REMOVAL OF DIRECT DYES FROM AQUEOUS

SOLUTION USING BAGASSE ASH

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CIVIL ENGINEERING UNIVERSITI TEKNOLOGI PETRONAS SEPTEMBER 2015

REMOVAL OF DIRECT BLUE DYES FROM AQUEOUS SOLUTION USING BAGASSE ASH

by

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Ssubmitted to the Civil And Environmental Engineering Programme in Partial Fulfillment of theRequirements for the Degree Bachelor of Engineering (Hons) (Civil And Environmental Engineering)

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by

Mohamad Saufi bin Sulaiman, 2015

CERTIFICATION OF APPROVAL

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Mohamad Saufi Bin Sulaiman

A project dissertation submitted to the Civil And Environmental Engineering Programme Universiti Teknologi PETRONAS in partial fulfillment of the requirement for the Bachelor of Engineering (Hons) (Civil And Environmental Engineering)

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August 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Mohamad Saufi Bin Sulaiman

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ABSTRACT

Industrial wastewater treatment covers the mechanisms and processes used to treat waters that have been beforehand being contaminated in some way by anthropogenic industrial or commercial activities prior to its release into the environment or its reuse.

The present study focuses on the adsorption of direct blue dye dye on bagasse ash ash. Batch studies were conducted to evaluate the influence of various experimental parameters namely initial pH (pH₀), contact time, adsorbent dose and initial concentration (C_0) on the removal of direct blue dye dye.

One of the main problems associated with wastewater from textile industries is basiccally colour. The main objective of this study is to determine and study the optimum combination of influencing factor levels for dye removal.

Then, this is the brief methodology for the study. Firstly, an adsorbent was prepared and characterized then a 1000 mg/l stock solution of direct blue dye dye was prepared then different dye concentrations i.e 20, 40, 60, 80 and 100 mg/l were prepared from the stock solution then it is continued with the effect of initial pH, contact time, adsorbent dose was studied, last and foremost the isotherm and kinetics studies were conducted.

Adsorbent has been prepared from sugarcane bagasse ash (1st objective). Optimum wavelength for color reading using spectrophotometer has been determined to be 620 Angstrom. The suitability of bagasse ash ash for removal of direct blue dye from aqueous solution is determined (2nd objective). The effect of pH, initial dye concentration and agitation time on the adsorption of direct blue dye on bagasse ash ash is finally determined (3rd objective). Optimum pH=2.0, contact time=90 minutes & adsorbent dosage= 0.8g. Maximum adsorption capacity= 3.89 mg/g. Adsorption isotherms follow Langmuir rather than Freundlich with R² values of 0.943 and 0.8135, respectively. Adsorption kinetics follows Pseudo second order kinetic model. The adsorption capacity of bagasse ash ash in the adsorptive removal of the direct blue dye from aqueous solution is assessed (3rd objective).

Dye concentration of 20 mg/L shows higher removal efficiency of about 99% within 1hour and followed by other concentrations (40-100 mg/L) in the descending order.

The contact time of 90 minutes exhibited significant removal of dye in all concentrations (20 mg/L-100 mg/L). In addition, adsorbent dosage of 0.8g is sufficient for the removal of dye. Beyond this value, the removal efficiency nearly constant. The pH of 2.0 is suitable for this experiment.

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CHAPTER 1

1.0 INTRODUCTION

1.1 Background Study

Industrial wastes such as fly ash, blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry, are currently being investigated and studied as potential adsorbents for the removal of the heavy metals from wastewater. It was found that some modified industrial wastes showed high adsorption capacity. The application of low-cost adsorbents obtained from the industrial wastes as a replacement for costly conventional methods of removing heavy metal ions from wastewater has been reviewed and studied before. It has been shown that certain industrial waste materials have high removal capacities for heavy metals and colour in wastewater. The adsorption capacities of these adsorbents vary depending on the characteristics of the adsorbents, the extent of chemical modification and the concentration of adsorbates. However there have been issues especially concerning the industrial application of these low cost adsorbents. Thus, more research needs to be conducted in this area.

Due to the ever-growing demands in textiles, synthetic organic dyes are widely used for dyeing textile fibers such as cotton and polyester. Approximately 10,000 different dyes and pigments are used for in industries and over 7×10^5 tons of these dyes are annually produced worldwide. Dyes and pigments represent one of the problematic groups; they are released into wastewaters from many industries; mainly from dye manufacturing and textile finishing and also from food colouring, cosmetics, paper and carpet industries. Synthetic dyes have complex aromatic structures which provide them physico-chemical, thermal and optical stability. Dyes in effluents, if not removed, can cause disturbance and interruption to ecological systems of the receiving waters. These materials can also pose certain health hazards and adverse environmental impact.

Direct blue dye dye is used for the production of cover paper in the paper industry. It causes irritation to the gastrointestinal tract, symptoms include nausea, vomiting and diarrhea. It may cause irritation to the respiratory tract, symptoms may be coughing and shortness of breath. Direct blue dye dye containing effluents are primarily generated from textiles, printing and dyeing, paper, rubber, plastic industries, etc.

Activated carbons are commonly used as adsorbents for the treatment of polluted water or wastewater. In these applications, adsorption capacity of activated carbons play an important role. Adsorption capacity of activated carbons mainly depends on pore characteristics including specific surface area, pore size, and its distribution. Most commercially available activated carbons are mainly microporous and of high surface area, and as the result, their property is to have high efficiency for the adsorption or removal of low molecular weight compounds. However, the adsorption of big molecules exhibiting high molecular weight on microporous activated carbon is very low. Nevertheless, adsorbent-grade activated carbon are often very difficult. As a result, many investigators have been studying the feasibility of using low cost adsorbents for the treatment of wastewater.

The sugar industry is an important agri-based industry in countries such as India, South America and Caribbean countries. Bagasse ash is a waste collected from the sugar industry with little reuse potential. Bagasse ash ash has good adsorptive properties and has been commonly used for the removal of COD (chemical oxygen demand) and colour from sugar mill and paper mill effluents. Several researchers have utilized it for both; the adsorptive removal of phenolic compounds and dyes. The aim of the present study is to explore the possibility of utilizing bagasse ash ash for the removal of direct blue dye dye from aqueous solution. The effect of many factors such as initial pH (pH₀), adsorbent dose (m), contact time (t), initial concentration (C_0) and temperature (T) were investigated. The kinetics of direct blue dye ash adsorption onto bagasse ash ash was analyzed by the method of fitting various kinetic models. Experimental equilibrium data were tested with the Freundlich, Langmuir, Redlich-Peterson (R-P), Dubnin-Radushkevich (D-R) and Temkin isotherm equations to determine the best-fit isotherm equation. Error analysis was being carried-out to test and study the adequacy and the accuracy of the model equations itself. The effect of temperature on direct blue dye adsorption on bagasse ash has also was also investigated. Thermodynamics of adsorption process have been studied, analyzed and data such as the change in Gibbs free energy, the enthalpy and the entropy of adsorption has also been determined. The purpose of this study was to evaluate the suitability of using bagass ash for the adsorption of direct blue dyes.

