	3.25
7	19.26	0.64	20.12	1.34	20.23	3.37
8	18.45	0.62	18.65	1.24	21.14	3.52
9	19.11	0.64	18.78	1.25	17.56	2.93
10	19.24	0.64	19.14	1.28	18.27	3.05

Table 36 Effect of pH and initial dye ion concentration on Rhodamine B adsorption by bengal gram husk (Adsorbent dose = 0.35g/100ml)

	10 mg/L		**20 mg/L**		**50 mg/L**	
pH	**% adsorbed**	**RB adsorbed (mg/g)**	**% adsorbed**	**RB adsorbed (mg/g)**	**% adsorbed**	**RB adsorbed (mg/g)**
2	5.47	0.16	4.28	0.24	3.85	0.55
3	29.49	0.84	22.84	1.31	15.88	2.27
4	49.87	1.42	45.33	2.59	31.58	4.51
5	61.59	1.76	54.79	3.13	44.84	6.41
6	83.19	2.38	78.85	4.51	72.84	10.41
7	91.58	2.62	86.87	4.96	79.85	11.41
8	92.88	2.65	87.15	4.98	78.38	11.20
9	91.89	2.63	87.21	4.98	79.27	11.32
10	92.18	2.63	86.98	4.97	79.48	11.35
11	92.71	2.65	87.09	4.98	79.37	11.34

Table 37 Effect of pH and initial dye ion concentration on Rhodamine B adsorption by tur dal husk (Adsorbent dose = 0.5g/100ml)

pH	10 mg/L % adsorbed	RB adsorbed (mg/g)	20 mg/L % adsorbed	RB adsorbed (mg/g)	50 mg/L % adsorbed	RB adsorbed (mg/g)
3	86.23	1.72	79.55	3.18	75.35	7.54
4	88.21	1.76	81.96	3.28	76.89	7.69
5	89.56	1.79	84.39	3.38	79.51	7.95
6	91.54	1.83	85.21	3.41	80.33	8.03
7	93.65	1.87	86.32	3.45	81.78	8.18
8	92.86	1.86	85.95	3.44	80.26	8.03
9	93.12	1.86	87.12	3.48	82.23	8.22
10	92.29	1.85	86.22	3.45	81.98	8.20
11	93.12	1.86	88.21	3.53	80.78	8.08

Table 38 Effect of pH and initial dye ion concentration on Rhodamine B adsorption by tamarind husk (Adsorbent dose = 0. 4g/100ml)

pH	10 mg/L % adsorbed	RB adsorbed (mg/g)	20 mg/L % adsorbed	RB adsorbed (mg/g)	50 mg/L % adsorbed	RB adsorbed (mg/g)
3	52.3	1.31	45.17	2.26	39.26	4.91
4	65.21	1.63	59.29	2.96	53.68	6.71
5	79.36	1.98	76.98	3.85	71.82	8.98
6	88.36	2.21	84.69	4.23	78.24	9.78
7	89.25	2.23	86.32	4.32	79.65	9.96
8	91.04	2.28	85.17	4.26	80.12	10.02
9	90.16	2.25	87.92	4.40	79.48	9.94
10	89	2.23	86.98	4.35	79.27	9.91
11	88.79	2.22	86.57	4.33	80.11	10.01

4.3.4 Adsorption Isotherms

Langmuir adsorption isotherms for amaranth adsorption by bengal gram husk, Tur dal husk and tamarind husk in Figures 43 to 45. Langmuir isotherms for methylene blue adsorption by the three adsorbents in Figures 46-48 and Figures 49 to 51 present the Langmuir isotherms for fast green adsorption. Langmuir plots for rhodamine B adosrption by BGH, TDH and TH are presented in Figures 52 to 54. The linear plots between Ceq vs Ceq/q shows that the three adsorbents namely BGH, TDH and TH followed Langmuir adsorption isotherm.

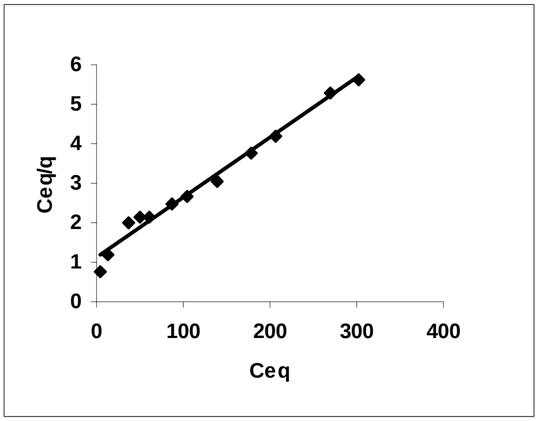


Figure: 43

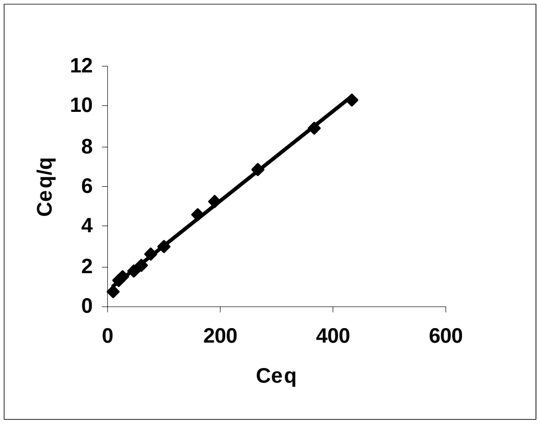


Figure: 44

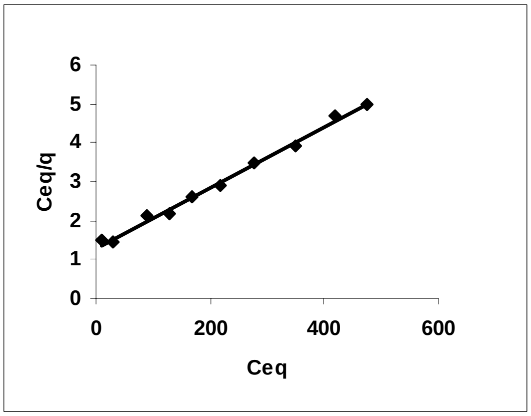


Figure: 45

Figure 43-45 Langmuir adsorption isotherm for Amaranth by BGH, TDH and TH respectively

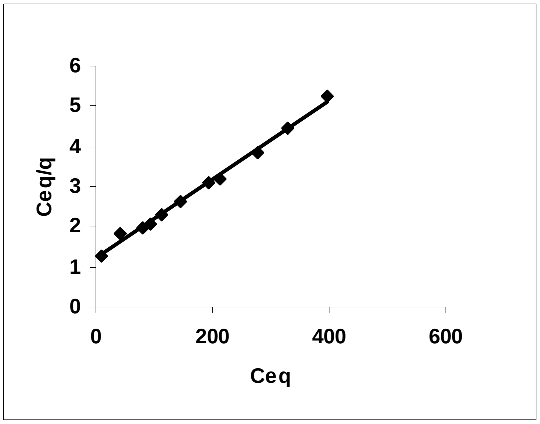


Figure: 46

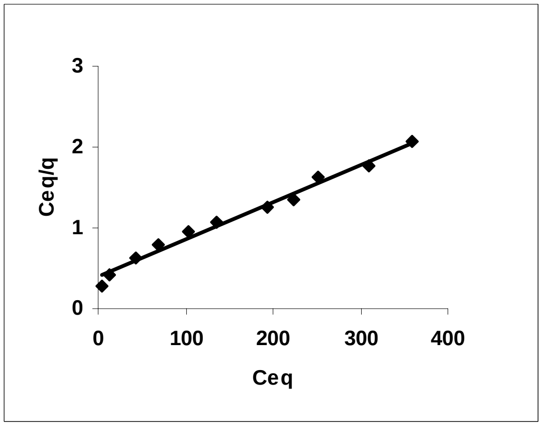


Figure: 47

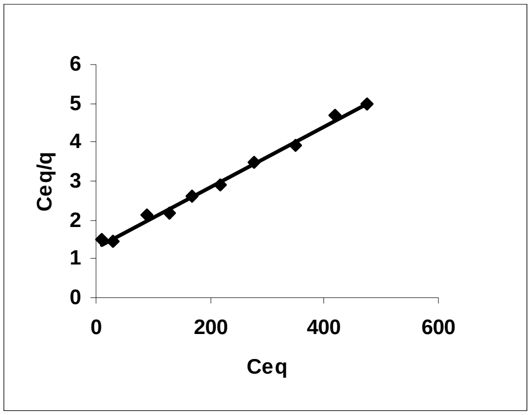


Figure: 48

Figure 46-48 Langmuir adsorption isotherm for Methylene blue by BGH, TDH and TH respectively

