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# Study of adsorption performance of BFA for removal of MG and MB dye mixture from aqueous solution

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***A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in Chemical Engineering under Environmental Engineering Stream.***

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## ACRONYMS

| | |
|---|---|
| BFA | Bagasse Fly Ash |
| BOD | Biochemical Oxygen Demand |
| $C_e$ | Equilibrium concentration of adsorbate (mg/L) |
| COD | Chemical Oxygen Demand |
| DO | Dissolved Oxygen |
| $K_L$ | Langmuir isotherm constant (L/mg) |
| MB | Methylene Blue |
| MG | Malachite Green |
| ppm | parts per million |
| $q_e$ | Amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g) |
| $q_m$ | Maximum monolayer coverage capacity (mg/g) |
| $R_L$ | Langmuir equilibrium parameter |
| UV/vis | Ultraviolet Visible |

# ABSTRACT

The excessive release of dye pollutants from the textile, paper, and leather industries are major sources of environmental pollution. Adsorption process is among the most effective techniques for color removal from wastewater. In this study, bagasse fly ash has been used as an adsorbent for the removal of Malachite Green (MG) and Methylene Blue (MB) mixture of dyes from aqueous solution. Characterization of the BFA was made by proximate analysis to determine the optimum particle size that should be used for the adsorption process and also Fourier Transform Infrared (FTIR) spectroscopy to reveal the functional group responsible for the process.

Particle size of less than 250 µm bagasse fly ash was employed for all experiments due to its high ash content of 81.63%. The raw bagasse fly ash obtained was treated using $H_2O_2$ and tested for its efficiency and compared with the untreated bagasse fly ash. The adsorption studies were carried out to assess the effect of various parameters such as initial dye concentration, contact time, adsorbent dose and pH and determine the maximum operating condition of the process for the removal of both dyes. Initial adsorption study carried out using 0.5 g adsorbent dose for concentrations (50, 75 and 100 ppm), pH (6, 8, and 10) and different time (10, 30, 60, and 90 min) resulted in a maximum adsorption capacity of 21.16 mg/g (79.39%) for MG and 16.59 mg/g (71.05%) for MB. This maximum values were all obtained at concentration of 100 ppm, pH 10, and time of 90 minute.

In order to understand the mechanism of the adsorption process, the sorption data were analyzed using Langmuir and Freundlich isotherm models. The linear form of both models was fitted with the data and resulted in good conformation with both models and for each dyes. Finally, the rate of the adsorption process was investigated using Pseudo-first order kinetics and Pseudo second-order kinetic models. Pseudo second-order kinetic model was found to be well fitted to the data obtained.

# 1. INTRODUCTION

## 1.1. Background

Water is vital requirement of life and used for various household as well as industrial activities. It is one of the most essential natural resources, unfortunately exploited the most. The key reason being increased human population, rapid industrialization, increased living standard and urbanization (Gupta & Ali, 2004). Today the whole world is facing water crises because of unrestricted and excessive exploitation of water (Karnitz et al., 2007). Rapid urbanization of natural resources like increase in number of industries, especially textile industries are posing a threat to the water bodies by discharging of contaminated wastewater (Isa et al., 2007). These discharge effluents contain various harmful and toxic components, heavy metals, BOD, COD and also dyes. This deteriorates the quality as well as quantity of water and makes it unsafe for further use (Amran et al., 2011; Yagub et al., 2014).

Many industries, such as dyestuffs, textile, paper, printing, cosmetics and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater (Kumar, 2004). It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater (Ramesh, 2013). The presence of very small amounts of dyes in water (less than 1 ppm) is highly visible and undesirable and may cause irregular coloration of surface waters as well as the pollution of the water with toxic compounds (Albanis et al., 2000; Deokar & Sabale, 2014). Color stuff discharged from these industries poses certain hazards and environmental problems. Rivers therefore must preserve their natural color and the clarity of water (Amran et al., 2011; Elgeundi, 1991).

Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade (Banerjee & Sharma, 2013). Non-biodegradable nature of most of the dyes reducing aquatic diversity by blocking the passage of sunlight through the water represents serious problems to the environment therefore, reduce the dissolved oxygen (DO) level in the water and may also increase the biochemical oxygen demand (BOD) of the contaminated water body (Wong et al., 2013; Babu et al., 2007). Since many dyes such as methylene blue and malachite green have adverse effect on human beings, the removal of color from the effluent or process has appeared of importance for ensuring healthy environment (Mohan et al., 2002; Rastogi et al., 2008).

Methylene blue and malachite green are cationic dyes, used in several industries such as textile, paper, leather, pulp, wool etc., for coloring their final products (Gong et al., 2013). Particularly, textile dyeing is becoming a major industry in Ethiopia consuming large quantity of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes (Beyene, 2014). The effluents of these industries containing huge amount of dyes, discharged into water bodies cause severe damage to the environment (Anbia, 2011; Makeswari & Santhi, 2013; Kanawade et al., 2011). Acute exposure to methylene blue will cause increased heart rate, vomiting, shock, Heinz body formation, and tissue necrosis in humans (Shahryari et al., 2010). Malachite green dye is extensively used all over the world in the fish farming industry as fungicide and disinfectant. Scientific evidence indicated that malachite green might persist in edible aquatic organisms, consumption of these organisms leads to toxicity of human beings for extended periods of time (Hameed & El-khaiary, 2008).

It has been cited that, adsorption of dyes using low cost adsorbents such as bagasse fly ash is the most economical and effective method for removal of dyes as a remedy to clean the water prior to release to the environment (Indra D Mall et al., 2006; Kanawade, 2010). Bagasse fly ash is a waste material obtained from the particular collection devices attached to the flue gas line of the sugar cane bagasse-fired boilers (Mane et al., 2007). It consists of fine, powdery particles predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The color of fly ash can vary from gray to black, depending on the amount of unburned carbon in the ash (Ahmaruzzaman, 2010).

Bagasse fly ash, although considered as environmental pollutant for most sugar manufacturing industries, it is an important raw material for various applications (Vinod K Gupta & Ali, 2000). The utilization of bagasse fly ash in construction (Kharade et al., 2014), removal of organic compounds (Lakdawala et al., 2012; Lokeshwari & Joshi, 2014), heavy metals (Taha, 2006; Vinod K Gupta & Ali, 2000; Singh et al., 2014) and dyes (Kanawade, 2010; Mane et al., 2007; Indra D Mall et al., 2006), can help a great deal in the reduction of environmental pollution. Therefore, Bagasse fly ash was selected for this study for removal of most widely used dyes in textile industry: Methylene blue and Malachite green dye mixtures.

## 1.2. Problem statement

Dyes do not only damage the aesthetics of the aquatic environment but also are toxic to the aquatic environment. There are more than 100,000 commercially available dyes and more than 700,000 tons per year are produced annually (Mane et al., 2007). Around 10-15% of dyes used in industry are discharged into the environment, which is harmful to the environment (Kanawade et al., 2011). Many of the dyes are resistant to oxidation, light, and aerobic digestion. Therefore, a suitable treatment method is required to bring the industrial wastewater within the acceptable concentration level prescribed by law in an economical fashion.

There are different methods for the removal of dyes from waste water effluents. The conventional methods can be categorized as biological, chemical and physical methods (Crini, 2006). The biological treatment methods include activated sludge, trickling filters, anaerobic process, oxidation ponding; which have an advantage of eco-friendly nature, minimum usage of chemicals and energy saving but these methods are not effective for treating dyestuff wastewater because many commercial dyestuffs are toxic to micro-organisms being used in the treatment process. Biological treatment methods also require large land area and minimum flexibility in design and operation (Karthik et al., 2014). Coagulation-flocculation, chemical precipitation, ion-exchange, ozone oxidation belongs to the group of chemical treatment methods, dyes can be removed completely by this method. But these methods have the limitations of high energy demand, large consumption of chemical reagents, high cost, and require additional treatment before disposal (Kharub, 2012). Physical treatment of wastewater includes membrane separation and adsorption techniques. Membrane separation has high separation efficiency, low energy consumption and easy operation as an advantage but have a downside of requiring special equipment, membrane fouling, and high investment cost (Ghaly et al., 2014). The process of adsorption has an edge over the other methods due to its low regeneration cost, sludge free operation, simplicity of design and operation, less land area requirement, not affected by toxic chemicals and does not form harmful substances (Amin, 2008).

Adsorption using a solid adsorbent is widely used to remove chemical pollutants especially that are unaffected by conventional biological methods. Among the most commonly used adsorbent is activated carbon due to its structural characteristics and porous texture which gives large surface area and great adsorption capacity for all kinds of pollutants. Activated carbon has high cost of production which is a constraint for the wide applicability of the process of adsorption. Activated carbon has another disadvantage of high regeneration cost when exhausted (Kharub, 2012). Consequently, there is a need to produce low cost and effective adsorbent with similar performance as activated carbon. The most common low cost adsorbents used for the removal of dyes include rice husk (Dalai et al., 2015), fruit waste (Ozsoy & Leeuwen, 2010), saw dust (Malik, 2004), bagasse fly ash (Vinod K Gupta & Ali, 2000; Kanawade, 2010; Rastogi et al., 2008), coconut shell (Wong et al., 2013), spent grain (Pedro et al., 2004) etc. Some of these materials require a carbonization step before use as an adsorbent and also there is usually a problem of collection of these wastes for their large scale application.

Bagasse fly ash, a waste collected from the particulate collection equipment attached to the bagasse fired boilers, cause a disposal problem. It is now mostly used for land filling but have shown good adsorptive properties. Bagasse fly ash does not require any further energy consuming process prior to use compared to some other low cost adsorbents. In addition to the easy collection of the material from bagasse fired boilers, currently it doesn’t have a potential application other than land filling. Therefore, the potential application of BFA as an adsorbent is being investigated by many researchers and shown promising results. The bagasse fly ash is currently being used as filler in building materials (Kharade et al., 2014), removal of organic compounds (Lokeshwari & Joshi, 2014), heavy metals (Taha, 2006; Vinod K Gupta & Ali, 2000; Singh et al., 2014) and dyes (Kanawade, 2010; Mane et al., 2007; Indra D Mall et al., 2006).

Many studies use a single dye aqueous solution for studying the efficiency of the adsorbent and does not consider the interaction that could exist between different pollutant molecules when adsorbed from a wastewater. In this study, the adsorption efficiency of bagasse fly ash from a mixture of malachite green and methylene blue dyes in aqueous solution will be investigated. To approach the treatment of real wastewater using bagasse fly ash which could help to reduce the cost of the process significantly. This could lead to the development of an effective technology for the treatment of wastewater containing dyes.

## 1.3. Objective

### 1.3.1. General objective

The main objective of this study is to investigate the potential application of bagasse fly ash for removal of cationic dye mixtures (Malachite green and Methylene blue) via adsorption process from aqueous solution.

### 1.3.2. Specific objective

The specific objectives of this study are:

- To characterize physical properties of raw bagasse fly ash obtained from the sugar cane bagasse-fired boilers of Wonji/Shoa Sugar Factory.
- To study the adsorption efficiency of the pretreated bagasse fly ash for cationic dye mixtures (Methylene blue and Malachite green) from aqueous solution.
- To investigate single and interaction effects of selected operating conditions (initial dye concentration, solution pH, adsorbent dose and adsorption time) on adsorption efficiency of bagasse fly ash and find optimal conditions using full factorial experimental design.
- To investigate surface property (functional group) of fresh and used bagasse fly ash using Fourier Transform Infrared Spectroscopy (FTIR).
- To perform the adsorption isotherm and kinetic studies for the bagasse fly ash.

## 1.4. Significance of the research

Discharged colored wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. One of the main concern about colored effluent is not only its toxicity but also its undesirable aesthetic impact on receiving waters. Since many dyes have adverse effect on human beings, the removal of color from the effluent or process has appeared of importance for ensuring healthy environment. Hence, the major significance of this study includes but not limited to:

- Removal of mixture of dyes using sugar industry waste material.
- Utilization of waste material, bagasse fly ash, as low cost and effective adsorbent.
- Gives important initial data of adsorption for mixture of cationic dyes using bagasse fly ash.
- Can help in the creation of industrial park by combining sugar industry and industries with dye containing wastewater.

# 2. LITERATURE REVIEW

## 2.1. Dyes

Dyes are ionic, aromatic organic compounds with structures including aryl rings with delocalized electron systems and also give color to the material. Mauveine, the first synthetic dye, was discovered in 1856 by William Henry Perkin (Gupta et al., 2015). Since then, thousands of new synthetic dyes have been produced. Unlike most organic compounds, dyes possess color because they absorb light in the visible spectrum (400–700 nm), have at least one chromophore (color-bearing group), have a conjugated system, i.e. a structure with alternating double and single bonds, and exhibit resonance of electrons, which is a stabilizing force in organic compounds. When any one of these features is lacking from the molecular structure the color is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (color helpers), such as carboxylic acid, sulfonic acid, amino and hydroxyl groups. While these are not responsible for color, their presence can shift the color of a colorant and they are most often used to influence dye solubility. Nowadays, the total annual world dye production is estimated at about $7*10^5$ tons, with more than 100,000 dyes available on the market (Mane et al., 2007). The largest consumer of these dyes is the textile industry accounting for around two thirds of its market. It is estimated that 10-15% of the dye is lost during the dyeing process and released with the effluent (Banerjee & Sharma, 2013).