A large amount (around 10^6 tons) of chemically different dyes are produced annually world-wide for the use in various industrial applications. They are used extensively in the dye and printing industries, and 5-10% of the dyestuffs are lost in the industrial effluents (Sanroman et al., 2005). As for textile industries itself, so many of aqueous waste streams are generated every day. These effluents usually posses colour, high electrolyte concentration and a substantial amount of residual dyes that can cause environmental issues and problems. Colour is usually the first contaminant to be recognized in wastewater; a very small amount of dye in water (10-20 mg/l) is also highly visible and can be easily seen and affects the water transparency and gas solubility of water bodies (Cameselle et al.,2005). These contaminated wastewater must first and foremost be treated before being released into the environment to prevent pollution and its adverse impacts. The treated wastewater must comply with the environmental regulatory standards set by the government.

Textile manufacturing begins with the production or harvest of raw fibre. After the raw natural or synthetic fibres are shipped from the farm or the chemical plant, they pass through four main stages such as processing; yarn production, fabric production, finishing and fabriction. For common utilization, these fabrics must undergo several further processing, which include bleaching, printing, dyeing, mechanical finishing, preshrinking, and shaping. Many different textures and several distinguished textures can also be obtained through the application of resins and sizings and the use of high temperature and pressure (Yang and Jared, 2005).

The textile industry produces large volume of wastewater in their dyeing and finishing processes. These effluents have several common properties due to their high colouration since a small amount of residual dye (of the order mg/l) can be sufficient and enough to cause a significant visual effect (Lopez and Gutierrez, 2005). The textile activities, as a consequence have an environmental impact, principally due to the release and production of large volume of wastewaters that contain high organic charge and strong colouration. Many dyes being used in textile processes exhibit toxicity to the aquatic biota (or can be biologically transformed to toxic species) and could cause interference and disturbance in natural photosynthetic processes (Ronaldo et al.,1999).

Textile dye processes are one of the major industrial water users where, this industry has the wastes that is difficult to treat satisfactorily. Textile dye wastewater is commonly known to contain strong colour, high pH, temperature and COD and low biodegrability, has its characteristics, especially the effluent from the dyeing stages of the dyeing and finishing process. The removal of dye is therefore a challenge to both the textile industry and the wastewater-treatment facilities that must treat it (Vlyssides et al., 1999).

Many methods have been utilized for the removal of dyes and colour from wastewater. Biological processes exhibit limited colour removal due to the toxic nature of some dyes and the high salt concentration, which makes a pre-treatment step mandatory. Adsorption on activated carbon is technically easy to conduct but, has a highly expensive waste disposal cost. The removal of colour from wastewater is a persistent problem. Researches are going on to search for an effective treatment method.

There are several treatment methods for colour removal such as physical treatment, adsorption (what this study is focussing), membrane process such as microfiltration (MF), ultrafiltration (UF), nanofiltration, reverse osmosis, biological treatment such as physical chemical treatment, and lastly chemical treatment such as ozonation and electrochemical method.

The adsorption process is a process has been applied and being used for concentrating organic compounds from industrial effluents for several years. The most widely used and commonly used adsorbent is granular activated carbon (GAC).GAC has been proven to be effective for the removal of colour from textile and plup and paper effluents (Yang and Jared, 2005).

However, the adsorption on activated carbon (C*) without prior pretreatment is difficult and very hard to achieve because the suspended solids rapidly clog the filter. This procedure is therefore only feasible when combined with a flocculation-decantation treatment or a biological treatment. This combination permits the reduction of suspended solids and organic substances as well as a slight influence on the colour but the cost of activated carbon is still high (Allegre et al., 2005).

Due to the high capital, regenaration, and disposal costs, full scale GAC adsorption systems for effluent decolorization have yet to be accepted by the industry. An adsorption capasity of 1g/g makes this material a suitable candidate for further development in the future. However, high pH and salt concentrations may have adverse effects on the adsorption (Yang and Jared, 2005).

The removal of direct blue dye dye was carried-out and experimented by using adsorbents. They are obtained from waste products of sugar mill. Aqueous solutions of direct blue dye dye were used in the experiment for the removal studies to determine the optimized conditions of amount of adsorbent, contact time, concentration of dye and temperature.

1.2 Problem Statement

Most industries produce some wet waste although recent trends in the developed world have been to minimise such production or recycle such waste within the production process. However, many industries remain dependent on processes that produce wastewaters. The present study deals with the adsorption of direct blue dye on bagasse ash ash. Because of the ever-growing demands in textiles, synthetic organic dyes are widely used for dyeing textile fibers for example cotton and polyester. Approximately 10,000 different dyes and pigments are being utilized in industries and over 7×10^5 tons of these dyes are annually produced worldwide. The dyes and pigments represent one of the problematic groups, which are emitted into wastewaters from several industrial branches, mainly from the dye manufacturing and textile finishing and also from food colouring, cosmetics, paper and carpet industries. Synthetic dyes have complex aromatic structures which provide them physico-chemical, thermal and optical stability. Excessive dyes in effluents, if not removed, can cause disturbance to the ecological systems of the receiving waters. These materials also have the tendency to pose certain health hazards and environmental pollution. Several industries such as textile, leather tanning, paper and pulp and food consume and used dyes extensively. Among them, textile industry ranks first in the usage of dyes for the colouration of fibre.

Colour can lead to hazards to the environment and surroundings due to the presence of a large number of contaminants like toxic organic residues, acids, bases and inorganic contaminants. Several of the dyes are carcinogenic and mutagenic, which are very dangerous, because they were formerly made from hazardous chemicals such as benzidine, metals. The discharge of coloured wastes into the receiving water bodies not only affects their aesthetic nature but also interferes with the transmission of sunlight and therefore reduces the photosynthetic activity. This disturbs the natural equilibrium by affecting the aquatic life and food chain. Due to the chemical stability of the dye components, conventional wastewater treatment technologies are often ineffective for handling waswater containing synthetic textile dyes.

Adsorption onto activated carbon has been shown beforehand to be an effective and reliable process for dye removal; but it is an expensive process. Consequently, several low cost alternatives have been proposed including peanut hulls, waste coir pith, corncob and barley husk, Indian Rosewood, sawdust and pine sawdust. For an adsorption procedure and technique to be truly low cost, not only the adsorption should be easy to get and cheaply available in abundance but it, on the other hand should require minimal or no pre-treatment, for expensive pre-treatment procedures would add to the overall treatment cost.



Figure 1.1: Sugarcane bagasse ash in Hainan, China

Bagasse ash means the fibrous matter that remains after sugarcane or sorghum stalks are crushed to extract their juice. It is used as a biofuel and in the manufacture of pulp and building materials.