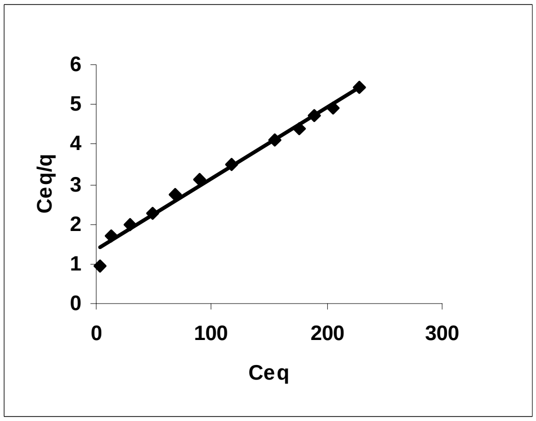


Figure: 49

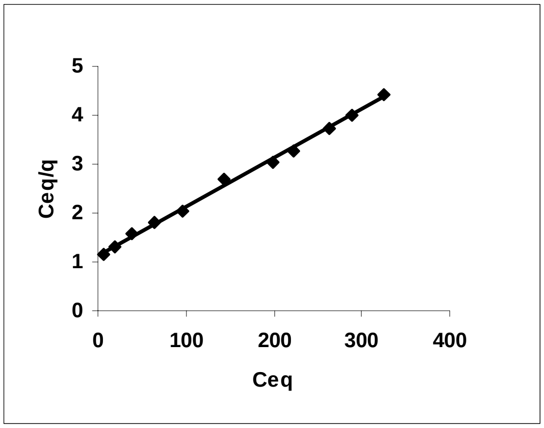


Figure: 50

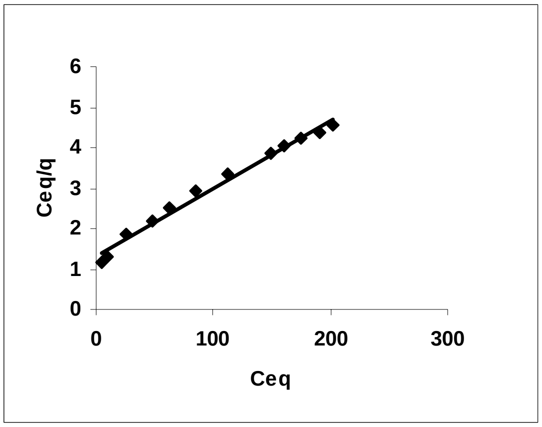


Figure: 51

Figure 49-51 Langmuir adsorption isotherm for Fast green by BGH, TDH and TH respectively

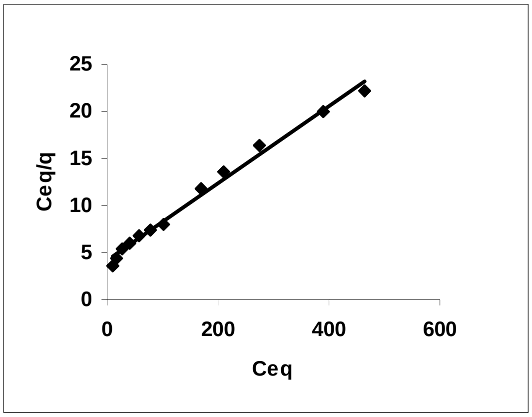
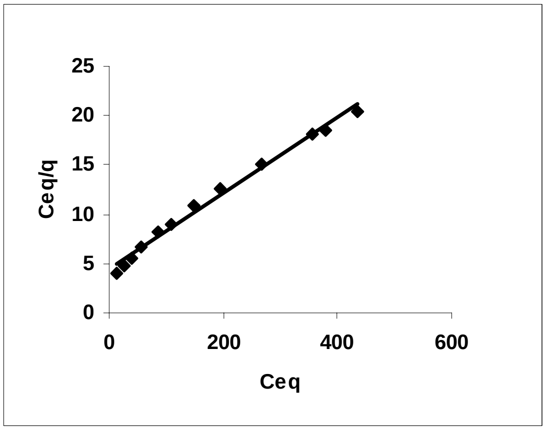


Figure: 52



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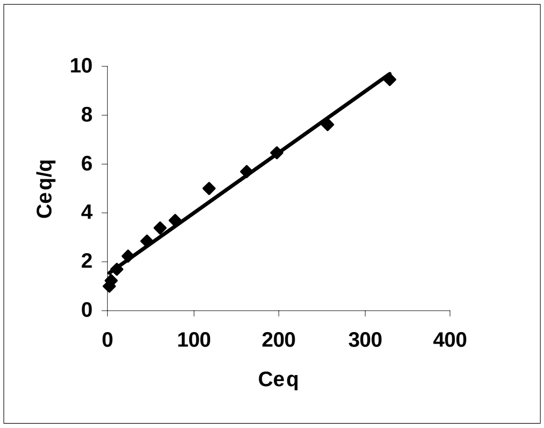
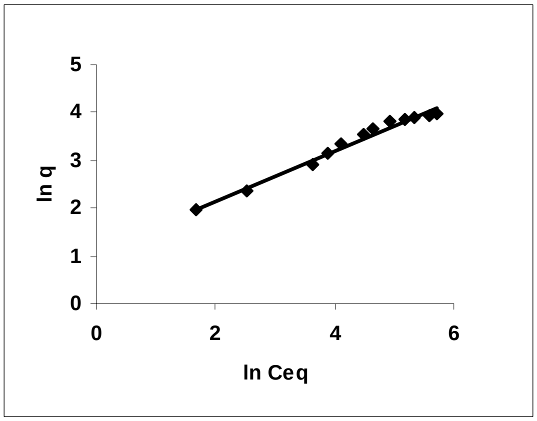


Figure: 54

Figure 52-54 Langmuir adsorption isotherm for Rhodamine B by BGH, TDH and TH respectively

The Freundlich plots for amaranth biosorption by the three husks namely BGH, TDH and TH are given in Figures 55 to 57, methylene blue adsorption in Figures 58 to 60; fast green biosorption in Figures 61 to 63 and rhodamine B adsorption by the three husks are given in Figures 64 to 66. The adsorption of dyes by the three husks namely BGH, TDH and TH followed Freundlich isotherms.



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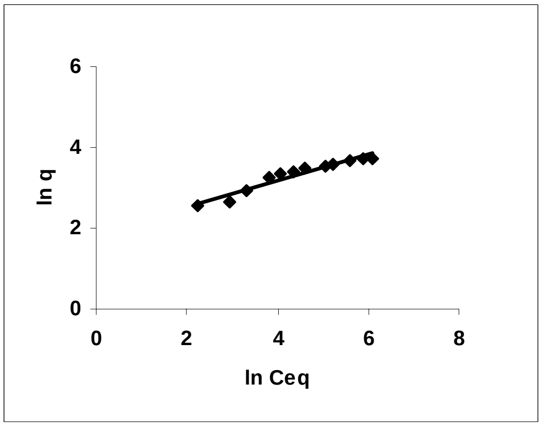

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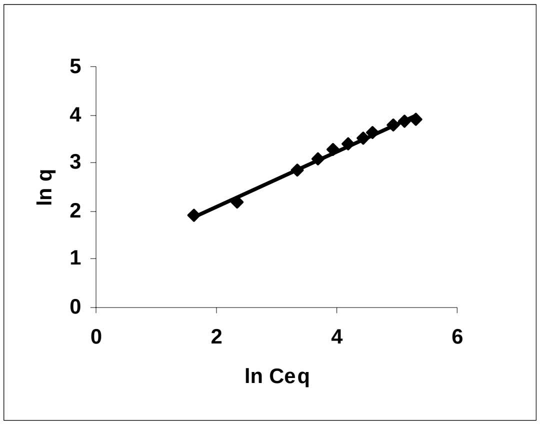
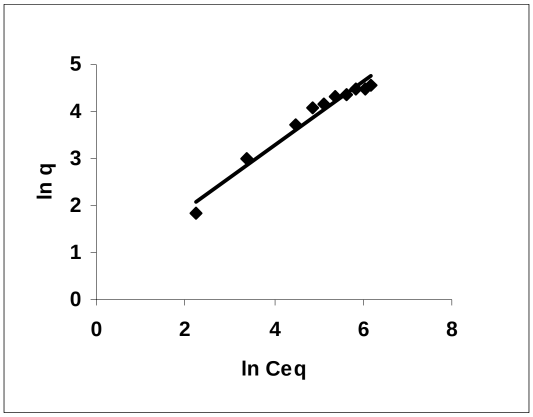


Figure: 57

Figure 55-57 Freundlich adsorption isotherm for Amaranth by BGH, TDH and TH respectively