Dyes are usually classified based on their particle charge upon dissolution in aqueous application medium such as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes) (Yagub et al., 2014). Anionic dyes are highly water soluble and difficult to remove by conventional methods. Nonionic dyes, also known as disperse dyes, do not ionize in an aqueous solution and their fused aromatic ring structure makes them highly resistant to degradation. However, a few cationic dyes like methyl blue can be easily removed by adsorption and advanced oxidation processes (Ahmad et al., 2015).

There are many harmful effects of dyes on ecosystem such as (Elgeundi, 1991):

- They pose acute as well as chronic effects on most of the exposed organisms.
- They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological activities.

- They are highly visible and even a minor amount may cause abnormal coloration of water bodies which appears displeasing to eyes.
- They have complex molecular structures which makes them difficult to treat with common municipal treatment operations.
- Consume dissolved oxygen and affect aquatic ecosystem.

***Malachite Green dye***

Malachite Green (MG), tri-phenyl methane dye, $C_{23}H_{25}N_2Cl$, is basically a cationic dye (Fig 2.1) (Indra Deo Mall et al., 2005). It is usually prepared by the condensation of benzaldehyde and dimethylamine to give leuco- malachite green (LMG).

$$C_6H_5CHO + 2\ C_6H_5N\ (CH_3)_2 \rightarrow C_6H_5CH\ (C_6H_4N\ (CH_3)_2)_2 + H_2O$$

Then this compound is oxidized to a cation that is MG (Fig. 2.1):

$$C_6H_5CH\ (C_6H_4N\ (CH_3)_2)_2 + HCl + 1/2\ O_2 \rightarrow [C_6H_5C\ (C_6H_4N\ (CH_3)_2)_2]\ Cl + H_2O$$

MG has been widely used for the dyeing of leather, wool, jute and silk, as a fungicide and antiseptic in aqua culture industry to control fish parasites and disease (Zhang et al., 2008).

MG is environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals. It is highly lethal to freshwater fish, in both acute and chronic exposures. It causes serious public health hazards and also poses potential environmental problem (Anbia, 2011). Both clinical and experimental observations reported so far reveal that MG is a multi-organ toxin. It decreases food intake, growth and fertility rates; causes damage to the liver, spleen, kidney and heart; inflicts lesions on the skin, eyes, lungs and bones; and produces teratogenic effects (Hameed & El-khaiary, 2008).

MG is highly cytotoxic to mammalian cells and acts as a tumor enhancing agent. This dye may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic effects on humans (Makeswari & Santhi, 2013).

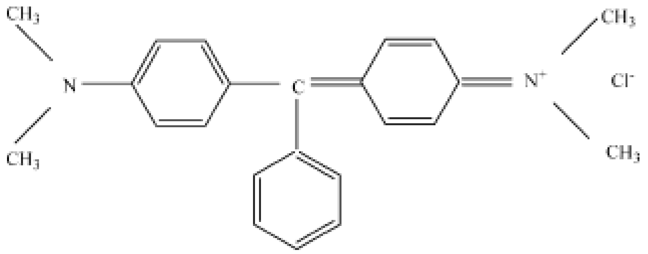


**Figure 2.1** Molecular structure of Malachite green (Indra Deo Mall et al., 2005).

***Methylene Blue dye***

Methylene Blue (MB) is a heterocyclic aromatic chemical compound with molecular formula, $C_{16}H_{18}N_3SCl$, (Fig. 2.2) and chemical name [3, 7-bis (Dimethylamino)-phenazathionium chloride Tetramethylthionine chloride] (Miclescu & Wiklund, 2010). MB is a basic aniline dye that forms a deep blue color in the oxidized state while it is colorless in its reduced form (leucomethylene blue). It is prepared by oxidizing dimethyl-phenylen diamine with ferric chloride in the presence of hydrogen sulphide (Gupta et al., 2011). It is utilized in coloring paper, dyeing cotton and wools, and coloring of paper stocks. It dissociates in aqueous solution in the same way that electrolytes dissociate into methylene blue cation and the chloride ion. The removal of methylene blue from any wastewater is most important due to the serious environmental damage that can occur as a result of contact with it, particularly in the case of human beings (Wong et al., 2013).

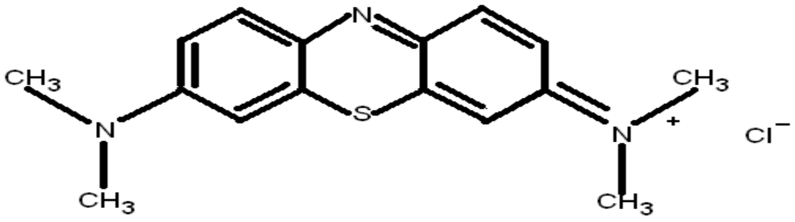


**Figure 2.2** Molecular structure of Methylene blue (Miclescu & Wiklund, 2010).

## 2.2. Dye removal technologies

With the growing rate of industrialization, the emission of effluents from different industries poses serious threats to several living forms due to their adverse effects. The serious environmental impact and increase of public awareness in environmental protection, created a need to remove pollutants from wastewater before it is discharged into the environment. Currently there are several methods that can be used in the removal of dyes from industrial effluents. However, due to the variety of existent dyes and to the effluents complexity, not all methods have the same efficiency and each method has its limitations. Generally, the treatment methods can be divided into three main categories namely physical, chemical and biological methods (Crini, 2006).

### 2.2.1. Physical method

A number of different physical methods are used such as membrane-filtration processes (Reverse osmosis, electrodialysis, nano-filtration) and various adsorption techniques. The major disadvantage associated with the membrane filtration processes is that they have a limited lifetime, the problem of membrane fouling and the cost of periodic replacement must thus be included in any analysis of their economic viability (Zheng et al., 2015).. The process of adsorption has an edge over the other methods due to its sludge free clean operation, completely removed dyes, convenience operation and simplicity of design (Elgeundi, 1991). Some physical methods are discussed below.

#### ***Membrane separation***

Membrane separation process is the method that uses the membrane's micropores to filter and makes use of membrane's selective permeability to separate certain substances in wastewater. Membrane separation has high separation efficiency, low energy consumption, easy operation, no pollution and so on. However, this technology is still not large-scale promoted because it has the limitation of requiring special equipment, and having high investment and the problem of membrane fouling (Ghaly et al.,2014). The important membrane separation processes are reverse osmosis and nano-filtration.

Reverse Osmosis is a technology that is used to remove a large majority of contaminants from wastewater by pushing the wastewater under pressure through a semi-permeable membrane.

Reverse osmosis permits the removal of all mineral salts, hydrolyzed reactive dyes, and chemical auxiliaries (Zheng et al., 2015).

Nanofiltration has been applied for the treatment of colored effluents from the textile industry. Nanofiltration membranes retain low molecular weight organic compounds, divalent ions, large monovalent ions, hydrolyzed reactive dyes, and dyeing auxiliaries (Babu et al., 2007). The treatment of dyeing wastewater by nanofiltration is also used for the treatment of solutions with highly concentrated and complex solutions (Ghaly, et al., 2014).

### 2.2.2. Chemical method

Chemical methods include coagulation-flocculation, precipitation, coagulation, conventional oxidation methods by oxidizing agents such as ozone, irradiation or electrochemical processes (Karthik et al., 2014). Dyes can be removed completely by this process, it is expensive and also accumulation of concentrated sludge creates another disposal problem. Recently, new emerging techniques, known as advanced oxidation process, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. But these methods are still costly & commercially unattractive. Common problems in these methods are the high electrical energy demand and the consumption of chemical reagents (Kharub, 2012). Common chemical methods are discussed below.

#### *Coagulation- flocculation*

Coagulation -flocculation is one of the most used method, especially in the conventional treatment process. Coagulation includes the use of suitable chemicals, through a chemical reaction, forms an insoluble end product. Active on suspended matter, colloidal type of very small size have electrical charge resulting in repulsion and prevent their aggregation. Adding in water coagulants such as aluminum sulphate, ferric sulphate, ferric chloride, giving hydrolysable metallic ions or organic hydrolysable polymers (polyelectrolyte) can eliminate the surface electrical charges of the colloids. This effect is called coagulation (Ayeche, 2012). Normally the colloids bring negative charges so the coagulants are usually inorganic or organic cationic coagulants. The metallic hydroxides and the organic polymers, besides giving the coagulation, can help the particle aggregation into flocks, thereby increasing the sedimentation (Ahmad et al., 2015).

The combined action of coagulation, flocculation and settling is named clariflocculation. Settling needs stillness and flow velocity, so these three processes need different reactions tanks. This processes use mechanical separation among heterogeneous matters, while the dissolved matter is not well removed (clariflocculation can eliminate a part of it by absorption into the flocks). The dissolved matter can be better removed by biological or by other physical chemical processes. But additional chemical load on the effluent (which normally increases salt concentration) increases the sludge production and leads to the uncompleted dye removal (Babu et al., 2007).

### *Chemical precipitation*

Chemical precipitation is a relatively simple wastewater treatment technique in which chemicals such as sulphides, hydroxides and carbonates react with organic and inorganic pollutants present in wastewater to form insoluble precipitates. Chemicals react with dissolved dye molecules to form insoluble precipitates and then can be removed. The general procedures involve the addition of chemicals into wastewater treatment to form the precipitate with dye molecules and waiting for the insoluble particles to settle. Then the wastewater can be decanted to separate the sludge. The most common chemical precipitation method for dye removal is hydroxide precipitation. Chemical precipitation is an efficient method for the removal of dyes from wastewaters, but generation of sludge and high chemical cost are the major hurdle for the application of this technology at industrial scale (Ahmad et al., 2015).

### *Ozone oxidation*

It is a very effective and fast decolorizing treatment, which can easily break the double bonds present in most of the dyes. Ozonation can also inhibit or destroy the foaming properties of residual surfactants and it can oxidize a significant portion of COD. Moreover, it can improve the biodegradability of those effluents which contain a high fraction of non-biodegradable and toxic components through the conversion (by a limited oxidation) of recalcitrant pollutants into more easily biodegradable intermediates (Ayeche, 2012). As a further advantage, the treatment does increase neither the volume of wastewater nor the sludge mass. Full scale applications are growing in number, mainly as final polishing treatment, generally requiring up-stream treatments such as at least filtration to reduce the suspended solids contents and improve the efficiency of decolorization.

Sodium hypochlorite has been widely used in the past as oxidizing agent. In textile effluent it initiates and accelerates azo bond cleavage. The negative effect is the release of carcinogenic aromatic amines and other wise toxic molecules and, therefore, it should not be recommended (Karthik et al., 2014).

***Ion exchange***

The ion exchange process is one of the most common techniques, which can effectively remove dyes from aqueous solutions through strong interactions between charged dyes and functional groups on ion exchange resins. This process involves the exchange of ions to form strong bonds between solutes and resins, thereby achieving effective separation. However, resins may be poisoned by unexpected constituents or rapidly exhausted by unexpectedly high loadings (Sharma et al., 2014).

### 2.2.3. Biological method

Biological treatment procedures for the removal of contaminations from wastewater are considered highly useful due to their eco-friendly nature, minimum usage of chemicals and energy saving nature. The principle of the biological treatment procedures is the conversion of biodegradable wastes into simpler and harmless species through biological processes by various microorganisms (Babu et al., 2007). There are many types of biological treatment methods such as trickling filters, activated sludge process, anaerobic process, oxidation ponding etc. Biodegradation methods such as microbial degradation, adsorption by living or dead microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents (Karthik et al., 2014). Biological process is cheaper than other methods. When compared to chemical methods, for biological process investment cost is 5-20 times less and operating costs are 3-10 times less than chemical methods (Ahmad et al., 2007). However, conventional biological processes are not effective for treating dyestuff wastewater because many commercial dyestuffs are toxic to organism being used and result in the problems of sludge bulking, rising sludge and pin flock, most dyes are designed to resist to microbial attack, require large land area and less flexibility in design and operation (Kharub, 2012).