Agave bagasse ash is a similar or might be the same material that consists of the tissue of the blue agave after extraction and production of the sap.



Figure 1.2: Process flow to obtain bagasse ash

Production, storage and composition



Figure 1.3: Production, storage and composition

Sugarcane being crushed beforehand in Engenho da Calheta, Madeira to produce bagasse ash ash. The bagasse ash falls down a chute and is removed on a conveyor belt below.

For every 10 tonnes of sugarcane crushed, a sugar factory typically produces approximately 3 tonnes of wet bagasse ash. The production in each country of sugarcane in every industries is in line with the quantity of bagasse ash produced since bagasse ash is a by-product of the cane sugar industry.

The high moisture content of bagasse ash, typically 40 to 50%, is detrimental to its use as a fuel. In general, the bagasse ash is stored beforehand prior to further processing. For the purpose of electricity production, it is stored under moist conditions, and the mild exothermic reaction that results from the degradation of residual sugars dries out and letting the water to be removed from the bagasse ash pile slightly. For the purpose of paper and pulp production, it is normally stored wet in order to assist in removal of the short pith fibres, which impede the papermaking process, as well as to remove any remaining sugar.

A typical chemical analysis of bagasse ash shows it consists of (on a washed and dried basis):

Cellulose (45–55%), hemicellulose (20–25%), lignin (18–24%), ash (1–4%), and waxes($<\!\!1\%$)

Bagasse ash is a material which is extremely nonhomogeneous, comprising around 30-40% of pith fibre, which is derived from the core of the plant and is primarily parenchyma material, and bast, rind, or stem fibre, in which comprises the balance and is largely derived from sclerenchyma material. These properties and characteristics make bagasse ash particularly problematic, as the bad impact for paper manufacture and have been the subject of a large body of literature.

Usage of bagasse ash



Figure 1.4: Usage of bagasse ash ash

Heaps of bagasse ash, covered with blue plastic, outside of a sugar mill in Proserpine, Queensland. (The picture is above)

Several research efforts have explored and determined using bagasse ash as a renewable power generation source and besides for the production of bio-based materials.

Fuel

Bagasse ash and often used as a primary fuel source for sugar mills, when burned in quantity, it generates and produces sufficient heat energy to supply all the needs of a typical sugar mill, with energy to spare. To this end, a secondary use for this waste product is in cogeneration, the use of a fuel source to produce both heat energy, used in the mill, and electricity respectively, which is typically sold on to the consumer electricity grid.

The CO_2 (carbon dioxide) emissions are less than the amount of CO_2 that the sugarcane plant absorbed from the surrounding atmosphere during its growing phase, which makes the process of cogeneration greenhouse gas-neutral as the advantage and good impact. In several countries such as Australia, sugar factories significantly contribute green power to the electricity supply. For instance, Florida Crystals Corporation, one of America's largest sugar companies, owns and operates the largest biomass power plant in the area of North America. The 140 MW facility uses bagasse ash and urban wood waste as fuel to generate sufficient energy to power and generate its large milling and refining operations as well as supply sufficient renewable electricity for nearly 60,000 homes. Hawaiian electric industries also used and burns bagasse ash for cogeneration.

Ethanol obtained from the sugar in sugarcane is a popular and well-known fuel in Brazil. The cellulose-rich bagasse ash is being widely investigated and studied for its potential for producing and generating the commercial quantities of cellulosic ethanol. For instance, BP is operating and generating a cellulosic ethanol demonstration plant based on cellulosic materials in the area of Jennings, Louisiana.

Pulp, paper, board and feed

Bagasse ash is commonly used as a substitute for wood in several tropical and subtropical countries for the production of pulp, paper and board, for example in countries like India, China, Colombia, Iran, Thailand and Argentina. It produces pulp with physical properties that are well suited for generic printing and writing papers as well as tissue products but it is also widely used for boxes and newspaper production.

It can also be used for making boards resembling plywood or particle board, called bagasse ash board and xanita board, and is considered a good substitute for plywood. It is usually being used for making partitions and furniture.

K-Much Industry for example, has patented a method of converting bagasse ash into cattle feed. The method involves mixing it with molasses and enzymes (example bromelain) and fermenting it. It is then introduced in the market of many countries such as Thailand, Japan, Malaysia, Korea, Taiwan and Middle East and Australia as "fiber rich". Xanita, a South African company, mixes 30% bagasse ash cellulose fibres in with recycled kraft paper fibre to make and produce the ultra lightweight composite boards. These are then sold in the market as an environmentally-friendly, formaldehyde-free alternative to MDF and particleboard.

The textile activities have a high potential environmental impact, principally due to the release of large volumes of wastewaters that consist of high organic charge and strong colouration. Many dyes utilized in textile processes impart toxicity to the aquatic biota (or can be biologically transformed to toxic species) and could cause disturbance in natural photosynthetic processes (Ronaldo et al.,1999). One of most major industrial water users is textile dye processes. In many areas, this industry has the wastes that are very difficult to treat satisfactorily. Besides being aesthetically displeasing, these synthetic dyes can cause considerable environmental pollution as the negative impact, and are toxic to some aquatic organisms and are of serious health risk to human beings. The synthetic dyes lead to greater public concern and present legislation problems.

1.3 **Objectives and Scope of Study**

- To prepare an adsorbent from agricultural byproduct, bagasse ash for the adsorptive removal of textile dyes
- To determine the suitability of bagasse ash for removal of direct blue dyes from aqueous solution
- To determine the effect of pH, initial dye concentration and agitation time on the adsorption of direct blue dyes on bagasse ash

This study is focused on the use of methodology of adsorption of bagasse ash to remove the direct blue dye from aqueous solution. These following steps are taken when conducting this study; the bagasse ash will prepare and characterized. Prepare the range of direct blue dyes are ranging from 20 mg/L to 80 mg/L from stock solution then the effect of initial pH, contact time, of adsorbent dose will be studied by bagasse ash then isotherm and kinetics studies will also be carried out.

CHAPTER 2

2.0 LITERATURE REVIEW

Many industries for example textile, leather tanning and food have dyes in their effluent. Textile industry effluents in particular are highly colored and have to be treated before discharge into the environment. There are several types of dyes which are acid dyes, disperse dyes, direct blue dyes, vat dyes, sulphur dye, cationic (basic) dyes, solvent dyes and reactive dyes but the study is only focusing on direct blue dye. Dyes in general can be described as a colored substance that has affinity to the substrate to which it is applied. Archaeological evidence shows that dyeing has been carried out for more than 5000 years, particularly in India and the Middle East. The first synthetic textile colorant was produced in 1860's when Perkin oxidized aniline to produce Mauvine. Synthetic dyes have been extensively used in many industries such textile, leather tanning, production, food technology, as paper photoelectrochemical cells, hair colorings and etc. although the exact number and amount of dyes produced in the world is not known, it is estimated that more than 10,000 dyes are commercially available with over 7 x 10^5 tons of dye-stuff produced annually (Lee et al., 2005).