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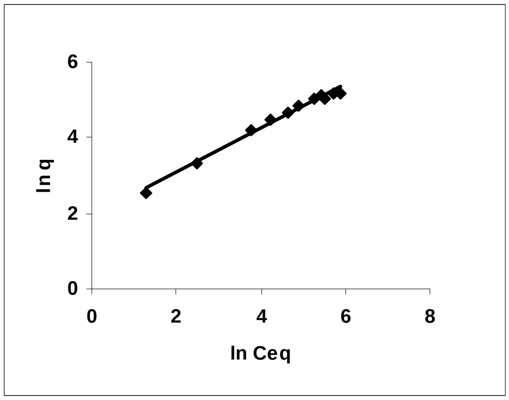

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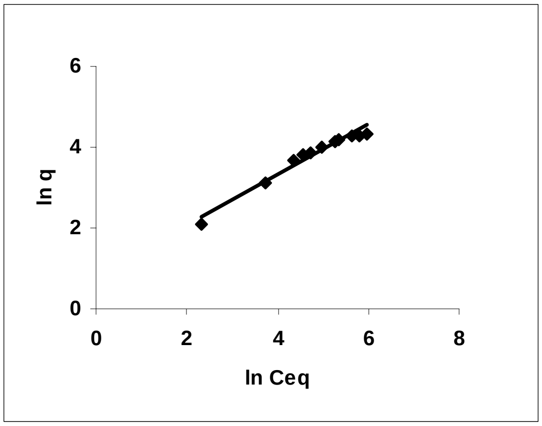
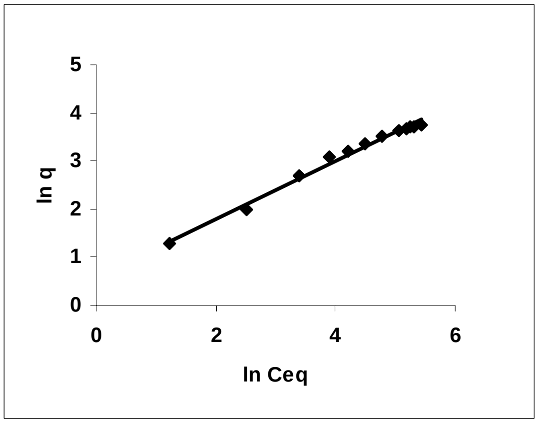


Figure: 60

Figure 58-60 Freundlich adsorption isotherm for Methylene blue by BGH, TDH and TH respectively



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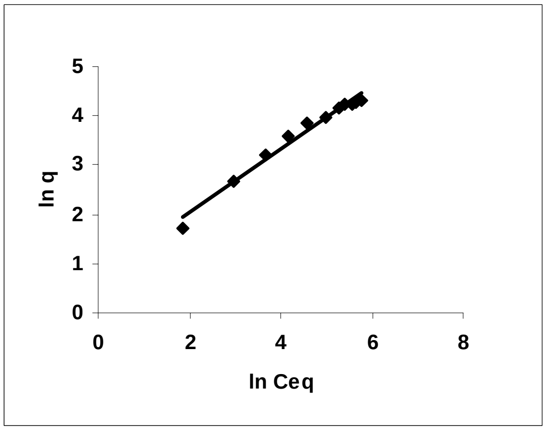

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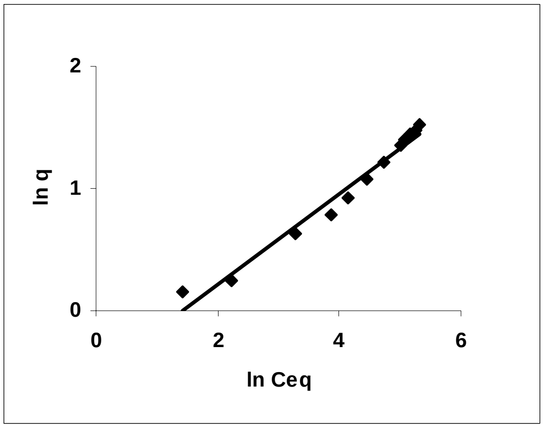
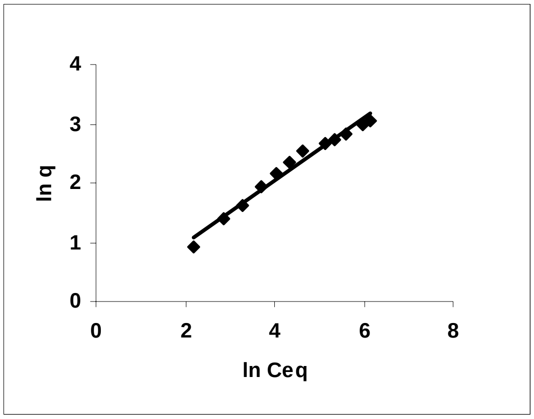


Figure: 63

Figure 61-63 Freundlich adsorption isotherm for Fast green by BGH, TDH and TH respectively



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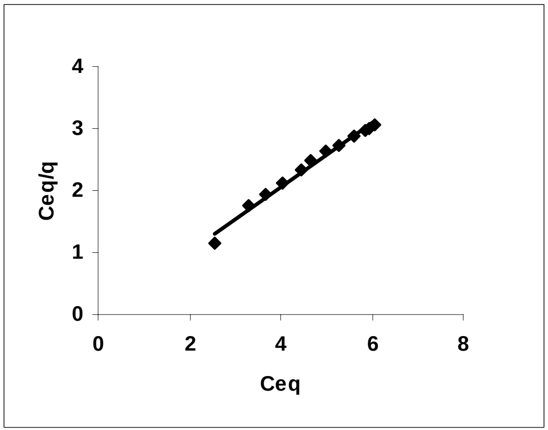

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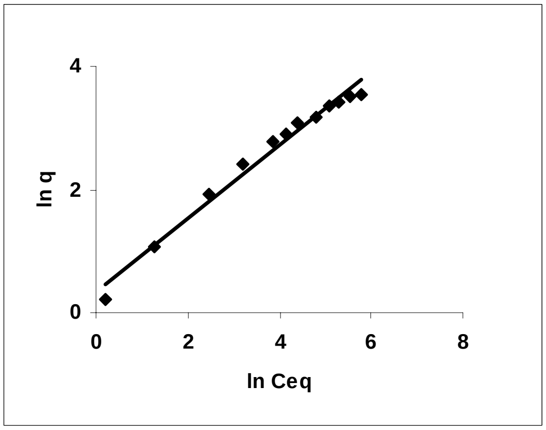


Figure: 66

Figure 64-66 Freundlich adsorption isotherm for Rhodamine B by BGH, TDH and TH

Table 39 Sorption isotherm constants and coefficients of determination for adsorption of dyes by TDH

	Langmuir equation			**Freundlich equation**		
	Q_{max} (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Amaranth	45.08	0.026	0.99	6.61	3.09	0.93
Methylene Blue	216.68	0.011	0.98	6.79	1.72	0.98
Fast green FCF	100.39	0.008	0.99	2.09	1.55	0.97
Rhodamine B	26.01	0.008	0.99	1.00	1.94	0.98

Table 40 Sorption isotherm constants and coefficients of determination adsorption of dyes for BGH

	Langmuir equation			Freundlich equation		
	Q_{max} (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Amaranth	65.89	0.01	0.98	2.97	1.89	0.98
Methylene Blue	129.18	0.005	0.99	1.79	1.48	0.96
Fast green FCF	56.06	0.013	0.98	1.77	1.65	0.98
Rhodamine B	24.39	0.009	0.99	1.88	1.09	0.97

Table 41 Sorption isotherm constants and coefficients of determination for adsorption of dyes by TH

	Langmuir equation			Freundlich equation		
	q_{max} (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Amaranth	65.04	0.01	0.97	2.58	1.74	0.99
Methylene Blue	60.11	0.012	0.98	2.02	1.53	0.96
Fast green FCF	101.58	0.008	0.99	2.7	1.68	0.97
Rhodamine B	40.26	0.016	0.98	1.40	1.68	0.98

Table 42 Equilibrium parameter (R_L) for adsorption of dyes

Adsorbent	**Adsorbate**	**R_L**
Bengal gram husk (BGH)	Amaranth	6 x 10^{-1} – 6 x 10^{-2}
	Methylene Blue	7.8 x 10^{-1} – 6 x 10^{-2}
	Fast green	8.3 x 10^{-1} – 1.7 x10^{-1}
	Rhodamine B	8.3 x 10^{-1} – 1.7 x10^{-1}
Tur dal husk (TDH)	Amaranth	8.3 x 10^{-1} – 1.4 x10^{-1}
	Methylene Blue	9 x 10^{-1} – 2.5 x10^{-1}
	Fast green	7.9 x 10^{-1} – 1.1 x10^{-1}
	Rhodamine B	1.8 x 10^{-1} – 1.5 x10^{-1}
Tamarind husk (TH)	Amaranth	7.6 x 10^{-1} – 1.25 x10^{-1}
	Methylene Blue	7.3 x 10^{-1} – 1.21 x10^{-1}
	Fast green	8.06 x 10^{-1} – 1.7 x10^{-1}
	Rhodamine B	6.7 x 10^{-1} – 8.19 x 10^{-2}

Adsorption kinetics

Lagergren plots of log10 (qe-q) vs t for the adsorption of The Lagergren plots are shown in Figures 67 to 75 for adsorption of amaranth by BGH, TDH and TH; Figures 67 to 69 give the Lagergren plots for adsorption of methylene blue by BGH, TDH and TH respectively; Figures 70 to 72 present the Lagergren plots for adsorption of fast green and Figures 73 to 75 give the Lagergren plots and their rate constants for rhodamine B adsorption.