**Table 2.1** Summary of conventional treatment methods for dye removal (Ghaly et al., 2014; Crini, 2006; Kharub, 2012).

| Treatment methodology | Advantages | Disadvantages |
|---|---|---|
| Membrane filtration | Removes all dye types.<br>Recovery and reuse of chemicals and water.<br>Wider application for complex wastes. | Concentrated sludge production.<br>Dissolved solids are not separated in this process.<br>High running cost |
| Coagulation/Flocculation | Good removal efficiencies.<br>Elimination of insoluble dyes | Cost of coagulants and chemicals for pH adjustment.<br>Dewatering and sludge handling problems. |
| Adsorption on activated Carbon | Good removal efficiency.<br>Suspended solids and organic substances well reduced. | Regeneration process with high cost.<br>Excessive solid waste generation. |
| Ion-exchange | Regeneration with low loss of resins. | Specific application.<br>Not effective for all dyes. |
| Electrochemical Oxidation | No additional chemicals required and end products are non-hazardous.<br>Capacity of adaptation to different volumes and pollution loads. | Process with high cost.<br>Iron hydroxide sludges. |
| Advanced oxidation Processes | Complete mineralization ensured.<br>Effective pretreatment methodology in integrated systems and enhances biodegradability. | Expensive process. |
| Ozonation | Effective for azo dye removal. No alteration in volume. | Releases aromatic amines.<br>Short half-life (20 min.). |

| | | |
|---|---|---|
| Photocatalysis | Process carried out at ambient conditions.<br>Complete mineralization with shorter retention times.<br>Inputs are non-toxic and inexpensive. | Effective for small amount of colorants.<br>Expensive process. |
| Aerobic biodegradation | Color removal is facilitated along with COD removal. | Longer retention times.<br>Less resistant to recalcitrant compounds. |
| Anaerobic biodegradation | Resistant to wide variety of complex colorants. Bio gas produced is used for electricity and steam generation. | Longer acclimatization phase. |
| Bacterial, fungal and algal biodegradation | Good removal efficiency for low volumes and concentrations.<br>Very effective for specific colorant removal. | Culture maintenance is expensive.<br>Cannot cope up with large volumes of colored effluents. |

## 2.3. Principles of adsorption

Adsorption is a surface phenomenon in which adsorbate molecules or ions (liquid or gas) are concentrated on the surface of a solid. It is a process of binding molecules or particles onto the external surface of solid or internal surface, if the material is porous in a very thin layer (Kandasamy et al., 2011). The binding to the solid are usually weak and reversible. The substance that accumulates at the interface is called ‘adsorbate’ and the solid on which adsorption occurs is known as ‘adsorbent’ (Bhatnagar & Sillanpää, 2010). Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. Separation occurs because of differences in molecular weight, shape or polarity, causes some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid (Elgeundi, 1991). In the adsorption process, dye molecules may be adsorbed on the surface of an adsorbent through several forces such as hydrogen bonding, electrostatic interactions, van der Waals forces, hydrophobic interactions etc. Generally, adsorption process is classified as physisorption and chemisorption (Kandasamy et al., 2011).

Physisorption is a type of adsorption in which the forces of attraction are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and do not involve a significant change in the electronic orbital patterns of the species involved. The adsorbed molecules are not fixed to a specific site at the surface of adsorbent but are free to undergo translational movement within the interface. It is predominant at low temperature and is characterized by relatively low energy of adsorption (Kalderis et al., 2008).

Chemisorption is adsorption in which the forces involved are forces of the same kind as those operating in the formation of chemical compounds. Generally, adsorbents possess porous structures to increase the total exposed surface area and allow fluid to pass through faster (Beyene, 2014).

Adsorption process is an attractive and effective alternative treatment for dye removal from wastewater (Sun et al., 2013). There are many advantages of adsorption process, such as:

- Less land area (half or a quarter of what is required in a biological system),
- Lower sensitivity to diurnal variation,
- Toxic chemicals do not affect the process,
- Greater flexibility in the design and operation,
- Superior removal of organic contaminants,
- High dye removal efficiency,
- Dose not form harmful substances, and
- Easy of operation

### 2.3.1. Factors affecting adsorption process

The initial dye concentration, solution pH, temperature, contact time and adsorbent dosage are usually the main factors that govern the performance of most of the adsorption process. Optimization of such conditions will greatly help in the development of industrial-scale dye removal treatment process. Some of the factors affecting adsorption of dyes are discussed below.

### *Effect of dye concentration*

The amount of adsorption for dye removal is highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. In general, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand, the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration (Yagub et al., 2014).

### *Effect of contact time*

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases (Indra D Mall et al., 2006).

### *Effect of adsorbent dose*

Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions. Generally, removal efficiency increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. The effect of adsorbent dosage gives an idea for the ability of a dye sorption to be adsorbed with the smallest amount of adsorbent, to recognize the capability of the adsorbent from an economical point of view (Sartape et al., 2014).

### *Effect of solution pH*

Another important factor affecting the capacity of adsorbent in dye removal is solution pH. The efficiency of adsorption is dependent on the solution pH, since variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent (Yagub et al., 2014). pH value of the solution will determine the surface charge of the adsorbent which will affect the interaction between the adsorbate and adsorbent. There are two possible mechanisms for the effect of pH on adsorption of dyes on any adsorbent: electrostatic interaction between the protonated or deprotonated groups of adsorbents with dyes, and the chemical reaction between the adsorbate and the adsorbent. The hydrogen ion and hydroxyl ions are adsorbed quite strongly, and therefore, the adsorption of other ions is affected by the pH of the solution. The change of pH affects the adsorptive process through dissociation of functional groups on the active sites of the adsorbent. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process. It is a common observation that the surface adsorbs anions favorably at lower pH due to presence of $H^+$ ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of $OH^-$ ions (Amran et al., 2011).

### *Effect of temperature*

Temperature is also a significant physico-chemical process parameter because temperature will change the adsorption capacity of the adsorbent. If the amount of adsorption increases with increasing temperature, then the adsorption is an endothermic process. This may be due to increasing mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature. Whereas the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process. This may be due to increasing temperature decreases the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result decreasing the amount of adsorption (Yagub et al., 2014).

### 2.3.2. Types of adsorbents

Adsorbents can be classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities (Babel & Kurniawan, 2003). Synthetic adsorbents are adsorbents prepared from Agricultural products and wastes, household wastes, industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces (Crini, 2006; Rafatullah et al., 2010). Many waste materials used include fruit wastes, coconut shell (Wong et al., 2013), sawdust (Malik, 2004), rice husk (Malik, 2003; Dalai et al., 2015; Mane et al., 2007), fertilizer wastes, bagasse fly ash (Vinod K Gupta & Ali, 2000; Kanawade, 2010; Rastogi et al., 2008), clays (Babel & Kurniawan, 2003), red mud, zeolites, sediment and soil, ore minerals etc. The removal of dyes from water and wastewater is generally carried out by adsorption using activated carbon, low cost adsorbents and other types of adsorbents (Rafatullah et al., 2010).

***Activated carbon***

Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus have a very large surface area available for adsorption or chemical reactions. Activated carbons are well known for their high surface area (up to 3000 $m^2$ $g^{-1}$) and great adsorption ability for all kind of pollutants. The excellent adsorption abilities and economic promise of activated carbons can be attributed to their origin from natural materials such as biomass, lignite and coal, which exhibit high sorption properties (Rafatullah et al., 2010). In aqueous solution, an electric charge is generated on the surface of activated carbon, either due to dissociation of the functional group of the carbon or due to the adsorbed ions which greatly depend on the solution conditions such as surface characteristics and solution pH. Various kinds of atoms or functional groups can be found on the surface of activated carbon which are responsible for adsorption, such as hydroxyl, carboxylic and epoxy, depending on the source of precursor materials (Ahmad et al., 2015).

### *Low cost adsorbents*

Activated carbon has been popular choice as an adsorbent for the removal of a variety of contaminants from wastewater. In spite of that, there is a major disadvantage of high cost regeneration, associated with it to allow for further use. Therefore, there is a need for the development of low cost and easily available materials, which can be used more economically on large scale. Due to the problems mentioned above, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years (Rafatullah et al., 2010). Attention has focused on various natural solid materials, which are able to remove pollutants from the contaminated wastewater at low cost. The cost is actually an important parameter for the comparison and selection of adsorbents. An adsorbent can be considered as low cost if it requires little processing and abundant in nature. It may also be defined as a by-product or waste material from the industry and needs additional disposal cost. Certain waste products from industries and agricultural operations, natural materials and bioadsorbents represent potentially economical alternative adsorbents (Mohan et al., 2002). Some low cost adsorbents are discussed below.

*Natural materials*

*Clays*: The clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks and water and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. The clays invariably contain exchangeable ions on their surface and play important role in the environment by acting as a natural scavenger of pollutants by taking up cations and/or anions either through ion exchange or adsorption or both. The prominent ions found on clay surface are $Ca^{2+}$, $Mg^{2+}$, $H^+$, $K^+$, $NH_4^+$, $Na^+$, and $SO_4^{2-}$, $Cl^-$, $PO_4^{3-}$, $NO_3^-$. These ions can be exchanged with other ions easily without affecting the structure of clay mineral (Rafatullah et al., 2010).

*Zeolites and other siliceous materials*: Zeolites are highly porous aluminosilicates with different cavity structures. They consist of a three dimensional framework, having a negatively charged lattice. High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites more attractive adsorbents (Babel & Kurniawan, 2003). The use of natural siliceous adsorbents such as silica, glass fibers and perlite for wastewater is increasing because of their high abundance, easy availability and low cost. Among inorganic materials, amorphous silica deserves particular attention, 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 adsorbents for decontamination (Babel & Kurniawan, 2003).

*Bioadsorbents*

The accumulation and concentration of dyes from aqueous solutions by the use of biological materials is termed bioadsorption. Biomass used as an adsorbent in order to remove dye from solutions. The bioadsorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce dye concentration to small levels (Rafatullah et al., 2010).

*Agriculture and industry waste materials and by-product*

*Agricultural solid wastes*: Agricultural materials are basically composed of cellulose, hemicellulose, lignin, lipid, protein etc. and due to the presence of cellulose most of these materials show good sorption capacity for various pollutants. Agricultural waste materials are preferred due to their unique chemical composition, availability in abundance, renewable nature and low cost (Ramesh, 2013). In addition, with their being economic and eco-friendly are viable option for water and wastewater remediation. Also it is a rich source for activated carbon production due to its low ash content and reasonable hardness, therefore, conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems and also to reduce the preparation costs (Bhatnagar & Sillanpää, 2010).

Previously, various agricultural wastes have been explored as low-cost adsorbent. Some of them include leaves, fibers, fruits peels, seeds etc. and waste materials from forest industries such as sawdust, rice husk, papaya seeds, bark etc. have been used as adsorbents. These materials are available in large quantities and may be potential adsorbents due to their physico-chemical characteristics and low cost (Crini, 2006).

*Industrial solid wastes*: Industrial solid wastes such as sludge, bagasse fly ash, red mud etc. are classified as low-cost materials because of their low cost and local availability and can be used as adsorbents for dye removal. Among the various adsorbents used for removal of dyes the bagasse fly ash is an effective adsorbent (Rafatullah et al., 2010).

## 2.4. Bagasse fly ash

Bagasse fly ash is a waste collected from the particulate separation equipment attached to the flue gas line of the sugarcane bagasse-fired boilers (Taha, 2006) . Sugar industry produces 30% bagasse for each lot of crushed sugar cane, the potential production capacity of burnt sugarcane bagasse residue is around 7–8% of total bagasse consumed (Madurwar et al., 2014). The high percentage of silica and alumina in bagasse fly ash make it a good candidate for utilization as an inexpensive adsorbent for bulk use (Kharade et al., 2014).

The bagasse fly ash is currently being used as filler in building materials (Kharade et al., 2014). It has been used previously for the COD removal from sugar mill and paper mill effluents (Lakdawala et al., 2012). Various researchers have utilized it for the adsorptive removal of phenolic compounds, metals and dyes (Indra Deo Mall et al., 2005).The major components in bagasse fly ash are shown in Table 2.2.

**Table 2.2** Composition of bagasse fly ash (Kharade et al., 2014).

| **Description of Properties** | **Percentage (%)** |
|---|---|
| Silica ($SiO_2$) | 59.5 - 86.0 |
| Alumina ($Al_2O_3$) | 7.0 - 14.26 |
| Calcium (CaO) | 2.0 - 11.67 |
| Iron ($Fe_2O_3$) | 2.2 - 4.56 |
| Potassium ($K_2O$) | 3.57 - 4.04 |
| Sodium ($Na_2O$) | 1.05 - 3.14 |
| Magnesium (MgO) | 0.85 - 2.3 |

Indra, Vimal et al. studied the adsorptive removal of MG dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses. Batch adsorption studies were conducted to evaluate the effect of various parameters such as pH, adsorbent dose, contact time and initial MG concentration on the removal of MG. The initial pH of the dye solution strongly affected the chemistry of both the dye molecules and adsorbents in an aqueous solution. Equilibrium reached in about 4 h contact time. The adsorption followed pseudo-second-order Kinetics (Indra Deo Mall et al., 2005).

The removal of lead and copper from aqueous solution by bagasse fly ash was investigated under various experimental conditions, e.g. contact time, pH and temperature. The level of uptake of $Pb^{2+}$ and $Cu^{2+}$ by the fly ash generally increased, but not in a progressive manner, at higher pH values. The effect of temperature on the uptake of $Pb^{2+}$and $Cu^{2+}$ revealed that the adsorption was enhanced on lowering the temperature. The experimental results emphasized the potential of fly ash for the recovery of metal ions from wastewater. The main mechanisms involved in the removal of heavy metal ions from solution were adsorption at the surface of the fly ash and precipitation (Gupta & Ali, 2004).