However, it has to be emphasized that the overwhelming majority of synthetic dyes currently utilized are the highly water soluble azo-reactive dyes. Azo dyes are characterized by the existence of nitrogen-nitrogen double bonds and the presence of bright color is due to these azo bonds and associated chromospheres. Even the presence of very low concentrations of dyes (less than 1mg/l) in the effluent is highly visible and is considered undesirable (Lee et al., 2005).

Besides being aesthetically displeasing these synthetic dyes can cause considerable environmental pollution, are toxic to some aquatic organisms and moreover can cause serious health risk to human beings. They can cause greater public concern and present legislation problems. Thus, removing these dyes from wastewater is a major environmental challenge and there is a constant need to have an effective process or technique that can efficiently remove these dyes (Lee et al., 2005).

Direct blue dye is as a water-soluble anionic dye, when dyed from aqueous solution in the presence of electrolytes, are substantive to, i.e, have high affinity for. Their principal use is the dyeing of cotton and regenerated cellulose, paper, leather, and, to a lesser extent, nylon. Most dyes in this class are polyazo compounds, alongside with some stilbenes, phthalocyanines, and oxazines. After being treated, frequently applied to the dyed material to improve washfastness properties, include chelation with salts of metals and treatment with formaldehyde or a cationic dye-complexing resin (Hunger,2003).

The dye removal by adsorption onto activated carbon is effective but expensive due to the use of commercial activated carbon. Hence, there is a need for cheaper alternative adsorbents. Sugar cane bagasse ash is therefore an agricultural waste that is cheap, easily available and to get and can be converted into an adsorbent for dye removal.

It is advantageous and beneficial to consider the classification of dyes by the usage or method of application before considering the chemical structures in detail because of the dye nomenclature and jargon that arises from this system. Classification by usage or application is the principal system adopted by the colour index. Since the most important and foremost textile fibers are commonly cotton and polyester, the most important dye types are those used for dyeing these two fibers, including the polyester-cotton blends. Other textile fibers are the nylon, polyacrylonitrile, and cellulose acetate (Hunger, 2003)

Toxic pollutants either organic or inorganic in nature enter the environment through various ways. Many of the organic compounds eventually degrade, regardless of the rate and the level of decomposition. Biodegradation process focusses and depends on the ability of the microorganism to develop enzymatic mechanism for attacking complex organic structures, while inorganic materials such metal elements present harder challenge (Isa *et al.*, 2008).

Adsorption

One of the physiochemical treatment processes, adsorption is found to be highly effective and trusted, cheap and easy to adapt and available. Activated carbon in several cases has been utilized as an adsorbent for reclamation of municipal and industrial wastewater for last few decades but the high cost of activated carbon has inspired investigators, especially in several developing countries, to search for suitable and appropriate low-cost adsorbents.

Adsorption phenomena are operative in most natural physical, biological, and chemical systems. Adsorption operations employing and concerning of solids such as activated carbon, metal hydrides and lastly synthetic resins are commonly used in industrial applications for purification of waters and wastewaters. The process of adsorption involves the separation of a substance from one phase followed by its accumulation or concentration at the surface of another. Physical adsorption is caused primarily by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface (Thomas *el at.*,2007). The adsorbate is the substance which is being removed from the liquid phase at the interface. The adsorbent is the solid, liquid or gas phase onto which the adsorbates accumulate (George *et al.*, 2004). Thus, as the conclusion the adsorbents are characterized by surface properties such as surface area and porosity.

Generally, batch and column adsorption studies are conducted to study the feasibility of using materials for purification of heavy metals (Arrayapan *et al.*, 2005; Ajmal *et al.*, 2003; Wong *et al.*, 2003). The researchers determined and finally made a conclusion that the efficiency and effectiveness of the adsorption is based on several parameters such as pH, contact time, initial concentration, adsorbent particle size, adsorbent dosage, flow rate and bed depth. Wong *et al.* (2003), had utilized tartaric acid modified rice husk as adsorbent and have carried-out and experimented batch studies for the removal of lead and copper. The effect of various parameters such as pH, initial concentration of adsorbate, particle size, temperature and etc has been reported and being studied for future usage. Arrayapan *et al.*, (2005) also investigated and studied on the effects on initial metal concentration, contact time, pH and adsorbent dose on the removal of direct blue dye from aqueous solution. Therefore this study also investigates these parameters for direct blue dye removal.

Effect of shaking time

The optimum contact time was selected as 35. 5 min to 35 min for SB, C-SB and FA-SB systems as shown in Fig. 2.



Figure 2.2: Effect of shaking time

Optimization of shaking time of Malachite green adsorbate systems.

Effect of concentration

The optimum concentration of direct blue dye dye was 8×10^{-6} , 1.4×10^{-5} and 8×10^{-6} M at which maximum adsorption was observed by using SB, C-SB and FA-SB systems.

Adsorption isotherm

The adsorption isotherm represents or is a graphical representation showing the relationship between the amount adsorbed by the unit weight of adsorbent and the equilibrium concentration remaining in the solution. It maps and showing the distribution of adsorbed solute between the liquid and solid phases at various equilibrium concentrations (Tahir et al., 2008a and Tahir et al., 2008b).

The adsorption experiments were run at different temperatures ranges from 303 to 318 K and adsorption isotherms were drawn at each specific temperature as the result.

The inspection and examination of adsorption isotherms show a decrease and decline in the rate of adsorption of dyes with the increase value in temperature. It shows and proved that adsorption of MG on SB, C-SB and FA-SB systems was found to be an exothermic process which release heat from the product.

CHAPTER 3

3.0 METHODOLOGY AND MATERIALS

Firstly, an adsorbent was prepared and characterized then a 1000 mg/l stock solution of direct blue dye was prepared then different dye concentrations i.e 20, 40, 60, 80 and 100 mg/l were prepared from the stock solution then it is continued with the effect of initial pH, contact time, adsorbent dose was studied, last and foremost the isotherm and kinetics studies were conducted

Adsorption studies

Batch adsorption studies were carried out by shaking 100 mL of dye solution of desired concentration with 0.2 g of bagasse ash ash in a conical flask at room temperature (22°C), using an orbital shaker at 150 rpm. Then, after a predetermined contact time, the flask was removed from the orbital shaker and the supernatant was filtered through 0.45 μ m membrane filter and analyzed spectrometically for residual dye concentration. The effects of contact time (10 to 260 min), dye concentration (20-40 mg/L) and pH (2-9) on adsorption were determined. The pH of the solution was adjusted with 0.1N NaOH or 0.1 N HCl solutions.

Adsorption isotherm was studied by batch equilibrium test using optimum and suitable contact time and pH for adsorption. Kinetic study was then conducted.