The rate constants that are derived from the Langergren equation are given dyes in Tables 43-53 for dyes. The linear plots of log10 (qe-q) vs t show that the adsorption follows a pseudo first order reaction.

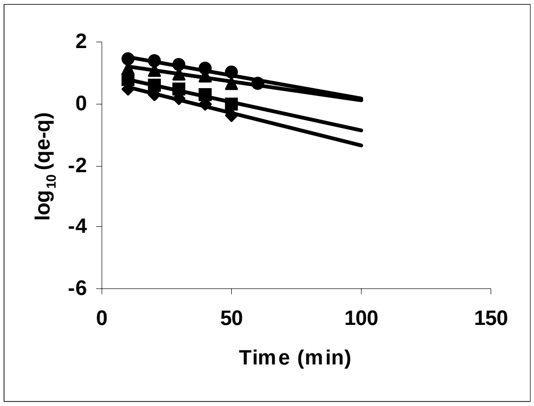


Figure: 67

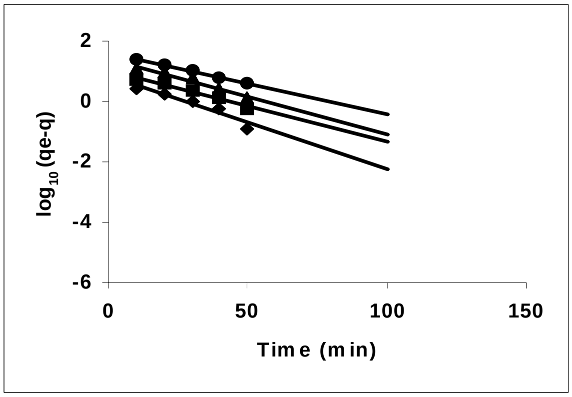


Figure: 68

Figure: 69

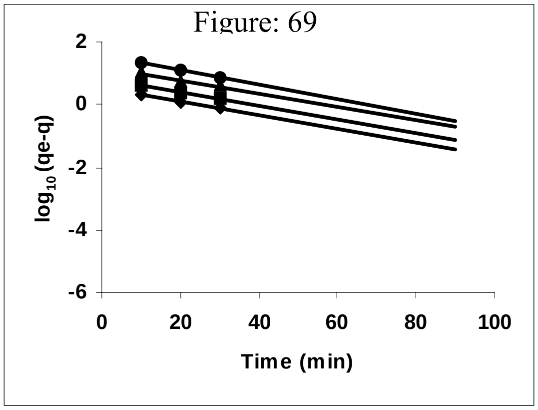
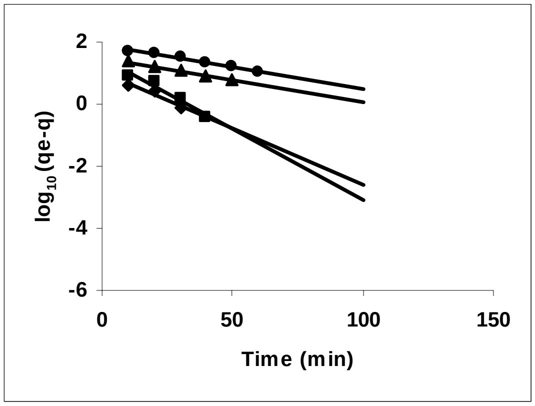


Figure 67-69 Lagergren plots for Amaranth adsorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)



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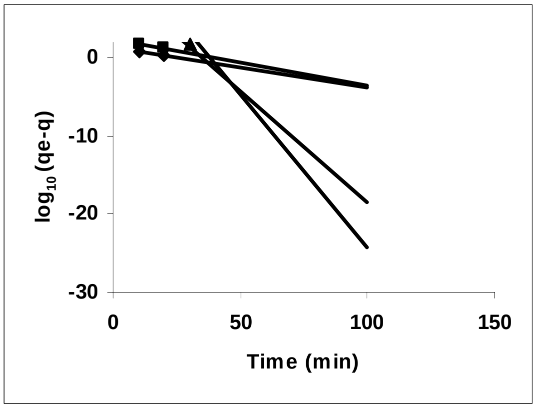

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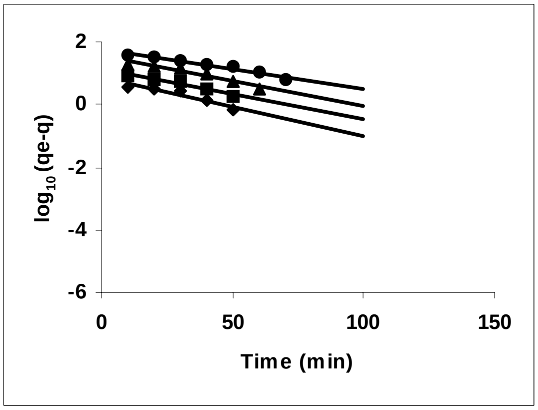
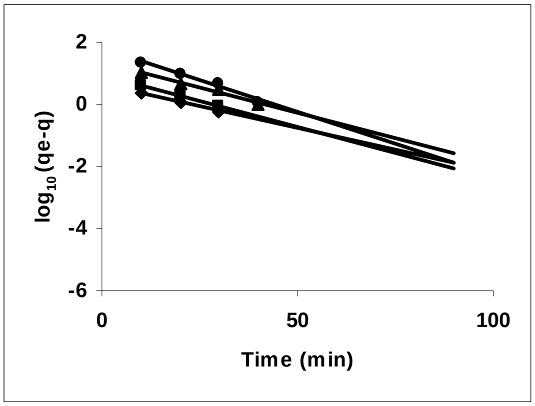


Figure: 72

Figure 70-72 Lagergren plots for Methylene blue adsorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)



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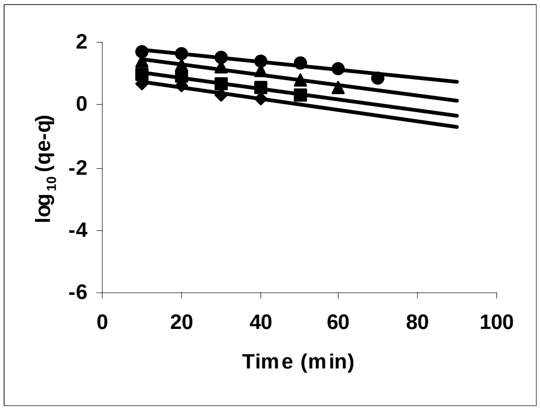

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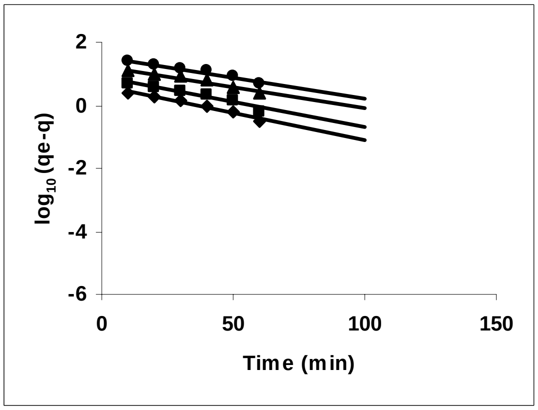
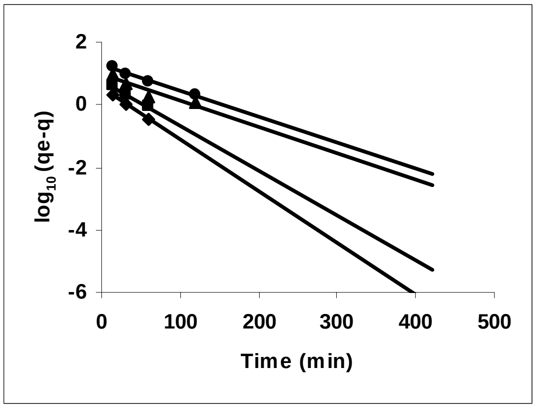


Figure: 75

Figure 73-75 Lagergren plots for Fast green adsorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)