Zinc removal from aqueous solutions using bagasse fly ash has also been done. The fly ash was converted into an efficient adsorbent. The removal of $Zn^{2+}$ reached 100% at low concentration and 60-65% at higher concentration at an optimum pH of 4, using 10g/L of adsorbent in 6-8 h of equilibration time. The uptake decreases with increasing temperature. In addition, cadmium and nickel were also removed from wastewater with 90% efficiency in about 60 and 80 min respectively. The optimum PH value was 6.0 and 6.5, respectively. A dose of 10g/L was sufficient for both metal ions (Vinod K Gupta & Sharma, 2003).

The bagasse fly ash has also been used for the removal of pesticides, lindane and malathion from wastewater. The optimum contact time needed to reach equilibrium was found to be 60 min. maximum removal takes place at a pH of 6. The removal improved with an increase in adsorbent dose and decrease with particle size. The optimum adsorbent dose is 5 g/L of particle size 250 microM. 97-98% removal of the two pesticides was achieved at optimum condition. The material followed both Langmuir and Freundlich models (Vinod et al., 2002).

### 2.4.1. Availability of bagasse fly ash in Ethiopia

Assessment of the availability of bagasse fly ash can be made by rough estimation of the bagasse fly ash generated in the currently operating sugar factories in the country. These are Wonji/Shoa, Methara and Finachaa. It’s planned to increase the capacity of these plants as a consequence, the new expected capacity of the plants is taken for calculation. On average, the amount of sugar produced from a certain amount of cane sugar is only 12.4%. The bagasse produced from processing cane sugar is about 30% while out of that 8% of the bagasse is returned as bagasse fly ash from the boiler. The expected new production capacity of the major sugar industries is in Table 2.3.

**Table 2.3** Amount of BFA available in Ethiopia.

| Factory | Total annual sugar production capacity (ton/year) | Total cane sugar used (ton/year) | Bagasse available (ton/year) | Bagasse fly ash available (ton/year) |
|---|---|---|---|---|
| Wonji/Shoa | 1,437,500 | 11,592,742 | 3,477,822.58 | 278,225.81 |
| Methara | 1,219,000 | 9,830,645 | 2,949,193.55 | 235,935.48 |
| Finchaa | 2,760,000 | 22,258,065 | 6,677,419.35 | 534,193.55 |
| Total | 5,416,500 | 43,681,452 | 13,104,435.48 | 1,048,354.84 |

Hence the annual generation of bagasse fly as from these industries is 1,048,354.84 tons. But this annual production capacity of sugar is not sufficient to satisfy even the local sugar demand forcing the government to annually import 1.5 million quintals from abroad. To prevent this shortage of sugar, the government has plans of expanding the sugar industry by building 10 other sugar industries. These industries are on their construction phase and are expected to start operation in the next years. So the production of bagasse fly ash would increase more than double in the near future.

## 2.5. Adsorption isotherm models

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. It is the relationship that shows the distribution of adsorbate between the adsorbed phase and the solution phase at equilibrium (Banerjee & Sharma, 2013). If the adsorbent and adsorbate are contacted long enough, an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by adsorption isotherms. Equilibrium data can be analyzed using commonly known adsorption systems. Several mathematical models can be used to describe experimental data of adsorption isotherms. The most commonly used isotherms are the Langmuir and Freundlich isotherms (Karnitz et al., 2007).

### 2.5.1. Langmuir isotherm model

Langmuir adsorption isotherm is one of the most popular isotherm for the removal of heavy metals, dyes, organic pollutant by adsorption onto activated carbon, clay, agricultural waste, industrial waste, etc. It is valid for monolayer adsorption on specific homogenous sites containing a finite number of identical sites (Banerjee & Sharma, 2013). The basic assumptions underlying Langmuir's model which is also called the ideal localized monolayer model are that the molecules are adsorbed on definite sites on the surface of the adsorbent and each site can accommodate only one molecule (monolayer). The area of site is fixed, quantity determined solely by the geometry of the surface, and the adsorption energy is the same at all sites. In addition, the adsorbed molecules cannot migrate across the surface or interact with neighboring molecules. The Langmuir isotherm model estimates the maximum adsorption capacity produced from the complete monolayer coverage on the adsorbent surface. Based upon the above assumptions, Langmuir isotherm model equation can be represented by equation 2.1 (Ramachandran et al., 2011).

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad \ldots\ldots 2.1$$

Langmuir adsorption parameters were determined by transforming the above equation into linear form.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad \ldots\ldots 2.2$$

Where:

$q_e$ = amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g).

$q_m$ = maximum monolayer coverage capacity (mg/g)

$C_e$ = equilibrium concentration of adsorbate (mg/L)

$K_L$ = Langmuir isotherm constant (L/mg)

The values $q_m$ and $K_L$ can be computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter $R_L$, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Indra Deo Mall et al., 2005).

$$R_L = \frac{1}{1+(1+K_L C_o)} \quad \ldots\ldots 2.3$$

Where:

$R_L$= Langmuir equilibrium parameter

$C_0$ = initial concentration (mg/L)

$K_L$ = constant related to the energy of adsorption, Langmuir Constant (L/mg)

$R_L$ value indicates the adsorption nature to be either unfavorable if $R_L>1$, linear if RL =1, favorable if $0< R_L<1$ and irreversible if $R_L=0$.

### 2.5.2. Freundlich isotherm model

Freundlich isotherm model assumes that the adsorption occurs on a heterogeneous surface and non-uniform distribution of the heat of adsorption over the adsorbent surface takes place (Banerjee & Sharma, 2013). Freundlich equation suggests multilayer adsorption and the sorption energy exponentially decreased on completion of the sorption centers of an adsorbent. It is assumed that the stronger binding sites are initially occupied with the binding strength decreasing with increasing degree of site occupation (Sun et al., 2013).

The linearized form of Freundlich model is expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad \text{2.4}$$

Where:

$q_e$ = amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)

$C_e$ = equilibrium concentration of adsorbate (mg/L)

$K_f$ = Freundlich isotherm constant (mg/g)

n = adsorption intensity

## 2.6. Adsorption kinetics models

The dynamics of the adsorption can be studied by the kinetics of adsorption in terms of the order of the rate constant. The adsorption rate is an important factor for a better choice of material to be used as an adsorbent; where the adsorbent should have a large adsorption capacity and a fast adsorption rate. Most of adsorption studies used Pseudo-first-order and Pseudo-second-order models to study the adsorption kinetics (Amran et al., 2011).

### 2.6.1. Pseudo first-order kinetics model

Pseudo first-order kinetics model is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. The linear form of pseudo first-order rate is given in equation 2.5 (Ramachandran et al., 2011).

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \text{2.5}$$

Where:

$q_e$ and $q_t$ = adsorption capacity at equilibrium and at time t, respectively (mg/g)

$K_1$ = rate constant of pseudo first-order kinetics ($\text{min}^{-1}$)

The plot of log ($q_e$ – $q_t$) versus t should give a linear relationship from which $K_1$ and $q_e$ can be determined from the slop and intercept of the plot, respectively.

### 2.6.2. Pseudo second-order kinetics model

The adsorption kinetics was also described as pseudo-second order kinetics using equation 2.6.

$$\frac{\mathrm{t}}{\mathrm{qt}} = \frac{1}{\mathrm{K2qe}^2} + \left(\frac{1}{\mathrm{qe}}\right)\mathrm{t} \quad \text{2.6}$$

Where:

$q_e$ and $q_t$ = adsorption capacities at equilibrium and at time t, respectively (mg/g)

$K_2$ = rate constant of pseudo-second-order sorption (g/mg/min)

If Pseudo-second order kinetics are applicable, the plot of t/$q_t$ against t should give a linear relationship, from which $q_e$ and $K_2$ can be determined from the slope and intercept of the plot (Wahyu et al., 2011)

# 3. METHODOLOGY

## 3.1. Materials and Equipments

All chemicals used in this study are reagent grade and include; hydrogen peroxide, hydrochloric acid, sodium hydroxide, methylene blue ($C_{16}H_{18}N_3SCl$), malachite green ($C_{23}H_{25}N_2Cl$), and bagasse fly ash.

The major equipments used were UV-Vis spectrophotometer (Perkin Elmer 950), furnace (Box-type Resistance Furnace, Model SX-2f.12), centrifuge (Universal 320 R), orbital Shaker (Excella E24R), pH meter, digital balance, oven and sieving equipment. The laboratory wares used were volumetric flask, teflon sheets, vacuum desiccators, beaker, conical flask, micropipettes and burette.

## 3.2. Collection and pretreatment of bagasse fly ash

Bagasse fly ash was collected from Wonji/Shoa sugar factory located in Oromiya Regional State – North Eastern Ethiopia. The material was then washed with distilled water to remove dust, dirt, clay and other non-bagasse material. The cleaned BFA was sieved to fractionate the material into different particle sizes (<250 µm, between 250 µm and 500 µm, and between 500 µm and 850 µm). The needed particle size was treated with concentrated hydrogen peroxide (30% w/v) to remove heterogeneously distributed organic matter. The treatment was carried out at room temperature for a period of 24 hrs. Then, the pretreated bagasse fly ash was filtered, washed several times with distilled water and finally dried at 100°C for 24 hrs. Afterwards, pretreated fly ash were stored in polyethylene plastic bag till use. The treated bagasse fly ash, from now on, will be referred to as BFA.

## 3.3. Characterization of BFA

### 3.3.1. Proximate analysis of BFA

The proximate analysis of a substance is a means of determining the distribution of products obtained when the sample is heated under specified conditions. Proximate analysis (ash content (ASTM D 3174), volatile matter (ASTM D 3175), fixed carbon (ASTM D 3172) and moisture content) of the bagasse fly ash were measured using the method of ASTM (ASTM, 1989).

**Determination of ash content**

Ash is an inorganic residue remaining after the material has been completely burnt at a temperature of 600°C in furnace. It is the aggregate of all non-volatile inorganic elements. About 1 g of dried sample was weighed into a crucible ($W_1$) and incinerated at 600°C for 2 hrs in furnace. The crucible was cooled in desiccators and reweighed ($W_2$) (ASTM, 1989).

The % ash content of the sample was calculated as follows:

$$\text{Ash content } (\%) = \frac{W_2}{W_1} * 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. \ 3.1$$

Where:

$W_1$ = weight of sample before incineration (gram)

$W_2$ = weight of sample after incineration (gram)

**Determination of volatile matter**

About 1 g of dried sample was weighed into a crucible ($W_1$) and incinerated at 850°C for 10 minute in furnace. This procedure is undertaken without contact with air under standardized conditions. The crucible was then cooled in desiccators and reweighed ($W_2$) (ASTM, 1989).

The % volatile of the sample was calculated as follows:

$$\text{volatile matter} (\%) = \frac{W_1 - W_2}{W_1} * 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \ 3.2$$

Where:

$W_1$= weight of sample before incineration (gram)

$W_2$= weight of sample after incineration (gram)

**Determination of moisture content**

The moisture content of the sample was determined by weighing 1 g of sample into a pre-weighed crucible and drying it in an oven at a temperature of 105 ± 5 °C till the constant weight dry matter was obtained. The percentage moisture content was computed as follows:

$$\text{Moisture content } (\%) = \frac{W_1 - W_2}{W_1} * 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \ 3.3$$

Where:

$W_1$ = weight of sample before drying (gram)

$W_2$ = weight of sample after drying (gram)

#### Determination of fixed carbon content

Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture content, ash content, and volatile matter content subtracted from 100 (ASTM,1989).

Fixed carbon (%) = 100 – [moisture (%) + ash (%) + volatile matter (%)] ……………… 3.4

### 3.3.2 Surface functional group analysis by Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was carried out in order to identify the functional groups that might be involved in the binding of dye ions. The functional groups of bagasse fly ash (fresh and used) were determined using FTIR Spectrometer (Spectrum 65 FT-IR, PerkinElmer) at wave number range of 4000-400 cm$^{-1}$. First, the dried adsorbent was mixed with KBr particles to make it suitable to infrared analysis. The mixture was then pressed to a small thickness, slightly below 1 mm, required for FTIR analysis. FTIR analysis was done at Addis Ababa university, College of Natural Science, Chemistry Laboratory.

## 3.4. Malachite Green (MG) and Methylene Blue (MB) adsorption study

### 3.4.1. Adsorption experimental setups

Batch adsorption experiment was performed by contacting a certain concentration of dye with the BFA at specified process conditions. For this set of experiments, a 0.0050 M equimolar stock solution of MG and MB was first prepared and the needed concentrations were diluted from it in 250 ml volumetric flask. The pH of the solution was adjusted by using 0.1 M HCl and 0.1 M NaOH to bring to the required pH. The appropriate concentration of the dyes were mixed with the BFA and put on an orbital shaker at 200 rpm for different times. The solution obtained after adsorption were centrifuged at 5000 rpm for 10 min to separate the adsorbent from the supernatant. The supernatant is then measured for its remaining concentration using a UV/Vis spectrophotometer.