Adsorption isotherm

The quantity of absorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. Generally, the amount of material adsorbed is studied as a function of the concentration at a fixed temperature, and the resulting function is called an adsorption isotherm. Adsorption isotherms are developed by exposing a given amount of adsorbate in a fix volume of liquid to varying amounts of adsorbent (George et al., 2004). The isotherms that most commonly used to describe adsorption characteristics are the empirical relationship developed by Freundlich and the theoretically derived Langmuir relationship.

Freundlich isotherm is expressed as

$$\frac{x}{m} = K_f C_e \frac{1}{n}$$
 Eq (1)

The Langmuir equation, derived based on equilibrium between condensation and evaporation of adsorbed molecules, considering a monomolecular adsorption layer (Isa,et,al.,2007) as follows :

$$\frac{x}{m} = \frac{abC_e}{1+bC_e}$$
 Eq (2)

where

x/m= amount of adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent)

Ce = equilibrium concentration of adsorbate in solution after adsorption (mg/L)

Kf,n,a and b are constants

The straight-line form of the Freundlich isotherm is

$$\log(\frac{x}{m}) = \log K_f + \frac{1}{n} \log C_e$$
 Eq (3)

Langmuir equation adsorption isotherm was developed by assuming : (1) a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy, (2) adsorption are reversible (George, et al., 2004)

Adsorption Kinetics

The rate of processes involved in batch adsorption can be analyzed using kinetic modeling such as pseudo-first order and pseudo-second order model. The pseudo-first order and pseudo-second order models can be respectively described as:

$$\frac{dq}{dt} = k'_1(q_e - q)$$
 Eq (5)

$$\frac{dq}{dt} = k'_2(q_e - q)$$
 Eq (6)

Where

 q_e = amount of solute adsorbed at equilibrium per weight of adsorbent (mg/g)

q = amount of solute adsorbed at time t per weight of adsorbent (mg/g)

$$k'_1, k'_2$$
 are constant

The following linearised time dependent function can be obtained by integrating and rearranging Equation 2.3a and 2.4a.

$$\log(q_e - q) = \log(q_e) - \frac{k'_1}{2.303} t$$
 Eq (7)

The equipments to be used are pH meter, spechtrophotometer and orbital shaker. pH measurements were made with a pH meter. For the batch test.the direct blue dye solutions and adsorbent mixture were shaken with an orbital shaker. The final dye concentrations were tested by using a spectrophometer. Figure 3.1-3.3 show the equipments used for this study. Figure 3.4 shows the flow of the research.



Figure 3.1 pH meter

Figure 3.2 spechtrophotometer



Figure 3.3 Orbital shaker

Figure 3.4: Flow of the research

Batch test

Batch tests were conducted at room temperature; $27 \pm 2^{\circ}C$ for studying the effect of contact time, pH, initial concentration of direct blue dye dye and adsorbent dosage. 250 ml of shaker bottles containing direct blue dye dye solutions were used in all batch experiments.

The procedures of getting the bagasse ash ash/activated carbon are as follows:

Sugar-cane bagasse ash collection, purification and storage

Sugarcane bagasse ash was collected from Pasar Malam Wednesday market at Seri Iskandar, Tronoh, Malaysia. The bagasse ash was manually sized to 10 cm and then washed thoroughly with tap water to remove ligneous and trapped impurities. Bagasse ash was further washed several times with deionized water in order to achieve further purity and for decontamination purpose.

The purified bagasse ash was oven dried at a temperature of 105°C for a period of 24 hours until constant weight was achieved. Dried bagasse ash was ground to a size of 2.5 cm using a mechanical grinder. Bagasse ash material was stored in an airtight container before further use.

Production of adsorbents

About 10 g of the purified sugarcane bagasse ash sample was placed in an alumina ceramic crucible (sample holder). Thermal incineration of the bagasse ash was carried out by

carbonization using nitrogen flow regulated at a flow rate of about 10 mL/min. Carbonization and activation of sugarcane bagasse ash was carried out at high temperature of 900°C at a heating rate of 10°C/min for 3 hours. Temperature, time and heating rate were selected based on preliminary studies. High temperature horizontal tube furnace (OTF-1200X) with a length of 1000 mm, internal diameter of 74.5 mm and external diameter of 80 mm was used. The tube was placed within the horizontal furnace and its two ends were sealed with alumina foam blocks 70 mm diameter. The inlet enclosure was used for nitrogen gas supply with a flow rate regulator attached. At the end of the activation run time, system temperature was set to cool to 500°C within 20 mins and subsequently allowed to cool to about 50°C under slow nitrogen flow.

Adsorbent characterization

Average pore diameter and Brunauer – Emmett- Teller (BET) surface area of the prepared adsorbent was determined using Micrometrics ASAP 2020 V3.04 H. Surface morphology of the adsorbents (before and after study) was analyzed with supra 55 VP Variable Pressure Field Emission Scanning Electron Microscope, FESEM (Carl-Zeiss AG, Germany). Fourier Transform Infrared spectroscopy (Perkin Elmer, wave range 7800-350 cm-1) was used to observe the functional group that can be found in the adsorbents, the functional groups of the adsorbent before and after experimental study was obtained.

Batch Tests

 \rightarrow 200 mg bagasse ash ash will be agitated with 100 ml of synthetic wastewater samples on an orbital shaker.

 \rightarrow Room temperature (28 ± 1 °C). Shaker speed, 350 rpm.

 \rightarrow Samples will be filtered (Whatman No. 1 filter paper) prior to colour determination using DR2010.

 \rightarrow pH range, 2.0 – 7.0

 \rightarrow Contact/shaking time, 10 – 240 minutes

Langmuir Isotherm

$$q_{e} = \frac{x}{m} = \frac{bQ_{0}C_{e}}{1+bC_{e}} \qquad \qquad \frac{C_{e}}{q_{e}} = \frac{1}{Q_{0}b} + \frac{1}{Q_{0}}C_{e} \qquad \qquad \text{Eq (9)}$$

Freundlich Isotherm

$$q_e = \frac{x}{m} = K_f C_e^{1/n}$$
 $\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$ Eq (10)

 $q_e = mass$ of solute adsorbed at equilibrium per unit mass of adsorbent (mg/g)

x = mass of material adsorbed (mg)

m = mass of adsorbent (mg)

 $C_e = \text{conc. of adsorbate in solution after adsorption is complete (mg/l)}$

 Q_0 , b, K_f , n = constants, to be calculated from straight line graphs of the isotherm equations.

The procedure of are experiment regarding the effect of pH and the absorbance as follows:

Frstly 0.1g of bagasse ash ash was measured using the electronic balance and put 18 several different conical flasks. Then, the solutions of pH 2.12,3.15,4.13,5.22,6.13 and 7.19 were poured into different conical flask containing the bagasse ash ash. Then, the 18 conical flasks were put on the orbital shaker to shake and mixed the bagasse ash ash with the solution of direct blue dye for approximately 120 minutes. Then, all of the conical flasks were removed from orbital shaker and final pH were measured using pH meter. The bagasse ash ash were filtered out before taking the reading of final pH. Lastly, measurements were made in triplicate to find the average.