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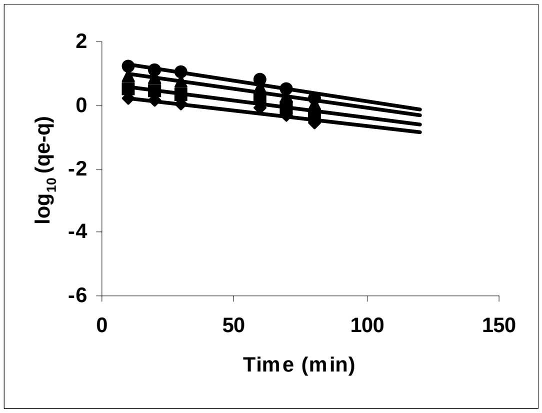

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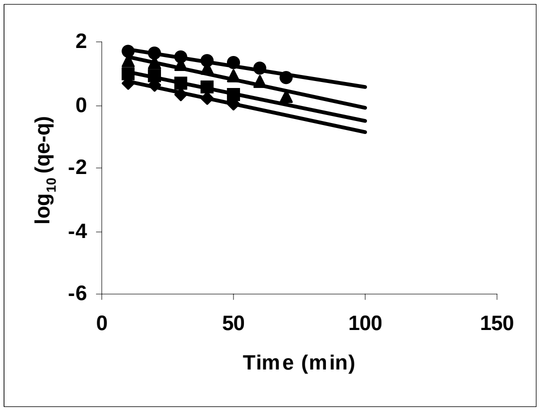

Figure: 78

Figure 76-78: Lagergren plots for Rhodamine B adsorption by BGH, TDH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

Table 43 Effect of initial Amaranth concentration on Lagergren rate constant by Tur dal husk (Adsorbent dose-0.3g/100 mL; pH – 2.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	7.1×10^{-2}	0.927
20	5.45×10^{-2}	0.9717
50	5.7×10^{-2}	0.9709
100	4.7×10^{-2}	0.9962

Table 44 Effect of initial Amaranth concentration on Lagergren rate constant by Tamarind husk (Adsorbent dose-0.25g/100 mL; pH – 2.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	5.13×10^{-2}	0.9999
20	5.07×10^{-2}	0.9912
50	4.9 X 10-2	0.9839
100	5.3 X 10-2	0.9967

Table 45 Effect of initial Methylene Blue concentration on Lagergren rate constant by bengal gram husk (Adsorbent dose-0.15g/100 mL; pH – 9.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	8.25×10^{-2}	0.9399
20	1.05×10^{-1}	0.9627
50	3.25×10^{-2}	0.9989
100	3.17×10^{-2}	0.9762

Table 46 Effect of initial Methylene Blue concentration on Lagergren rate constant by Tur dal husk (Adsorbent dose-0.10 g/100 mL; pH – 9.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	1.17×10^{-1}	1
20	1.33×10^{-1}	1
50	6.5×10^{-1}	0.9498
100	8.9×10^{-1}	0.9862

Table 47 Effect of initial Methylene Blue concentration on Lagergren rate constant by tamarind husk (Adsorbent dose-0.2 g/100 mL; pH – 9.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	4.28×10^{-2}	0.9205
20	3.61×10^{-2}	0.9404
50	3.63×10^{-2}	0.9236
100	2.83×10^{-2}	0.9414

Table 48 Effect of initial Fast green concentration on Lagergren rate constant by bengal gram husk (Adsorbent dose-0.30g /100 mL; pH – 2.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	6.5×10^{-2}	0.9997
20	7.6×10^{-2}	0.9996
50	7.5×10^{-2}	0.9867
100	9.45×10^{-2}	0.9717

Table 49 Effect of initial Fast green concentration on Lagergren rate constant by Tur dal husk (Adsorbent dose-0.15g/100 mL; pH – 2.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	4.1×10^{-2}	0.9341
20	4×10^{-2}	0.967
50	3.8×10^{-2}	0.9238
100	3.06×10^{-2}	0.9282

Table 50 Effect of initial Fast green concentration on Lagergren rate constant by Tamarind husk (Adsorbent dose-0.30g/100 mL; pH – 2.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	3.9×10^{-2}	0.9637
20	3.7×10^{-2}	0.9312
50	3.1×10^{-2}	0.9743
100	3.05×10^{-2}	0.9572

Table 51 Effect of initial Rhodamine B concentration on Lagergren rate constant by bengal gram husk (Adsorbent dose-0.35g/100 mL; pH – 8.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	3.8×10^{-2}	0.9999
20	3.3×10^{-2}	0.9972
50	1.92×10^{-2}	0.8693
100	1.91×10^{-2}	0.8695

Table 52 Effect of initial Rhodamine B concentration on Lagergren rate constant by Tur dal husk (Adsorbent dose-0.5g/100 mL; pH – 8.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	4×10^{-2}	0.9617
20	4×10^{-2}	0.967
50	4.14×10^{-2}	0.989
100	3.06×10^{-2}	0.9282

Table 53 Effect of initial Rhodamine B concentration on Lagergren rate constant by Tamarind husk (Adsorbent dose-0.4g /100 mL; pH – 2.0)

Initial dye concentration (mg/L)	**Kad (l/min)**	**R^2**
10	2.23×10^{-2}	0.903
20	2.44×10^{-2}	0.8938
50	2.72×10^{-2}	0.9185
100	2.99×10^{-2}	0.91

4.3.6 Desorption studies

Figure 79-82 presents the desorption of dyes –Amaranth, Methylene blue, Fast green and Rhodamine B by BGH, TDH, and TH at different initial pH.

Among the dyes, methylene blue was desorbed the least and amaranth the most. Among the adsorbents, the maximum amount of dyes was desorbed from tamarind husk.

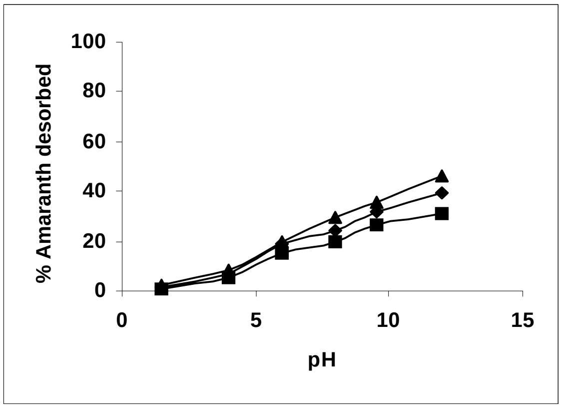

Figure 79

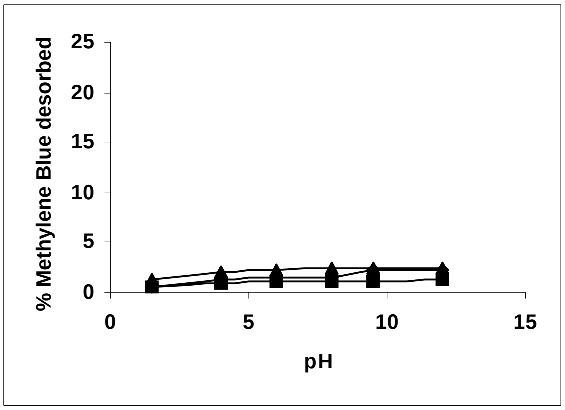

Figure 80

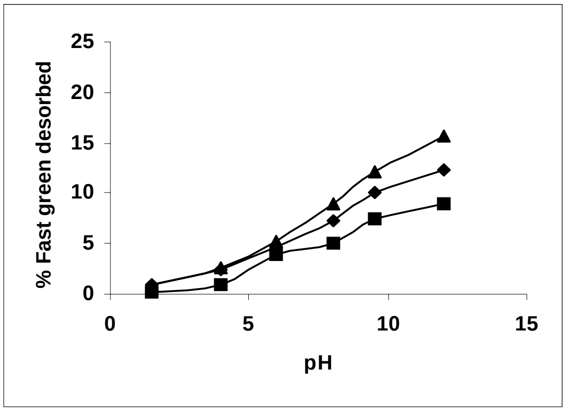

Figure 81

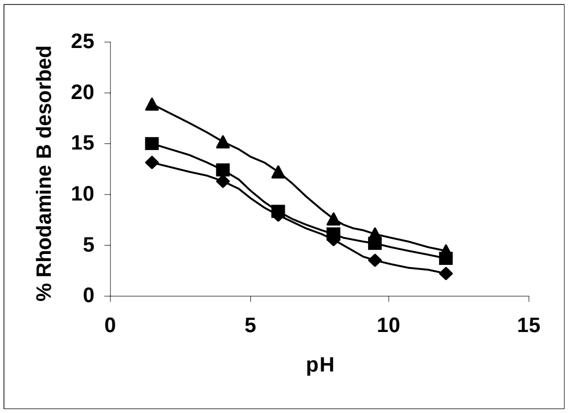

Figure 82

Figure 79-82
Effect of pH on the desorption of Amaranth, Methylene Blue, Fast green and Rhodamine B
(♦ BGH ■ TDH ▲ TH)

5.0 Discussion

5.1 **Characteristics of the adsorbent**

The approximate percentages of total carbon, nitrogen and hydrogen in the four adsorbents namely bengal gram husk (BGH); tur dal husk (TDH); coffee husk (CH) and tamarind husk (TH) are shown in Table 25. The relatively low percentage of nitrogen (0.86% for BGH, 1.13% in TDH; 0.63 % in CH and 0.94% in TH) in comparison to the carbon quantities, indicates that few nitrogen containing compounds are involved in the adsorption of dyes. A relatively larger percentage of hydrogen in comparison to nitrogen compounds indicates that carbon-hydrogen groups might be available for adsorption of dyes. The relatively low percentage of nitrogen shows that very less percentage of protein might be present in the husks. This is advantageous over protein rich adsorbents since proteinious materials are likely to putrefy under moist conditions (Ahalya *et al.,* 2006).