### 3.4.2. Analysis of MG and MB dyes concentration using UV/Vis spectrophotometer

To measure the concentration of MG and MB in aqueous solution using UV/Vis spectrophotometer, a calibration curve was needed to be set up. The calibration curve is constructed by preparing orderly increasing concentration solutions and measuring the absorbance of this solutions. MB absorbs UV/Vis light at a wavelength of 665 nm while MG absorbs at a wavelength of 617 nm. An absorbance versus concentration linear graph was drawn and equation of the straight line was determined. So samples from the absorption studies are brought and their absorbance measured. The concentration of the solutions was then determined from the calibration graph. For our case two calibration curves, for MB and MG were constructed.

### 3.4.3. Adsorption performance study

Various adsorption experiments were carried out to investigate the effects of the factors that influence the adsorption process.

#### 3.4.3.1. Effect of $H_2O_2$ pretreatment on the performance of BFA

The first experiment is to determine the effect of the treatment of the bagasse fly ash, a mixture of MB and MG solution with a concentration of 75 ppm was prepared. The prepared solution and 0.5 g bagasse fly ash (raw or treated) was mixed in a 500 ml flask and setup on the orbital shaker at room temperature. The agitation was stopped after 2 hrs and sample was taken. Before measuring the absorbance of the solution, centrifugation of the samples is needed. The concentration of the supernatant was measured using a UV/Vis spectrophotometer.

The next part of the experiment was to determine the adsorption capacity of the bagasse fly ash for the individual dyes; MB and MG. For testing of single dyes 40 ppm concentration of MG and 35 ppm concentration of MB was prepared. The prepared solutions were mixed with 0.5 g bagasse fly ash (treated) and put on an orbital shaker. The solutions were agitated for 2 hrs and samples were taken at the end of the process. The samples were centrifuged and their absorption measured using the UV/Vis spectrophotometer. The concentration is then calculated from their respective calibration curves.

#### 3.4.3.2. Interaction effects of process variables on performance of BFA

Adsorption study for the three factors of the study was carried out in the same way as the previous experiments. The effect of time, pH, and concentration of the dye was investigated.

The chosen concentrations are 50, 75, and 100 ppm of binary solution of MB and MG consisting of nearly half MB and half MG by mass but equal moles of the two dyes. An adsorbent dose of 0.5 g BFA was added in each of the prepared solutions and set up on the orbital shaker and samples were taken from each flask at times of 10 min, 30 min, 60 min, and 90 min. These experiments were done at solution pH of 6, 8 and 10.

The sample analysis was also carried out similarly; first samples were taken from the process at different times, concentration and pH and then centrifuged. The concentration of the supernatant was determined by UV/Vis spectrophotometer at the wavelength for maximum absorbance ($\lambda_{max}$) which is 617 nm and 665 nm for MG and MB, respectively.

After obtaining of the optimum time, pH and concentration from the above experiment for the removal of the mixture of dyes, the values were used to assess the effect of dye concentration and adsorbent dose. Finally, the adsorption capacity and removal efficiency were determined for all samples as follows. Dye concentration retained in the adsorbent can be calculated as: -

$$q_e = (C_o - C_e) * V/W \ldots\ldots 3.1$$

Percentage removal efficiency can be calculated as:

$$\% R = \frac{C_o - C_e}{C_o} * 100\% \ldots\ldots 3.2$$

Where:

Co and Ce = initial and equilibrium concentrations (mg/L) of the dye in solution, respectively

V= volume of the solution (L)

W = mass of dry adsorbent used (g)

### 3.4.3.3. Data analysis using Design Expert software

Data analysis also was performed by Design Expert 6.0.8 software using full factorial design. The experiment was designed to investigate the single and interaction effects of selected operating conditions (initial dye concentration, pH and contact time with constant adsorbent dose) on adsorption capacity and removal efficiency of the BFA. The analysis resulted in 36 experiments and the experiment were replicated two times to improve reliability of the data. The factors and levels are illustrated in Table 3.1.

**Table 3.1** Factors and levels of process variables.

| Factors | Level | | | |
|---|---|---|---|---|
| Concentration (ppm) | 50 | 75 | 100 | - |
| pH | 6 | 8 | 10 | - |
| Time (min) | 10 | 30 | 60 | 90 |

### 3.4.4. Determination of equilibrium time

Initial dye concentration of 50, 75 and 100 ppm and contact time of 10 min, 30 min, 1 hr, 2 hrs, 3 hrs, 4 hrs and 24 hrs with constant pH was used to determine equilibrium time of the adsorption process.

### 3.4.5. Effect of adsorbent dose

To study the effect of adsorbent dose on dye adsorption, another set of adsorbent doses were investigated. 1 g, 2 g, and 3 g were used with optimum concentration and pH of the mixture of the dyes. Samples were taken with a time of 1 hr, 2 hrs, 3 hrs and 4 hrs, centrifuged and measured for its absorbance in the UV/Vis spectrophotometer. The experiment was carried out at room temperature.

### 3.4.6. Effect of process variables at optimum BFA dose

The maximum adsorption capacity that could be achieved using optimum BFA dose for the removal of the mixture of dyes (MG and MB) was done repeatedly for different solution pH (6, 8, 10), dye concentration (50, 75, 100) with a contact time of 1, 2, 3 and 4 hrs. All experiments were performed in the same way as section 3.4.3.2.

### 3.4.7. Effect of higher dye concentration

The effect of dye concentration on the adsorption uptake of the bagasse fly ash was further investigated by taking higher concentration values than the preliminary adsorption analysis. Values for initial concentrations of 200, 300, 400 and 500 ppm were prepared using the mixture of dyes (MB and MG) and adsorption experiment was carried out at constant pH, time and adsorbent dose. The samples were taken from all tests and analyzed for their absorbance.

## 3.5. Adsorption isotherm models and kinetics

After the selection of the optimum values for the concentration, pH, and time, isotherms and kinetics of adsorption were studied. Different dye concentration of 50, 75 and 100 ppm were prepared and mixed with 0.5 gram per 250 ml of adsorbent. The adsorption processes were carried out until equilibrium is achieved. The results obtained from adsorption experiments were analyzed by Langmuir and Freundlich models.

The kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from the aqueous solution at different time intervals. The same adsorption kinetic data were treated with pseudo-first order kinetic model and pseudo-second order kinetic models.

# 4. RESULT AND DISCUSSION

## 4.1. Proximate analysis of BFA

The result of the proximate analysis done on the bagasse fly ash is tabulated in Table 4.1. Moisture content, ash content, volatile matter, fixed carbon and density was determined as a function of the particle size of BFA. The particle size that is going to be used for adsorption should be small enough for higher surface area. Larger surface area provides accessibility to the pores thereby improving the adsorption efficiency. Ash content was also used in the selection of the appropriate particle size of bagasse fly ash. Smaller particle size with larger ash content BFA is promising for the adsorption purpose.

**Table 4.1** Proximate analysis of bagasse fly ash with different particle size.

| | Particle size of bagasse fly ash (µm) | | |
|---|---|---|---|
| Proximate analysis (%) | 500 <BFA< 850 | 250 <BFA<500 | BFA< 250 |
| Moisture content | 7.8 | 6 | 6 |
| Ash content | 20.57 | 35.78 | 81.63 |
| Volatile matter | 25.77 | 21.38 | 4.9 |
| Fixed carbon | 47.66 | 36.84 | 7.47 |
| Density (g/cm$^3$) @ particle size <250 µm | | | 1.01 |

As shown in the table, particle size of bagasse fly ash less than 250 µm had high ash content (81.63%) and low volatile matter (4.9%). Fly ash consists of trace metals, with the main constituents being oxides, silicates, and aluminosilicates of calcium, iron, and other bases. Because these constituents, which are responsible for the adsorption process, the particle size of BFA that has the highest ash content is used for the subsequent experiments. Finally, the density of the adsorbent of particle size less than 250 µm was found to be 1.01 g/cm$^3$.

## 4.2. Adsorption performance of BFA

### 4.2.1. Effect of $H_2O_2$ treatment on BFA

Adsorption experiments were carried out after the pretreatment of BFA and before treatment to determine the influence of $H_2O_2$ treatment on the adsorption process. The tests were carried out using a 75 ppm of mixed dyes and 39.97 ppm of MG and 35.03 ppm of MB single dyes in aqueous solution using 0.5 g of adsorbent dose and at existing solution pH.

The result for both single dye aqueous solutions with treated BFA have higher capacity than the adsorption process using untreated BFA. The untreated bagasse fly ash contains inorganic and dirt materials with it therefore the actual active site available for the adsorption process is lower than the treated bagasse fly ash hence a lower performance due to filling of active sites.

The adsorption capacity for the mixed dye BFA (treated) is lower than the value for a single dye with BFA (treated). This may be due to some interaction between the two molecules as both are cationic dye, so that their interaction inhibit adsorption of both dyes on neighboring sites of the surface. The interaction between the dye and the adsorbent must have been similar for both treated and untreated adsorbents since the result shows just small improvement in adsorption capacity on the treated BFA than untreated. The involvement of organic, unwanted and dirt materials can be the reason for the reduced performance of the untreated BFA. The result is illustrated in Table 4.2.

**Table 4.2** Comparison of adsorption capacity for treated and untreated BFA.

| | $q_e$(mg/g) | |
|---|---|---|
| | **MG** | **MB** |
| Untreated bagasse fly ash (Single dye solution) | 8.135 | 7.045 |
| Treated BFA (Single dye solution) | 18.13 | 16.16 |
| Treated BFA (Binary dye solution ) | 14.33 | 11.65 |

### 4.2.2. Effects of process variables

#### 4.2.2.1. Data analysis using Design Expert software

Effect of concentration, pH, adsorbent dose and contact time on the adsorption capacity and removal efficiency was analyzed using Design-Expert 6.0.8 software in order to determine the significant of the model and the factors. Adsorption capacity and removal efficiency obtained from the experiment work was an input data for the software.

The significance of the model was justified by the analysis of variance (ANOVA). The ANOVA summary for MG is given in Table 4.3 the analysis was done by means of Fisher's 'F'-test. The model F-value observed was 320.508 enlightening that the model was significant. The parameters having an F-statistics probability value less than 0.05 are said to be significant. In this present study the probability of model F statistics value was <0.0001 indicating that the model suggested by the software was highly significant. In this case A, B, C, $A^2$, $B^2$, $C^2$, AB, AC, BC are are statistically significant ($P<0.05$) model terms at the 95 % confidence level.

**Table 4.3** Analysis of variance (ANOVA) for adsorption capacity for MG.

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 1626.22 | 9 | 180.691 | 320.508 | < 0.0001 | significant |
| A | 1215.81 | 1 | 1215.807 | 2156.593 | < 0.0001 | |
| B | 282.411 | 1 | 282.411 | 500.939 | < 0.0001 | |
| C | 53.7809 | 1 | 53.781 | 95.396 | < 0.0001 | |
| $A^2$ | 3.6784 | 1 | 3.678 | 6.525 | 0.0131 | |
| $B^2$ | 11.8599 | 1 | 11.86 | 21.037 | < 0.0001 | |
| $C^2$ | 22.988 | 1 | 22.988 | 40.776 | < 0.0001 | |
| AB | 13.2596 | 1 | 13.26 | 23.520 | < 0.0001 | |
| AC | 34.2068 | 1 | 34.207 | 60.676 | < 0.0001 | |
| BC | 6.49067 | 1 | 6.491 | 11.513 | 0.0012 | |
| Residual | 34.9533 | 62 | 0.564 | | | |
| Lack of Fit | 31.2774 | 26 | 1.203 | 11.781 | < 0.0001 | significant |
| Pure Error | 3.67591 | 36 | 0.102 | | | |
| Cor Total | 1661.17 | 71 | | | | |

A= concentration, B= time, C= pH

The ANOVA summary for MB is given in Table 4.4. The analysis was done similar to MG (Fisher's 'F'-test). The model is significant with F-value of 139. 252. The parameters having an F-statistics probability value less than 0.05 are said to be significant. In this present study, the probability of model F statistics value was <0.0001 indicating that the model suggested by the software was highly significant. In this case A, B, C, $C^2$, AB, AC, BC are significant ($P<0.05$) model terms at the 95 % confidence level.