CHAPTER 4

4.0 **RESULTS AND DISCUSSIONS**

4.1 Preparation of stock standard solution.

Table 4.1 shows the concentration versus the absorbance.

concentrations				
(mg/L) vs				
absorbance				
Readings	1	2	3	
concentrations				
(mg/L)	absorbance	absorbance	absorbance	Average
(8,)				Be
0	0	0	0	0
0 15	0 0.728	0 0.718	0 0.71	0 0.7187
0 15 20	0 0.728 0.981	0 0.718 0.97	0 0.71 0.958	0 0.7187 0.9697
0 15 20 25	0 0.728 0.981 1.172	0 0.718 0.97 1.166	0 0.71 0.958 1.14	0 0.7187 0.9697 1.1593

Figure 4.1: Concentration versus absorbance

This is the result of several wavelengths versus the absorbance and the purpose of this experiment is to determine the optimum wavelength based on the maximum value of absorbance by using spechtrophotometre. It shows the optimum wavelength to be used throughout the experiment is 620 Angstrorm.

Table 4.2: Wavelength versus absorbance

absorbance

Wavelength (abs)

400	0.083
500	0.031
600	0.504
610	0.588
620	0.64
630	0.633
640	0.574
660	0.596
680	0.416
700	0.188

Figure 4.2: Wavelength versus absorbance

Figure 4.2 shows the result of different pH; 2.0-7.0 versus absorbance. And using pH meter, the pH of the solution can be determined. Hydrochloric acid, HCl was used to reduce the pH and of sodium hydroxide, NaOH was used to increase the pH.

initial	final	final	final	average	absorbance	absorbance	absorbance	average
pН	pН	pН	рН					
2.12	2.18	2.16	2.14	2.1600	0.121	0.115	0.112	0.1160
3.15	3.52	3.51	3.49	3.5067	0.143	0.155	0.148	0.1487
4.13	6.13	6.29	6.2	6.2067	0.302	0.416	0.36	0.3593
5.22	7.12	7.25	7.32	7.2300	0.41	0.425	0.412	0.4157
6.13	7.61	7.66	7.75	7.6733	0.427	0.402	0.425	0.4180
7.19	7.66	7.68	7.84	7.7267	0.432	0.409	0.451	0.4307

Table 4.3:Initial and final pH versus absorbance

Figure 4.3: Initial pH versus absorbance

Figure 4.4: Final pH versus absorbance

And as mentioned before, the absorbent need to be characterized and the results presented in Table 4.4:

4.2 Characterization of adsorbent.

Table 4.4: BET surface area

Properties	Adsorbents			
BET surface area (m^2/g)	599.0208			
Langmuir surface area (m ² /g)	866.3480			
Microspore surface area (m ² /g)	452.2628			
External surface area (m ² /g)	146.7580			
Total pore volume (cm ³ /g)	0.338335			
Microspore volume (cm ³ /g)	0.230443			
Average pore size (Å)	40.536			

4.2.1 BET surface area

4.2.2 FTIR analysis

The FTIR spectra for adsorbent exhibits four different peaks, the strong peak at 3423.07 cm^{-1} indicates the stretching of –OH phenol group of cellulose and lignin, this is similar to the strong peak observed for raw sugarcane bagasse ash, the peak at 2142.85 cm^{-1} can be assigned to C=C stretching vibration in acetylenic (alkyne) groups, the peak at 1558.31 can be assigned to C=C stretching vibration in aromatic rings and the peak at 1037 cm⁻¹ represents C-O stretching of ether group of cellulose.

Figure 4.5: FTIR analysis

4.2.3 FESEM analysis

It has been observed that after thermal treatment, SEM showed the existence of heterogeneous and vastly porous openings in excess above the honey comb surface of adsorbent, showing good probability for the adsorption of pollutants.(Figure 4.6)

Figure 4.6: FESEM analysis

The results of dye removal in percentage when direct blue dye concentration was 20 mg/L.

Contact						Dye
Time	Initial					removal
(min)	absorbance	Fin	al absorba	nce	Average	%
5	0.922	0.5300	0.5300	0.5170	0.5257	43.0
10	0.922	0.3620	0.3650	0.3750	0.3673	60.2
20	0.922	0.3570	0.3400	0.3300	0.3423	62.9
30	0.922	0.2015	0.2025	0.2170	0.2070	77.5
60	0.922	0.0179	0.0198	0.0197	0.0191	97.9
90	0.922	0.0190	0.0174	0.0186	0.0183	98.0
120	0.922	0.0188	0.0180	0.0169	0.0179	98.1

Table 4.5: Concentration of 20 mg/L versus contact time

Figure 4.7: Dye removal (%) versus contact time

About 90% removal in 1 hour at 20 mg/L dye cone.

Then, this is the result at concentration of 40 mg/L direct blue dye and the graph itself.

	Table 4.6:	Concentration	of 40	mg/L	versus	contact	time
--	------------	---------------	-------	------	--------	---------	------

						Dye
	Initial					removal
Time	absorbance	Fin	al absorba	nce	Average	%
5	1.708	1.0920	1.0960	1.1030	1.0970	35.8
10	1.708	1.0540	1.0620	1.0820	1.0660	37.6
20	1.708	0.9770	0.9830	0.9980	0.9860	42.3
30	1.708	0.5610	0.5770	0.5990	0.5790	66.1
60	1.708	0.4360	0.4480	0.4630	0.4490	73.7
90	1.708	0.3710	0.3540	0.3820	0.3690	78.4
120	1.708	0.3460	0.3490	0.3460	0.3470	79.7

Figure 4.8: Dye removal (%) versus contact time

About 80% removal in 90 minutes at 40 mg/L dye cone.

Then, this is the result of different and separate concentration of 60 mg/L and the graph itself.

						Dye
	Initial					removal
Time	absorbance	Fin	al absorba	nce	Average	(%)
5	2.647	1.8630	1.8630	1.8620	1.8627	29.6
10	2.647	1.7280	1.7110	1.7320	1.7237	34.9
20	2.647	1.5980	1.5970	1.5980	1.5977	39.6
30	2.647	1.5462	1.5328	1.5430	1.5407	41.8
60	2.647	0.8390	0.8388	0.8385	0.8388	68.3
90	2.647	0.6060	0.6030	0.6020	0.6037	77.2
120	2.647	0.6405	0.6400	0.6402	0.6402	75.8

	Table 4.7:	Concentration	of 60	mg/L	versus	contact	time
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Figure 4.9: Dye removal (%) for 60 mg/L versus contact time

About 80% removal in 90 minutes at 60 mg/L of dye concentration.

Then, this is the result of different and separate concentration of 80 mg/L and the graph itself.