5.2 Infrared spectroscopic studies

Unreacted samples of the four adsorbents used in the present study namely bengal gram husk (BGH), Tur dal husk (TDH), coffee husk (CH) and tamarind husk (TH) were subjected to Fourier transform infrared spectroscopy (FTIR). The spectra obtained are presented in Figures 3 to 6 for BGH, TDH, TH and CH respectively.

The spectra of BGH sample (Figure 2) reveal the presence of several functional groups on the surface which facilitates the adsorption of dyes. Wavenumber of 3000 and 3750 cm^{-1} for BGH indicates the presence of OH groups on the husk surface. The trough that is observed at 2918.18 cm^{-1} and 893.25 cm^{-1}indicates the presence of C-H groups. The 1634.34 cm^{-1} band is a result of CO stretching mode, conjugated to a NH deformation mode and is indicative of amide 1 band. The trough at 1115.57 cm^{-1} is due to CO or CN groups (Ahalya *et al.,* 2005).

The absorption spectra of TDH (Figure 3) display a broad, intense --OH stretching absorption trough at 3431 cm^{-1}, although the bands are dominated by the -OH stretch due to bonded water. Weaker ---CH stretch bands are superimposed onto the side of the broad -OH band at 3000–2800 cm^{-1}. The strong peak at 1733 cm^{-1} is caused by the C=O stretching band of the carboxyl group. The peak at approximately 1100 cm^{-1} is due to either the C-O stretch of the -

OH bend. However, the N-H stretch (3300 cm^{-1}) and the C-N stretch (1000 cm^{-1}) are not seen in this spectra due to the dominance of the ---OH stretch (Ahalya *et al.,* 2006).

The spectrum of the pristine TH is complex due to the numerous and multifarious functional groups on the surface of the adsorbent (Figure 4). The broad and strong band ranging from 3200 to 3600 cm^{-1} may be due to the overlapping of OH and NH stretching, which is consistent with the peak at 1115 and 1161 cm^{-1} assigned to C–O and C–N stretching vibration, thus showing the presence of hydroxyl and amine groups on the adsorbent surface. The strong peak at 1674 cm^{-1} can be assigned to a C=O stretching in carboxyl or amide groups. The bands at 2936 and 1558 cm^{-1} are attributed to CH stretching and N–H bending, respectively.

The spectra of CH display a number of absorption peaks, indicating the complex nature of the material examined (Figure 5). The FTIR spectroscopic analysis indicated broad bands at 3412 cm−1, representing bonded –OH groups. The bands observed at about 2921–2851 cm^{-1} could be assigned to the C–H stretch. The peaks around 1733 cm−1 correspond to the C=H group and at 1652–1512 cm^{-1} C=O. This C–O band absorption peak is observed to shift to 1035 $cm–^{1}$.

5.3 Batch mode studies

In order to evaluate the feasibility and economics of adsorption, laboratory batch mode studies were conducted. In this study the optimum agitation speed i.e., good contact between the adsorbent and adsorbate was established at 120 rpm.

Parameters, which influence the extent of adsorption such as adsorbate concentration, agitation time, adsorbent dosage and pH were investigated. In addition to the above parameters, effect of pH on the desorption of dyes was investigated. The use of the adsorbent for continuous use was also determined by regeneration studies.

5.3.1 Effect of agitation time

Effects of agitation time and dye concentration on removal of rhodamine B, fast green, amaranth and methylene blue by the adsorbents shows that the amount of dyes adsorbed (mg/g) increased with increase in agitation time and reached equilibrium mostly after 60 minutes. But the time varied depending on the adsorbent and dye concentration. The percent dye removal at equilibrium time decreased with increase in dye concentration, although the amount of dye removed increased with increase in initial dye concentration. It is clear that the removal of dyes depends on the concentration of the dye.

Mameri *et al* (1999) reported that the available adsorption sites on the biosorbent are the limiting factor for dye uptake. The equilibrium time required by the adsorbents used in the present study is less, compared to others reported in literature. This is significant as equilibrium time is one of the important considerations for economical water and wastewater applications. In process application, this rapid (or instantaneous) biosorption phenomenon is advantageous since the shorter contact time effectively allows for a smaller size of the contact equipment, which in turn directly affects both the capacity and operation cost of the process.

5.3.2 Effect of adsorbent dosage on adsorption

The biosorption of dyes was studied at various biosorbent concentrations ranging from 0.5 to 5 mg/L. The percentage of dye removed increased with increase in adsorbent dosage due to increased adsorption surface area. For all the adsorbents studied adsorbent dosage of 1g – 2g/L was sufficient for adsorption of 90% of the initial dye concentration**.** Further increase in the adsorbent dosage did not show an increased removal of dye concentrations.

The percent removal of adsorbates increased with increase in adsorbent dosage and reached a particular constant value after a particular adsorbent dosage. This is also true for different pH values studied. A maximum removal of about 90% was obtained for all the adsorbates studied. However, the adsorbent dosage required for maximum percent removal varied with the concentration of initial dye ions. This is mainly due to the fact that a larger mass of adsorbent could adsorb larger amount of adsorbate due to the availability of more surface area of the adsorbent. But for each adsorbate (dye) studied the amount of adsorbate adsorbed after equilibrium per unit weight of adsorbent is different.

5.3.3 Effect of pH on the adosrption of dyes

(i) Methylene Blue (cationic): Effect of pH on methylene blue removal for different concentrations (10, 20, 50 and 100 mg/L) for the adsorbates namely bengal gram husk, tur dal husk, and tamarind husk, show that the percent removal was very efficient in the wide pH range of 6 to 11. However the percent removal decreased when the pH was reduced below 6.

The decreased adsorption of methylene blue, a cationic dye at highly acidic pH is probably due to the presence of excess H+ ions competing with dye cations for the adsorption sites. As the pH of the system increases the number of negatively charged surface site decreases and the number of negatively charged surface site increases. The negatively charged surface sites on the adsorbent favours the adsorption of dye cation due to electrostatic attraction.

Increase in percent removal with increase in pH has been reported on the adsorption of methylene Blue and Basic Blue by Hydrilla (Low *et al* , 1993) and Chara aspera (Low *et al* , 1994). Nawar and Doma, 1989 have reported that the adsorption capacity was constant in the pH range of 2-10 for the adsorption of Sandocryl orange (basic dye) by peat, rice hulls and activated carbon. Coconut husk showed quantitative removal of Methylene blue at pH 12.00 (Low and Lee, 1990).

(ii) Amaranth (anionic): The maximum removal of anionic dye, amaranth occurred at pH 2.0 for the different dye concentrations of 10, 20 and 50 mg/L and the percent removal decreased with increase in initial pH. The surface is positive at low pH where reaction (1) predominates, and is negative at higher pH when reaction (2) takes over.

$\text{M–OH} + \text{H+} = \text{MOH}^{2+}$ (1)

$\text{M–OH} + \text{OH}- = \text{MO}- + \text{H}_2\text{O}$ (2)

As shown in the figures and Tables, it is found that the amount of amaranth adsorbed decrease with increasing solution pH.
At low pH, the following equation predominates:

$\text{MOH}^{2+} + \text{Dye}^{-} = \text{MOH}^{2+}\text{Dye}^{-}$ (3)

With an increase in pH, positive charge at the oxide/solution interface decreases hence the adsorbent surface becomes negatively charged and will be associated with positively charged ions of the solution in the following manner:

$\text{MO}^{-} + \text{K}^{+} = \text{MO}^{-}\text{K}^{+}$ (5)

Thus, there are no exchangeable anions on the outer surface of the adsorbent at higher pHs and consequently the adsorption decreases. Similar trends were observed in the adsorption of Congo red on red mud (Namasivayam and Arasi, 1997) and wollastonite (Singh, *et al* , 1994) and waste Fe (III)/Cr (III) hydroxide (Namasivayam *et al* , 1994)

Similar trend on pH effect has been reported by Namasivayam and co-workers for the adsorption of acid violet (acid dye) by residual biogas slurry (Yamuna, 1990) and waste banana pith (Namasivayam and Kanchana, 1992) Gupta et al, 1988 have reported that the adsorption of chrome dye (acid dye) on fly ash decreased with increase in pH. Yoshida et al, 1991 have found that the adsorption capacity of chitosan for acid orange II (acid dye) decreased with increase in pH.