**Table 4.4** Analysis of variance (ANOVA) for adsorption capacity for MB.

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 1083.712 | 9 | 120.412 | 139.252 | $< 0.0001$ | significant |
| A | 746.8367 | 1 | 746.837 | 863.684 | $< 0.0001$ | |
| B | 210.5867 | 1 | 210.587 | 243.534 | $< 0.0001$ | |
| C | 58.17652 | 1 | 58.177 | 67.279 | $< 0.0001$ | |
| $A^2$ | 0.862886 | 1 | 0.863 | 0.998 | 0.3217 | |
| $B^2$ | 2.47007 | 1 | 2.470 | 2.857 | 0.0960 | |
| $C^2$ | 17.85626 | 1 | 17.856 | 20.650 | $< 0.0001$ | |
| AB | 8.850838 | 1 | 8.851 | 10.236 | 0.0022 | |
| AC | 31.70867 | 1 | 31.709 | 36.670 | $< 0.0001$ | |
| BC | 11.08716 | 1 | 11.087 | 12.822 | 0.0007 | |
| Residual | 53.61206 | 62 | 0.865 | | | |
| Lack of Fit | 39.76449 | 26 | 1.529 | 3.976 | $< 0.0001$ | significant |
| Pure Error | 13.84756 | 36 | 0.385 | | | |
| Cor Total | 1137.324 | 71 | | | | |

A= concentration, B= time, C= pH

*Regression modeling and Model analysis*

The dye adsorption capacity of BFA from aqueous solution on the interaction of three process factors (initial dye concentration (A), contact time (B) and pH (C)), were used for the model generation. The output of different model summary statistics, shown in Table 4.5 and 4.6, focus on obtaining larger Adjusted R-Squared and the Predicted R-Squared values so that model accuracy can be maximized. Therefore, quadratic model is suggested for model generation. Moreover, as shown in the Table 4.5, for MG, "Pred R-Squared" of 0.9716 is in reasonable agreement with the "Adj R-Squared" of 0.9759. In addition, as shown in the Table 4.6, for MB, "Pred R-Squared" of 0.9355 is in reasonable agreement with the "Adj R-Squared" of 0.9460. Similar trend was observed for both dyes adsorption experiment.

**Table 4.5** Model summary statistics for MG.

| Model type | Std. Dev. | R. squared | Adjusted R. squared | Predicted R. squared |
|---|---|---|---|---|
| Linear | 1.37 | 0.9233 | 0.9199 | 0.9134 |
| 2FI | 1.06 | 0.9558 | 0.9517 | 0.9472 |
| Quadratic | 0.75 | 0.9790 | 0.9759 | 0.9716 |

**Table 4.6** Model summary statistics for MB.

| Model type | Std. Dev. | R. squared | Adjusted R. squared | Predicted R. squared |
|---|---|---|---|---|
| Linear | 1.36 | 0.8888 | 0.8839 | 0.8737 |
| 2FI | 1.07 | 0.9342 | 0.9282 | 0.9187 |
| Quadratic | 0.93 | 0.9529 | 0.9460 | 0.9355 |

Regression analysis was performed to fit the response functions, i.e. MG adsorption capacity of BFA. An empirical relationship between the response and the input test variables in actual units can be expressed by the following equation:

**Adsorption capacity** = -9.55515 - 0.11318*Concentration + 0.024237*Time + 3.47148*pH + 7.67167E-4*Concentration$^2$-5.94202E-4*Time$^2$-0.29966*pH$^2$+6.93594E4*Concentration*Time +0.020678*Concentration*pH+6.06590E-3*Time*pH

Similarly, regression analysis was performed to fit the response functions, i.e. MB adsorption capacity of BFA. An empirical relationship between the response and the input test variables in actual units can be expressed by the following equation:

**Adsorption capacity** = -17.81105 + 0.026447*Concentration + 0.10448 * Time +3.68123 * pH - 3.71567E-4*Concentration$^2$ - 2.71174E-4*Time$^2$ - 0.26410*pH$^2$ + 5.66673E-4*Concentration * Time +0.019909 * Concentration * pH -7.92795E-3* Time * pH

### 4.2.2.2. Effect of independent process variables on performance of BFA

#### Effect of dye concentration

The effect of the initial concentration of MB and MG dyes on the adsorption efficiency of the bagasse fly ash was evaluated at concentrations of 50, 75 and 100 ppm. When the initial concentrations of MG and MB were increased from 50 to 100 ppm the amount of dye adsorbed per unit weight of the adsorbent ($q_e$, mg/g), at constant adsorbent dose of 0.5 gram, pH of 10 and 90 minute, increased from 8.38 mg/g to 21.16 mg/g for malachite green and from 6.38 mg/g to 16.59 mg/g for methylene blue (Fig. 4.1). These may be due to the greater availability and interaction of the sorbent molecules with the existing pores at higher concentration of the sorbent. From the dye concentration study, the maximum removal efficiency of 79.39% and 71.05% and adsorption capacity for malachite green and methylene blue dyes is observed at a concentration of 100 ppm respectively.

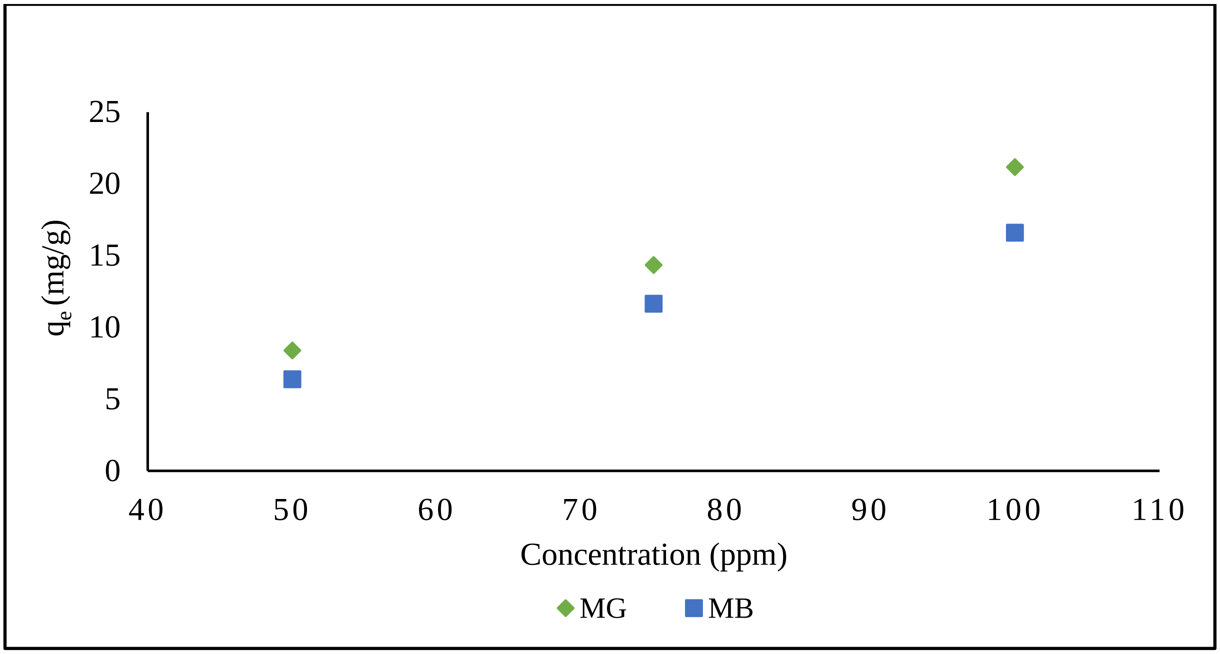


**Figure 4.1** Effect of initial dye concentration on adsorption capacity for MG and MB.

Figure 4.1 also shows the comparison of adsorption capacity for the two dyes at the same concentration. It shows that MG is more adsorbed per unit mass than MB, the difference in the adsorption capacity for the two dyes may be explained using the molecular structure of the dye molecule and morphology of the adsorbent. The pore size of the adsorbent may be more compatible with the molecular size and shape of the MG dye molecule.

### Effect of contact time

The effect of contact time on the adsorption capacity of both dyes was investigated at initial dye concentrations of 50, 75 and 100 ppm. For the investigation, again 0.5 gram per 250 ml of adsorbent dose and pH = 10 was used. The results show an increase in the adsorption capacity as the time of contact increases (Fig. 4.2 and 4.3). This is understandable because of the existence of an equilibrium for the process of adsorption, the process will continue until all active sites (pores) are filled with dye molecules. In addition, the adsorption process will be fast at the beginning due to availability of large area then the process will slow down as more pores are filled by molecules. The adsorption capacity increased from 13.48 mg/g to 21.16 mg/g for MG and from 11.48 mg/g to 16.59 mg/g for MB as time increased from 10 to 90 minute. The maximum adsorption capacity was found at 90 minute and 100 ppm concentration.

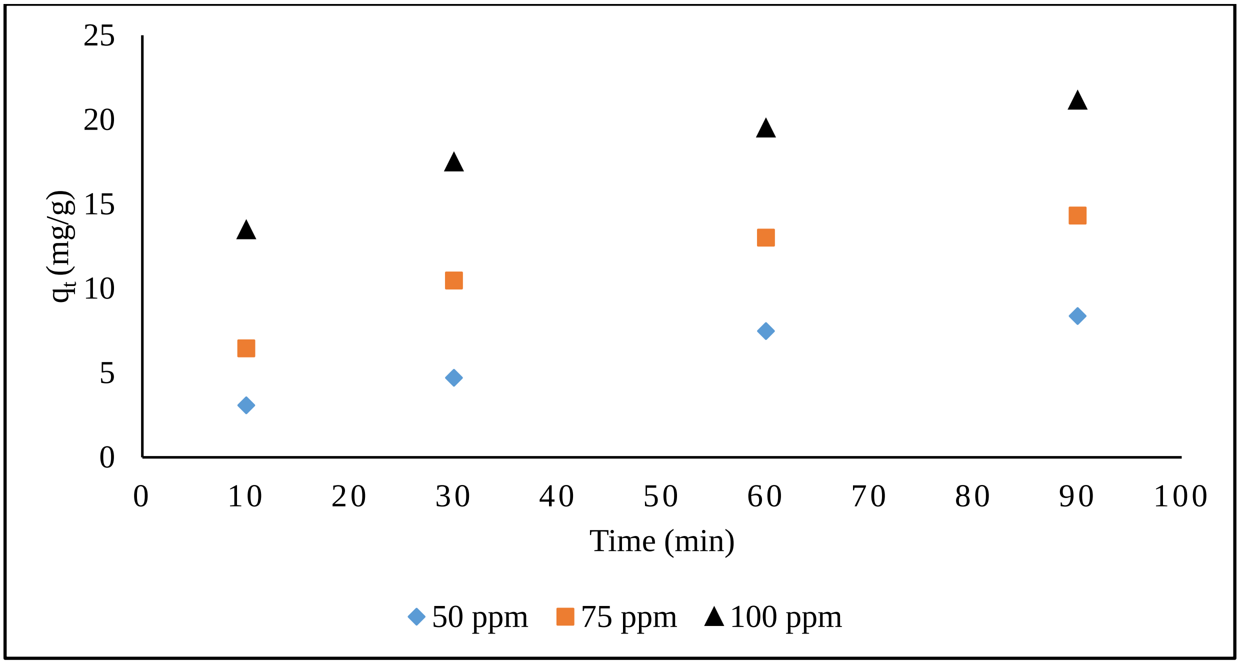


**Figure 4.2** Effect of contact time on adsorption capacity for MG.

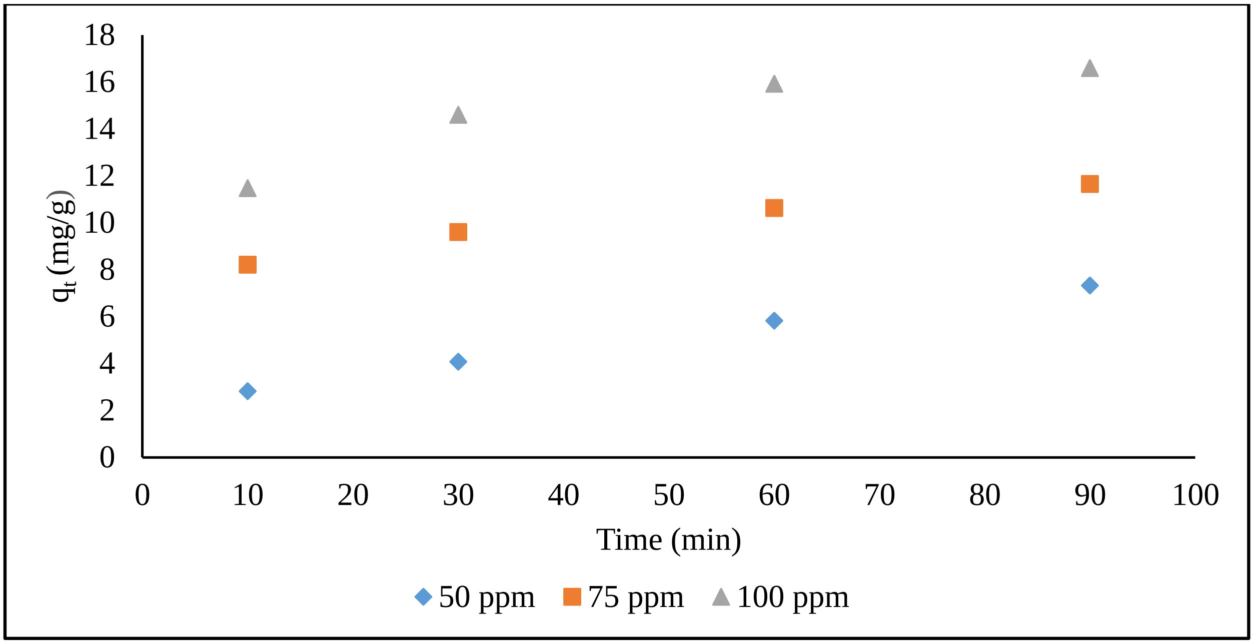


**Figure 4.3** Effect of contact time on adsorption capacity for MB.

**Effect of solution pH**

The pH of the dye solution plays an important role in the adsorption process, hence on the adsorption capacity. To reveal the effect of solution pH on the adsorption capacity of BFA, the adsorption process was carried out at different pH (6, 8, and 10).