	Initial					Dye removal
Time	absorbence	Final absorbence			Average	(%)-80 mg/L
5	3.493	2.3160	2.3140	2.3160	2.3153	33.7
10	3.493	2.2590	2.2550	2.2580	2.2573	35.4
20	3.493	2.2220	2.2210	2.2200	2.2210	36.4
30	3.493	2.1240	2.1240	2.1230	2.1237	39.2
60	3.493	1.2780	1.2750	1.2790	1.2773	63.4
90	3.493	1.1400	1.1490	1.1470	1.1453	67.2
120	3.493	1.2120	1.2000	1.2140	1.2087	65.4

Table 4.8: Concentration of 80 mg/L versus contact time

Figure 5.0: Dye removal (%) for 80 mg/L versus contact time

About 70% removal in 80 minutes at 80 mg/L dye cone.

Then, this is the result of different and separate concentration of 100 mg/L and the graph itself.

	Initial					Dye removal
Time	absorbence	Fin	al absorbe	nce	Average	(%)-100 mg/L
5	4.325	3.1440	3.1440	3.1420	3.1433	27.3
10	4.325	3.0490	3.0500	3.0480	3.0490	29.5
20	4.325	2.8630	2.8610	2.8640	2.8627	33.8
30	4.325	2.7640	2.7630	2.7650	2.7640	36.1
60	4.325	1.6130	1.6150	1.6140	1.6140	62.7
90	4.325	1.5400	1.5390	1.5500	1.5430	64.3
120	4.325	1.2120	1.5224	1.5222	1.5222	64.8

Table 4.9: Concentration of 100 mg/L versus contact time

Figure 5.1: Dye removal (%) for 100 mg/L versus contact time

About 60% removal in 60 minutes at 100 mg/L dye cone.

And then, this is the result for all combination of several concentrations starting from 20 mg/L, 40 mg/L,60 mg/L, 80 mg/L, and lastly 100 mg/L.

	20	40	60	80	100
Time	mg/L	mg/L	mg/L	mg/L	mg/L
5	43.0	35.8	29.6	33.7	27.3
10	60.2	37.6	34.7	35.4	29.5
20	62.9	42.3	39.6	36.4	33.8
30	77.5	66.1	41.8	39.2	36.1
60	97.9	73.7	68.3	63.4	62.7
90	98.0	78.4	77.2	67.1	64.3
120	98.1	79.7	75.8	65.4	64.8

Table 5.0: Several concentrations versus contact time

Figure 5.2: Several concentrations versus contact time

The findings are the dye concentration of 20 mg/L has the highest removal about 99% in 60 minutes/1 hour treatment duration. Followed by dye cone of 40 mg/L with removal of about 80% within approximately 90 minutes. Then, for 60 mg/L has the removal about 78% in 90 minutes treatment duration. For 80 mg/L has the removal about 65% in 90 minutes treatment duration and lastly for 100 mg/L has also the removal about 65% in 90 minutes treatment duration.

The lowest concentration of dye showed higher removal efficiency and the dye removal decreased gradually as the dye concentrations are increasing from 20 mg/L to 100 mg/L respectively.

	Initial	Adsorbent					20
Time	absorbence	dosage	Fin	al absorbe	ence	Average	mg/L
	0.914	0.2	0.5776	0.5777	0.5774	0.5776	36.8
2 hrs	0.914	0.4	0.2780	0.2710	0.2760	0.2750	69.9
	0.914	0.6	0.1633	0.1633	0.1621	0.1629	82.2
5 111 8	0.914	0.8	0.1250	0.1240	0.1270	0.1253	86.3
	0.914	1	0.1140	0.1130	0.1130	0.1133	87.6
	0.914	1.2	0.0980	0.0970	0.0990	0.0980	89.3

Table 5.1: Adsorbent dosage versus absorbance

Figure 5.3: Adsorbent dosage versus absorbance

The procedure of the experiment of adsorbent dosage and the relationship to the bagasse ash ash and the absorbance value is by firstly preparing the direct blue dye solution then putting different and several amount of bagasse ash ash in gram starting from 0.2 g, 0.4, 0.6, 0.8,1.0 and lastly 1.2 gram (firstly being weighted by electronic balance). Then filtered the bagasse ash ash then put them on the orbital shaker to be shaken for 3 hours then taken out for measuring the absorbance value using spechtrophotometre.

Then, this is the result for Langmuir and Freundlich isotherms.

	Langmuir and Freundlich isotherm analysis table								
ci	ce	ci-ce	v	Х	m	x/m (qe)	ce/qe	Log Ce	Log qe
0.914	0.578	0.3	0	0.034	0	0.2	3.4	-0.24	-0.77
0.914	0.275	0.6	0	0.064	0	0.2	1.7	-0.56	-0.80
0.914	0.163	0.8	0	0.075	1	0.1	1.3	-0.79	-0.90
0.914	0.125	0.8	0	0.079	1	0.1	1.3	-0.90	-1.01
0.914	0.113	0.8	0	0.080	1	0.1	1.4	-0.95	-1.10
0.914	0.098	0.8	0	0.082	1	0.1	1.4	-1.01	-1.17

Table 5.2: Langmuir and Freundlich isotherm analysis table.

Figure 5.4: The graph of Langmuir isotherm

Figure 5.5: The graph of Freundlich isotherm

Then, this is the result for kinetics.

	final absorbance							
	20	40	60	80	100			
Time	mg/L	mg/L	mg/L	mg/L	mg/L			
5	0.5257	1.0970	1.8627	2.3153	3.14333			
10	0.3673	1.0660	1.7237	2.2573	3.049			
20	0.3423	0.9860	1.5977	2.2210	2.86267			
30	0.2070	0.5790	1.5407	2.1237	2.764			
60	0.0191	0.4490	0.8388	1.2773	1.614			
90	0.0183	0.3690	0.6037	1.1453	1.543			
120	0.0179	0.3470	0.6402	1.2087	1.5222			

Table 5.3: Contact time for several concentrations versus final absorbance

Table 5.4: qt versus concentrations

		qt		
20	40	60	80	100
mg/L	mg/L	mg/L	mg/L	mg/L
0.1	0.1	0.2	0.2	0.2
0.1	0.1	0.2	0.2	0.3
0.1	0.1	0.2	0.3	0.3
0.1	0.2	0.2	0.3	0.3
0.2	0.3	0.4	0.4	0.5
0.2	0.3	0.4	0.5	0.6
0.2	0.3	0.4	0.5	0.6

		t/q		
20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L
63.1	4.6	31.9	21.2	21.2
90.1	9.4	54.2	40.5	39.2
172.5	20.3	95.3	78.6	68.4
209.8	51.8	135.6	109.5	96.1
332.3	133.6	165.9	135.4	110.7
498.0	243.9	220.2	191.7	161.8
663.6	345.8	299.0	262.7	214.1