Hwang and Chen, 1993 have reported that the removal efficiency of epichlorohydrin-cellulose polymer for acid blue 158 and acid orange 7 (both anionic dyes) decreased with increase in pH. Youssef , 1993 has reported that the acid dye stuffs – acid blue and acid violet showed maximum adsorption at acidic pH.

Bottom Ash and De-Oiled Soya was studied over a wide range of pH (2–7) for the adsorption of amaranth and it was found that in both the adsorbents the maximum uptake of dye occurred at pH 2.0 (Mittal *et al* , 2005). The anionic dyes namely amaranth, fast green and sunset yellow was maximally adsorbed by powdered peanut hull at pH 2.0 (Gong *et al* , 2005).

(iii) Rhodamine B (Cationic): The effect of solution pH on the adsorption of Rhodamine B by the different adsorbents are shown in Figures 88 to 90 and Tables 79 to 81. Adsorption of Rhodamine B increased with increase in pH. The maximum adsorption was found in the pH range of 7-11. The amount of the dye adsorbed decreased with the increase in the concentration of the dye molecules. As the pH of dye solution becomes higher, the association of dye cations with negatively charged functional groups in the adsorbent surface could be more easily take place as follows:

$\text{S–OH} + \text{OH}^- = \text{SO}^- + \text{H}_2\text{O}$ (6)

$\text{SO}^- + \text{Dye}^+ = \text{S–O–Dye}$ (7)

Lower adsorption of Rhodamine-B at acidic pH is due to the presence of excess H+ ions competing with the dye cation for the adsorption sites. When solution pH is low, the adsorbent surface and dye molecules both are highly in protonated form hence, there is electrostatic repulsion between cationic dye and protonated adsorbent surface which leads to lower removal of dye. Namasivayam and Kadirvelu (1994) have reported similar results. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases. The negatively charged sites favor the adsorption of dye cation. Similar results have been reported for the removal of Rhodamine-B using agricultural solid wastes as adsorbents such as coir pith carbon (Namasivayam *et al* , 2001), silk cotton hull (Radhika *et al* , 2001) and pyrite (Demirbas *et al* , 2002).

(iv) Fast green (Anionic): At acidic pH quantitative removal of dye occurs for different initial dye concentrations (10, 20 and 50 mg/L) and the percent removal for all the adsorbents decreased with increase in the initial pH. In highly acidic media the adsorbent surfaces are highly protonated (positively charged) and favour the uptake of negatively charged (anionic) dyes like amranth and fast green. With increase in the initial pH of the dye, the degree of protonation of the adsorbent surfaces decreases gradually. Namasivayam and Yamuna, 1992, have reported that the percent adsorption of Congo red (anionic, direct dye) decreased with increase in pH. The anionic dyes namely amaranth, fast green and sunset yellow was maximally adsorbed by powdered peanut hull at pH 2.0 (Gong *et al* , 2005).

5.3.5 Adsorption isotherms: Adsorption data for wide ranges of adsorbate concentrations and adsorbent doses have been treated by Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1907) isotherms, two widely used models. The Langmuir isotherm model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. Langmuir isotherms were obtained by agitating the adsorbent of fixed dose and the adosrbate solution of different concnetrations for a contact time greater than equilibrium time. The Langmuir isotherm represents the equilibrium distribution of dye molecules between the solid and liquid phases. The following equation can be used to model the adsorption isotherm:

$$q = q_{max} \, b \, C_{eq} / 1 + b \, C_{eq} \qquad (8)$$

where q is milligrams of dye accumulated per gram of the biosorbent material; C_{eq} is the dye residual concentration in solution; q_{max} is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates (Chong and Volesky, 1995). When the initial dye concentration rises, adsorption increases while the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation.

$$C_{eq}/q \;=\; 1/q_{max}.b + C_{eq}/\, q_{max} \qquad (9)$$

Thus a plot of $C_{eq}/$ q vs C_{eq} should be linear if Langmuir adsorption were operative, permitting calculation of qmax. The Langmuir isotherm model was followed by all the adsorbates and adsorbents in the present study. The comparison of sorption capacities of adsorbents (54 to 57) used in this study with those obtained in the literature shows that the four husks namely bengal gram husk, tur dal husk and tamarind husk are effective for the removal of dyes from aqueous solution.

Table 54 Comparison of adsorption capacity of Methylene Blue with other adsorbents

Adsorbent	**qmax (mg/g)**	**b (l mg−1)**	**References**
Raw clay	27.49	13.99	Ghosh and Bhattacharyya 2001
Pure clay	91.87	15.55	Ghosh and Bhattacharyya 2001
Calcined raw clay	13.44	7.59	Ghosh and Bhattacharyya 2001
Calcined pure clay	56.31	8.88	Ghosh and Bhattacharyya 2001
NaOH-treated raw clay	204.00	16.34	Ghosh and Bhattacharyya 2001
NaOH-treated pure clay	122.01	20.49	Ghosh and Bhattacharyya 2001
Fe (III)/Cr (III) hydroxide	5.1	0.1001	Namasivayam and Sumithra, 2005
Raw date pits	80.29	0.157	Banat *et al* , 2003
Bengal gram husk	129.18	0.005	Present work
Tur dal husk	216.68	0.011	Present work
Tamarind husk	60.11	0.012	Present work

Table 55 Comparison of adsorption capacity of Amaranth with other adsorbents

Adsorbent	**qmax (mg/g)**	**b (l mg−1)**	**References**
Peanut hull	14.90	0.766	Gong *et al* , 2005
Bengal gram husk	65.04	0.01	Present work
Tur dal husk	45.08	0.026	Present work
Tamarind husk	45.08	0.026	Present work

Table 56 Comparison of adsorption capacity of Fast green with other adsorbents

Adsorbent	**qmax (mg/g)**	**b (l mg−1)**	**References**
Peanut hull	15.60	0.571	Gong *et al* , 2005
Bengal gram husk	56.06	0.013	Present work
Tur dal husk	100.39	0.008	Present work
Tamarind husk	101.58	0.008	Present work

Table 57 Comparison of adsorption capacity of Rhodamine B with other adsorbents

Adsorbent	**qmax (mg g−1)**	**b (l mg−1)**	**Reference**
Sago waste carbon	16.2	0.0625	Kadirvelu *et al* , 2005
Waste banana pith	8.5	0.034	Kanchana, 1991
Chemically modified Orange peel	4.81	0.1188	Gayathri, 1996
Raw Orange peel	3.23	0.0490	Namasivayam *et al* , 1996
Coir pith carbon	2.56	2.743	Namasivayam *et al* , 2001
Silk cotton hull	2.10	0.9392	Radhika *et al* , 2001
Bengal gram husk	24.39	0.009	Present work
Tur dal husk	26.01	0.008	Present work
Tamarind husk	40.26	0.016	Present work

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

$R_L = 1/1+bCo$ (10)

Where Co is the initial adsorbate concentration (mg/L) and b is the Langmuir constant (L/mg). The parameter indicates the shape of the isotherm as follows:

Table 58 Type of Isotherm for various R_L

R_L	**Type of isotherm**
$R_L>1$	Unfavourable
$R_L=1$	Linear
$0< R_L<1$	Favourable
$R_L = 0$	Irreversible

The R_L values at different initial adsorbate concentrations indicate favorable adsorption for all the adsorbents and adsorbates studied.

The Freundlich equation is basically empirical, but is often useful as a means for data description. Freundlich isotherms were basically obtained by agitating the adsorbate solution of a fixed concentration and the adsorbent of different doses for a contact time greater than the equilibrium time. The Freundlich isotherm is represented by the equation (Freundlich, 1907):

$$q= K_f C_{eq}^{1/n} \qquad (11)$$

where C_{eq} is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The linearised forms of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$\ln q = \ln K_f + 1/n \ln C_{eq}$ (12)

K_f and n were calculated from the slopes of the Freundlich plots. The Freundlich isotherm basically indicates whether the adsorption proceeds with ease or difficulty.
Freundlich isotherm model was obeyed by all the adsorbates under the studied conditions. These results may be explained if adsorbent surface sites have a spectrum of different binding energies as suggested by Benjamin and Leckie, 1981.