As shown in Fig. 4.4., the adsorption capacity increased from 15.58 mg/g to 21.16 mg/g for malachite green dye and from 9.20 mg/g to 16.59 mg/g for methylene blue dye as the pH increased from 6 to 10. In terms of removal efficiency, a maximum value of 79.397 % was observed for malachite green and 71.051 % for methylene blue at initial concentration of 100 ppm, 0.5-gram adsorbent dose after 90 min of contact time. For both dyes the maximum adsorption capacity was attained at a pH of 10.

The reason for increasing adsorption capacity with increasing alkalinity may be because both dyes are cationic dyes and are protonated in the acidic medium and deprotonated at higher pH. At lower pH, the number of positively charged adsorbent surface sites increased at the expense of the number of negatively charged surface sites. The carboxylic groups of dyes were protonated and had high positive charge density at a lower pH (Seey et al., 2012). Consequently, electrostatic repulsion between the positively charged surface and the positively charged dye molecule increased with decreasing solution pH and hence resulting in the decrease of adsorption capacity of dyes to the adsorbent.

In addition, the competition of $H^+$ ion with the cationic dye molecules also decreased the adsorption. On the contrary, the functional groups such as hydroxyl and carbonyl groups can act as biosorbing agents or sites with negative charges. The surface of the adsorbent was negatively charged at higher pH, which favored for adsorption of the positively charged dye molecules through electrostatic force of attraction. If we compare this result with other research articles, similar result can be obtained with respect to pH. In many papers it is observed that cationic dyes are adsorbed efficiently at higher pH and vice versa, also in this paper a maximum adsorption capacity observed at pH of 10 (Gong et al., 2013; Indra D. et al., 2006; Jain &Arvind Kumar, 2008).

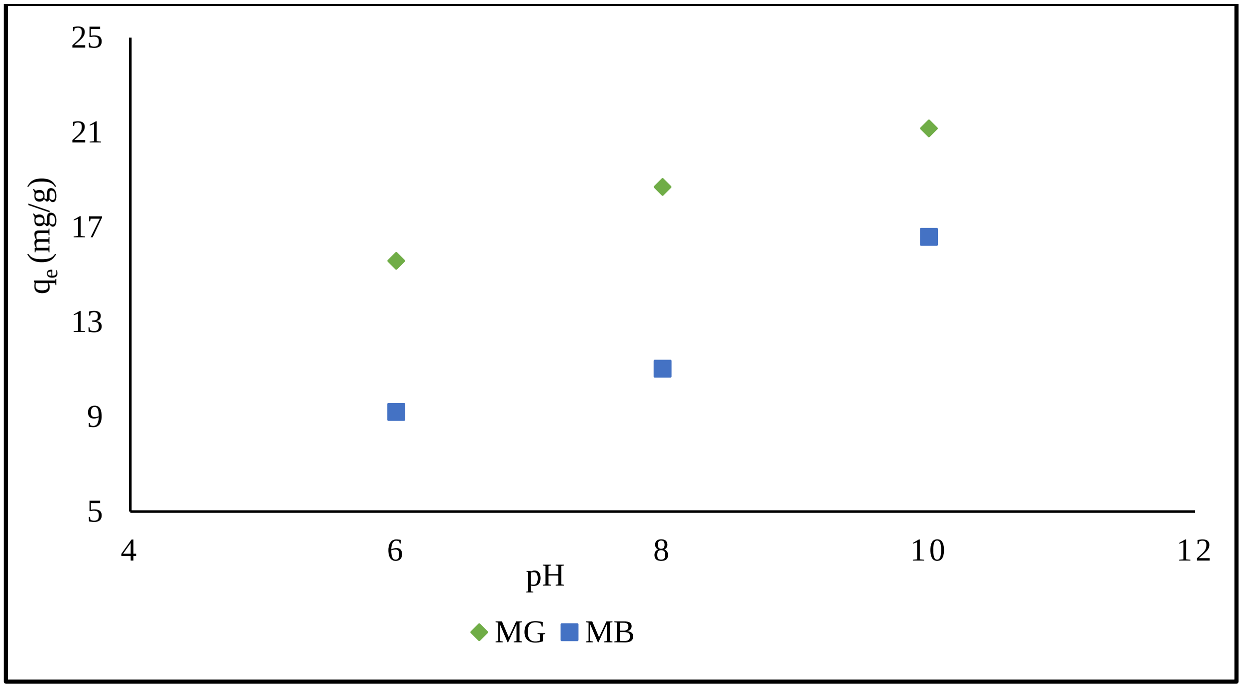
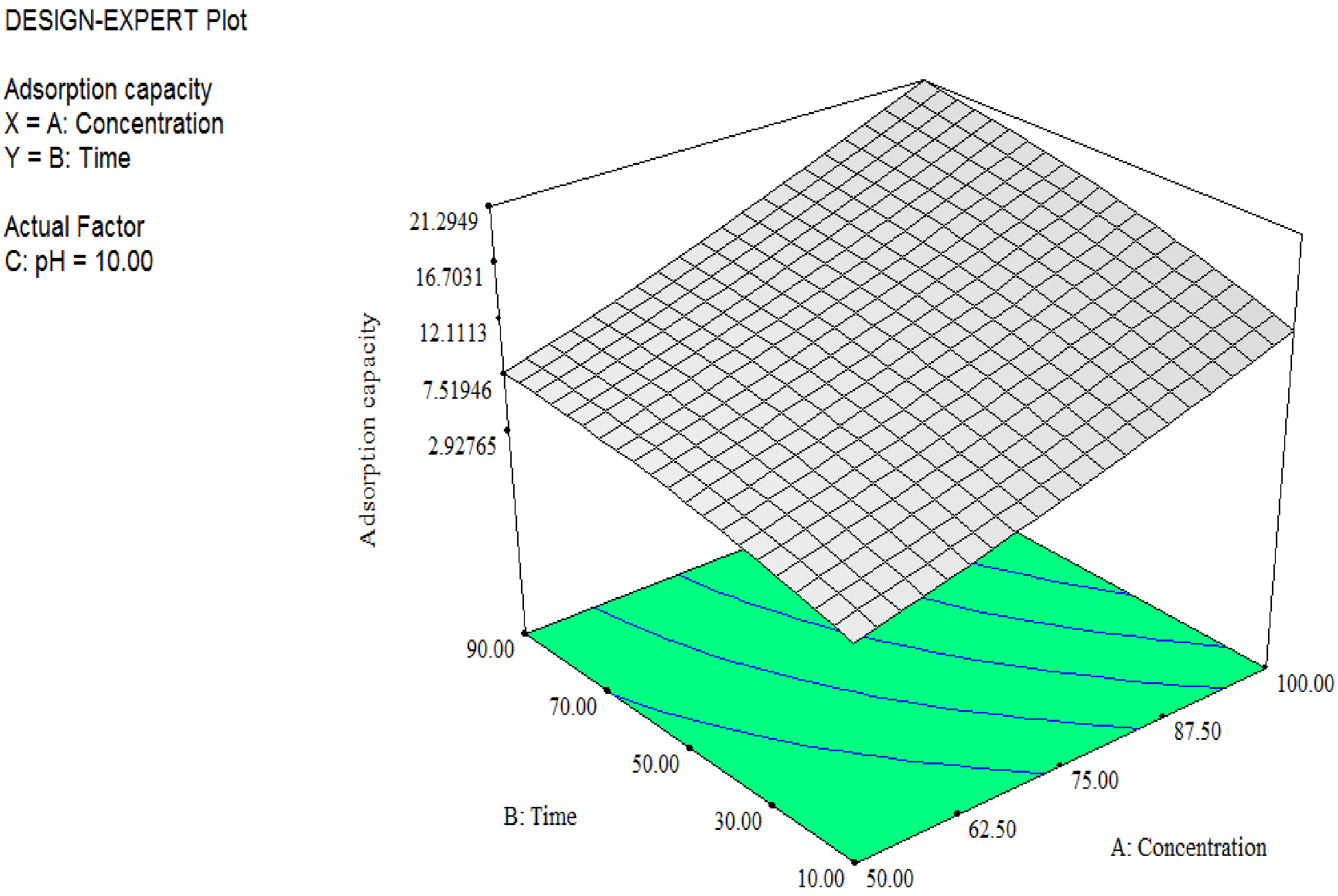


**Figure 4.4** Effect of pH on adsorption capacity for MG and MB.

#### 4.2.2.3. Interaction effects of process variables on adsorption performance of BFA

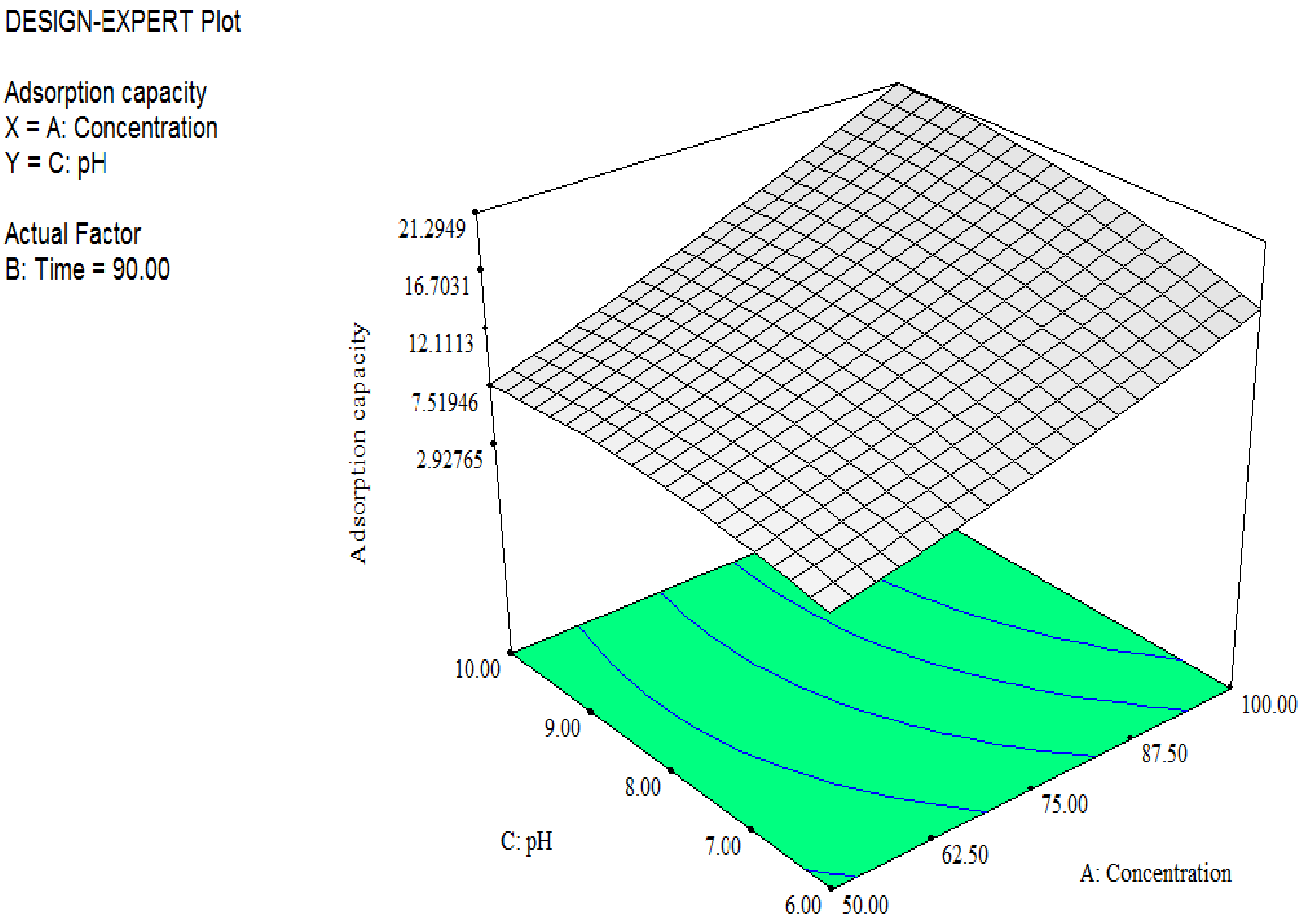
*Interaction effects of process variables on adsorption of MG*

The interaction effect of time and concentration is increasing the adsorption capacity of BFA as both parameters increase with constant pH of 10, as shown in Fig. 4.5(a). The effect of increasing the concentration on the adsorption capacity show a pronounced increase than time. The maximum adsorption capacity of 21.29 mg/g was obtained at time of 90 min and 100 ppm concentration and minimum value was observed at the 50 ppm concentration and 10 min time with a value of 3.09 mg/g.