Table 5.5: t/q versus concentrations

Table 5.6: log (qe-q) versus concentrations

	log (qe-q)							
20	40	60	80	100				
mg/L	mg/L	mg/L	mg/L	mg/L				
-0.92	-0.75	-0.61	-0.58	-0.44				
-1.05	-0.77	-0.67	-0.60	-0.46				
-1.08	-0.81	-0.72	-0.61	-0.51				
-1.24	-1.13	-0.75	-0.65	-0.54				
-1.71	-1.32	-1.42	-1.25	-1.24				
-1.72	-1.49		-1.52	-1.36				
-1.72	-1.56		-1.37	-1.40				

Table 5.7: Pseudo First order

Pseudo First order										
concentration (mg/L)	equation	\mathbf{R}^2								
20	y = -0.0075x - 0.9907	0.8381								
40	y = -0.0076x-0.7533	0.9123								
60	y = -0.0144x-0.4725	0.9085								
80	y = -0.0088x-0.5135	0.8556								
100	y = -0.0099x - 0.3788	0.8975								

Table 5.8: Pseudo Second order

Pseudo	o Second order	
concentration (mg/L)	equation	R^2
20	y = 5.0666x + 47.443	0.9956
40	y = 3.0288-29.321	0.9894
60	y = 2.1208x + 41.654	0.9681
80	y = 1.9215x+27.985	0.9725
100	y = 1.5308x+28.355	0.967

Figure 5.6: Graph of log (qe-q) versus times for several concentrations

Figure 5.7: Graph of t/qt versus times for several different concentrations

CHAPTER 5

5.0 CONCLUSION AND RECOMENDATION

Adsorbent has been prepared from sugarcane bagasse (1st objective). Optimum wavelength for color reading using spectrophotometer has been determined to be 620 Angstrom. The suitability of bagasse ash for removal of direct dye from aqueous solution is determined (2nd objective). The effect of pH, initial dye concentration and agitation time on the adsorption of direct dye on bagasse ash was finally determined (3rd objective). The optimum condition for the operating parameters such as pH, contact time and adsorbent dosage were 2, 90 minutes and 0.8 g, respectively.

Maximum adsorption capacity was 3.89 mg/g. Adsorption isotherms follow Langmuir rather than Freundlich with R² values of 0.943 and 0.8135, respectively. Adsorption kinetics follows Pseudo second order kinetic model. Dye concentration of 20 mg/L shows higher removal efficiency of 99% within 1hour and followed by other concentrations (40-100 mg/L) in the descending order. The contact time of 90 minutes exhibited significant removal of dye in all concentrations (20 mg/L-100 mg/L). In addition, adsorbent dosage of 0.8g is sufficient for the removal of dye. Beyond this value, the removal efficiency nearly constant. The pH of 2.0 is suitable for this experiment.

PROJECT KEY MILESTONE (1st semester)

PROJECT KEY MILESTONE (2nd semester)

GANTT-CHART & TIMELINE

(1st semester)

No	Details/	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Week														
1	Selection														
	of project														
	title														
2	Preliminary														
	Research														
	Work														
3	Submission														
	of														
	Extended														
	Proposal														
4	Proposal														
	Defence														
5	Project														
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REFERENCES

- Aharoni , C., Sideman, S., Hoffer, E. (1979). 'Adsorption of phosphate ions by colloid ion-coated alumina', 29, J Chem Technol Biotechnol, , pp. 404–412
- Bhattacharyya, K.G., Sarma, A. (2003), 'Adsorption characteristics of the dye, brilliant green, on neem leaf powder', Dyes Pigments, 57pp. 211–222
- Bishop, S., Seshadri, P.L., Agha, A.M. (1994) 'Anaerobic/aerobic treatment of selected azo dyes in wastewater', 15, Waste Manage, , pp. 127–137 & Mall, I.D., Mishra, N., Mishra, I.M. (1994), 'Removal of organic matter from sugar mill effluent using bagasse ash flyash activated carbon' & 39 (6), Res Ind, pp. 115–119
- Ho, Y.S., McKay, G. 'Pseudo-second order model for sorption processes, Process Biochem, 34 (1999), pp. 451–465
- Janos, P., H. Buchtova, M. Ryznarova(2003), 'Sorption of dyes from aqueous solutions onto fly ash', 37, Water Res, pp. 4938–4944
- Lagergren, S. (1898)'About the theory of so called adsorption of soluble substances', Ksver Veterskapsakad Handl, 24, pp. 1–6
- Malik, P.K., (2003), 'Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid yellow 36', Dyes Pigments, 56 pp. 239–249
- Mall, I.D., Srivastava, V.C., Agarwal N.K., Mishra I.M. (2005)
 'Adsorptive removal of malachite green dye from aqueous solution by bagasse ash fly ash and activated carbon-kinetic study and equilibrium isotherm analyses', Colloid Surf A, 26, pp. 17–28,
- Mall, I.D., Srivastava, V.C., Agarwal, N.K., Mishra, I.M. (2005), 'Removal of Congo red from aqueous solution by bagasse ash fly ash and activated carbon: kinetic study and equilibrium isotherm analyses', Chemosphere, 61 pp. 492–501
- Mall, I.D., V.C. Srivastava, N.K. Agarwal(2006), 'Removal of orange-G and methyl violet dyes by adsorption onto bagasse ash fly ash – kinetic study and equilibrium isotherm analyses', Dyes Pigments, 69, pp. 210–223

- 11. Mckay , G., Allen, S.J., Meconney, I.F., Ottrburn, M.S. (1981)'Transport processes in the sorption of colored ions by peat particles', J Colloid Interface Sci, 80 (2) pp. 323–339
- Srivastava, V.C., Mall, I.D., Mishra, I.M. (2005) 'Treatment of pulp and paper mill wastewaters with poly aluminium chloride and bagasse ash fly ash' & 260, Colloid Surf A, pp. 17–28
- Srivastava, V.C., Prasad, B., Mall, I.D., Mahadevswamy, M., Mishra, I.M. (2006), 'Adsorptive removal of phenol by bagasse ash fly ash and activated carbon: equilibrium, kinetics and thermodynamics', Colloid Surf A, 272 pp. 89–104
- Sun, Q., Yang, L. (2003), 'The adsorption of basic dyes from aqueous solution on modified peat resin particle', Water Res, 37 pp. 1535– 1544
- Tutem, E., Apak, R., Unal, C.F. 'Adsorptive removal of chlorophenols from water by bituminous shale', Water Res, 32 (1998), pp. 2315–2324
- Weber Jr., W.J., Morris, J.C. (1963), 'Kinetics of adsorption on carbon from solution', J Sanit Eng Div ASCE, 89 (SA2), pp. 31–59
- Y., Wong, Yu J. (1999), 'Laccase catalysed decolorisation of synthetic dyes', Water Res, 33 (16) pp. 3512–3520
- Zollinger, H. (1987) 'Color chemistry synthesis, properties and applications of organic dyes and pigments', VCH Publishers, New York, pp. 92–102