The magnitude of the exponent 'n' gives the indication of favourability and Kf, the capacity of the adsorbent/adsorbate system. The n values for the dyes were between 1 and 10 under the studied conditions, indicating beneficial adsorption (Yoshida, 1991)

5.3.6 Adsorption dynamics – adsorption rate constant

The rate constant of adsorption is determined from the following first order rate expression given by Lagergren (1898)

$\log_{10} (qe-q) = \log_{10} q_e - Kad\ t / 2.303$ (13)

where q and qe are amounts of adsorbate adsorbed (mg/g) at time, t (min) and at equilibrium, respectively, K_{ad} is the rate constant of adsorption (l/min). The linear plots of $\log_{10}$ (qe-q) vs t for all the dyes were studied at different concentration (Figures 147 to 172) shows the applicability of the above equation. Values of K_{ad} were calculated from the slope of the linear plots and are presented in Tables 105 to 116 for dyes. The rate constant for the dyes generally decreased with increase in adsorbate concentration. The rate constant for the adsorption of dyes is comparable with those in literature (Kadirvelu and Namasivayam, 2003; Periasamy and Namasivayam, 1994).

5.3.7 Desorption and Regeneration studies

Both incineration and land disposal represent possible options for final disposition of spent adsorbent material. However, both methods directly or indirectly pollute the environment. If regeneration of dyes from the spent adsorbent were possible then it would not only protect the environment but also help recycle the adsorbate and adsorbent and hence contribute to the economy of wastewater treatment. Desorption studies help elucidating the mechanism adsorption.

Desorption experiments were carried out at different pH values. Desorption of the dyes with water was not significant. If the adsorption is by physical bonding then the loosely bound solute can be easily desorbed with distilled water in most of the cases (Agarwal *et al.*, 2006). Hence, physical adsorption is ruled out. Among the three adsorbents used for adsorption experiments, the percentage dyes adsorbed on to tamarind husk were easily desorbed. Among the dyes, the percentage of amaranth desorbed was the highest with increase in pH. About 46.32% of the dye was desorbed from tamarind husk; 39.25% for bengal gram husk and 31.24% of amranth was desorbed from tur dal husk. The percentage of methylene blue desorbed did not exceed 2.45% for all the three adsorbents. Similarly low desorption percentages were observed in Rhodamine B and Fast green desorption.

From the desorption experiments, the following inference can be made. The negligible desorption of dyes with double distilled water indicates the predominance of chemical bonding between adsorbents and dyes. This implies that physical adsorption is not playing significant role in removal of dyes. This suggests either chemisorption or ion-exchange as the possible mechanism of dye removal. Since about 85% of dyes still remained on sorbents, which indicates that most of dyes are able to form strong bonds with the adsorbents.

5.4 Mechanism of adsorption

5.4.1 Dye adsorption

(i) Dye cation adsorption (Rhodamine B and Methylene Blue)

At acidic pH with an increasing concentration of the H^+ ion in dye solution, the surface OH^- ions would get neutralized by protonation, which facilitates the diffusion of dye molecules in the vicinity of the adsorbent. Consequently the positive charge density would be located more on the dye molecule at pH 4.0, and this accounts for the higher dye uptake on the negatively charged surface. Thus it is likely that the negative charge density on the surface will increase and will be associated with H^+ or Na^+ ions according to the pH of the solution. These positively charged ions in the presence of dye solution could then be exchanged with dye cations as follows (Davis and Leckie, 1978).

$$C_xOH_2^{2+} + 2\,Dye^+ \rightarrow C_x\,O\,(Dye)_2^{2+} + 2H^+ \qquad (14)$$

$$C_xOH^+ + Dye^+ \rightarrow Cx\ O\ (Dye)^{2+} + H^+ \qquad (15)$$

$$C_xO\ Na_2^{2+} + 2\ Dye^+ \rightarrow C_x\ O\ (Dye)_2^{2+} + 2Na^+ \qquad (16)$$

$$C_xO\ Na^+ + Dye^+ \rightarrow C_x\ O\ (Dye)^+ + Na^+ \qquad (17)$$

Adsorption by chemisorption is represented by:

$$C_xO + Dye^+ \rightarrow C_x\ ODye^+ \qquad (18)$$

(ii) Dye anion adsorption (Fast green and Amaranth)

When dye anions are introduced in the system containing adsorbents, they may be adsorbed onto the positively charged surface in two ways (Sharma and Forster, 1994):

The first way:

$$C_xOH_2^{2+} + 2\ Dye^- \rightarrow C_x\ OH_2\ dye^+ \qquad (19)$$

This however, does not account for the change in pH of the solution after dye adsorption compared to the blank i.e. in the absence of dye anion.

The second way:

$$C_xOH^+ + Dye^- \rightarrow Cx\ O\ (Dye)^+ + OH^- \qquad (20)$$

This accounts for the increase in pH of the solution after dye adsorption.

From the above observations, it is clear that the adsorption of Amaranth, Methylene blue, Fast green and Rhodamine B on bengal gram husk, tur dal husk and tamarind husk is predominantly chemisorption (Eq 5) and ion exchange is less operative (Eq 6). Moreover if ion exchange mechanism were operative, then the adsorption and desorption of the dyes would be reversible, when the operating pH ranges of these processses are reversed. As the binding is predominantly irreversible for all the dyes tested, it is concluded that ion exchange is not the predominant mechanism. Sometimes this kind of phenomenon is good, since the dye loaded adsorbent can be further employed for metal ion removal (Shukla and Sakherdande, 1990).

6.0 Conclusions

The present investigation shows that the agricultural by-products like bengal gram husk, tur dal husk, and tamarind husk can be used as an effective adsorbent in the adsorption of dyes. Adsorption dynamics, isotherms, pH effect and adsorbent dosage on the removal of dyes for all the adsorbates were examined. In addition desorption of the dyes from the loaded adsorbents were also carried out.

The uptake of dyes increased with increase in the agitation time till the equilibrium was reached. At any contact time, increase in initial adsorbate concentration decreased the percent adsorption and increased the amount of adsorbate uptake (q) per unit weight of the adsorbent.

The effect of adsorbent dosage on the adsorption of dyes showed that the percentage of dye removed increased with increase in adsorbent dosage due to increased adsorption surface area. For all the adsorbents studied adsorbent dosage of 1g – 2g/L was sufficient for adsorption of 90% of the initial dye concentration.

Irrespective of the type of the adsorbent, the optimum pH for the removal of methylene was 6-11; rhodamine B - 7-11. Amaranth and fast green, both anionic dyes were absorbed at pH 2.0. The amount of the dye removed at optimum pH increased with increase in initial dye concentration but the percentage absorbed decreased with increase in initial dye concentration.

Adsorption data for wide ranges of adsorbate concentrations and adsorbent doses were treated by Langmuir and Freundlich isotherms. All the adsorbents and adsorbates followed the Langmuir and Freundlich isotherms. Comparison of the adsorption capacity of the four adsorbents with that cited in literature reveals that bengal gram husk, tur dal husk and tamarind husk had a higher biosorption capcity than the adsorbents reported in literature.

Values of the equilibrium parameter (R_L) from Langmuir isotherm and n values from the Freundlich isotherm indicate that the adsorption process is favorable for all the dyes. The equilibrium data also fit well with the Freundlich adsorption isotherm for all the adsorbents and adsorbates (dyes) studied.

The Lagergren rate constant of absorption for different concentrations for the dyes by the adsorbents used in the study are generally in the range of 9.00 X 10^{-3} to 1.03 x 10^{-1} L/min.

Desorption and regeneration studies of the adsorbates showed that regeneration and recovery of the adsorbates is possible. Chemisorption/ion exchange was the main mechanism by which the adsorbates (dyes) were attached to the adsorbents. Physical adsorption played a minimal role in the process. Since about 85% of dyes and 70 % of the dyes still remained on sorbents, it indicates that most of dyes are able to form strong bonds with the adsorbents.

The infrared spectral analysis of the adsorbents showed that Carbon bonded with hydrogen and oxygen atoms played a major role in the adsorption of dyes. The absorption spectra revealed that –C-O, C-N and C=O bonds were predominant in the surface of the adsorbents and played a major role in the adsorption process.

The analysis of the carbon, hydrogen and nitrogen content of the husk, showed relatively low percentage of nitrogen, revealing the low content of protein in the adsorbents. This is advantageous over the protein rich algal and fungal biomass projected as dye biosorbents, since proteinious materials are likely to putrefy under moist conditions. Further, most dye sorption reported in literature is based on algal and fungal biomass, which must be cultured, collected from their natural habitats and pre-processed, if available as discards and transported under special conditions, thus introducing the factor of additional costs. In contrast, BGH, TDH, TH and CH as agro-industrial wastes have negligible cost and have also proved to be an efficient biosorbent for the removal of dyes. Furthermore, these adsorbed dyes can be easily desorbed and the biomass be incinerated for final disposal. These biosorbents are of low cost; its utility will be economical and can be viewed as a part of a feasible waste management strategy.

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8.0 References

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