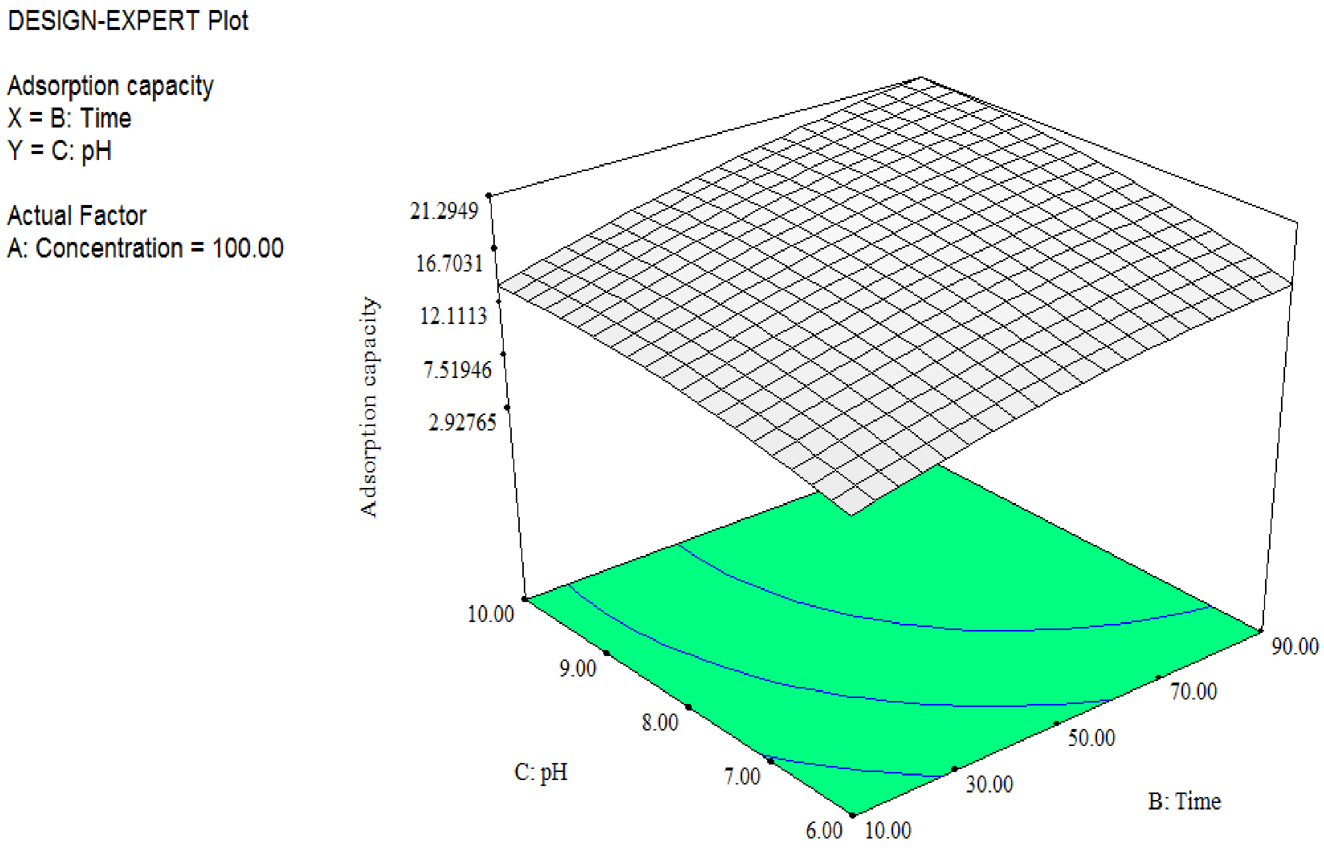
a)

The interaction effect of pH and concentration was seen in Fig. 4.5(b) at constant time of 90 min. The result indicates that increasing both concentration and pH improves the adsorption capacity but the contribution of concentration is more significant than pH. The maximum value was observed when solution pH is 10 and concentration is 100 ppm, 21.29 mg/g while the minimum is obtained at pH 6 and 50 ppm concentration, 3.74 mg/g.



**b)**

The overall effect of pH and time was also shown in Fig. 4.5(c) at constant concentration of 100 ppm. The result can be explained as increasing both time and pH improves the adsorption capacity but the contribution of time is more significant than pH in comparison. The maximum adsorption capacity is observed at largest time (90 min) and alkaline condition (pH 10), it has a value of 21.29 mg/g while the minimum is at slightly acidic condition (pH 6) and smallest time (10 min) with a value of 10.0 mg/g.



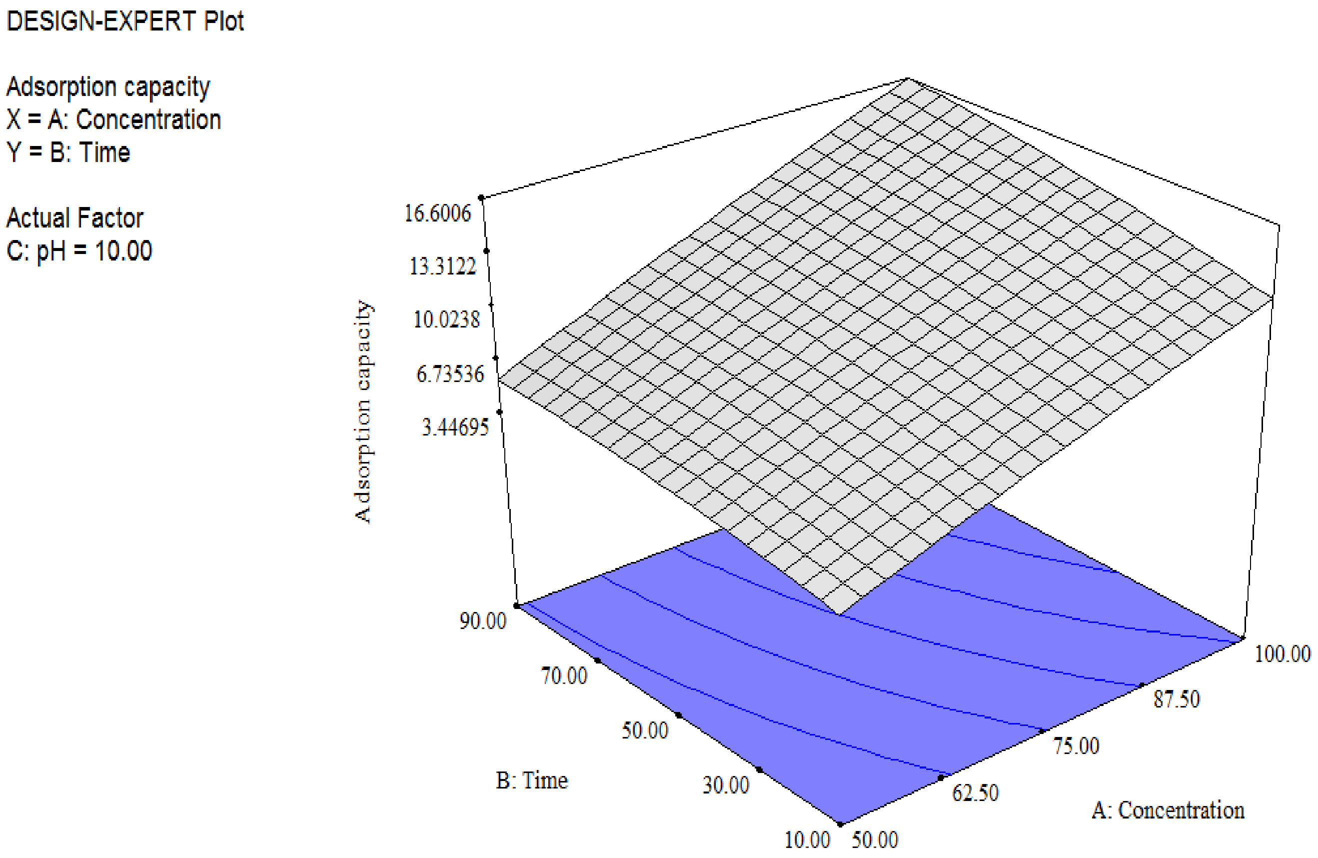
c)

**Figure 4.5** Interaction effects of process variables on adsorption capacity (3D surface plot) for MG.

a) Interaction effect of concentration and time b) Interaction effect of concentration and pH and c) Interaction effect of time and pH

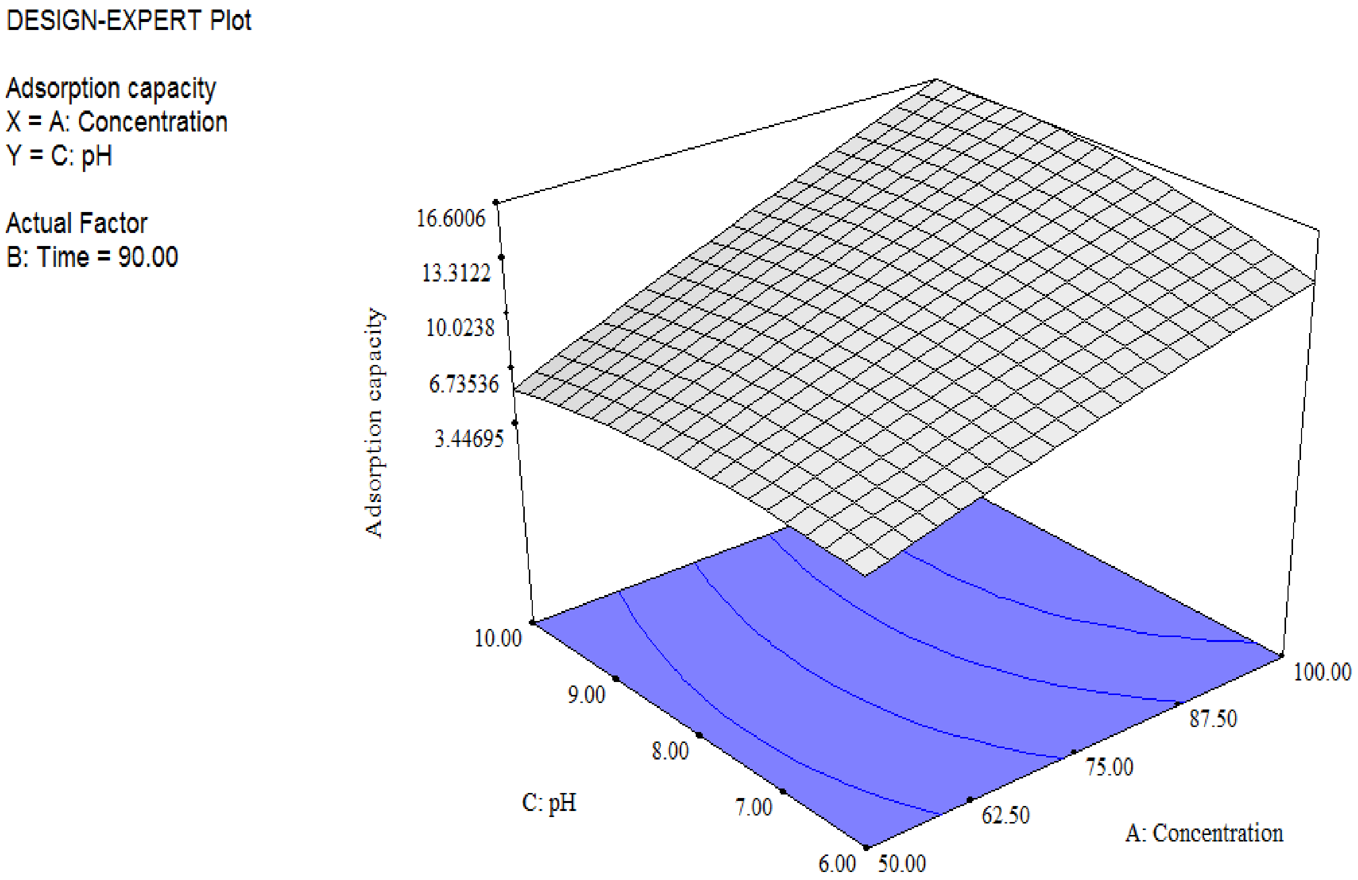
*Interaction effects of process variables on adsorption capacity for MB*

As shown in Fig 4.6(a), the adsorption capacity of BFA increased as both time and concentration increase with constant pH of 10. The effect of concentration on the adsorption capacity was significant than time. The maximum adsorption capacity of 16.60 mg/g was obtained at time of 90 min and 100 ppm concentration and minimum value was observed at 50 ppm concentration and 10 min time with a value of 2.82 mg/g.



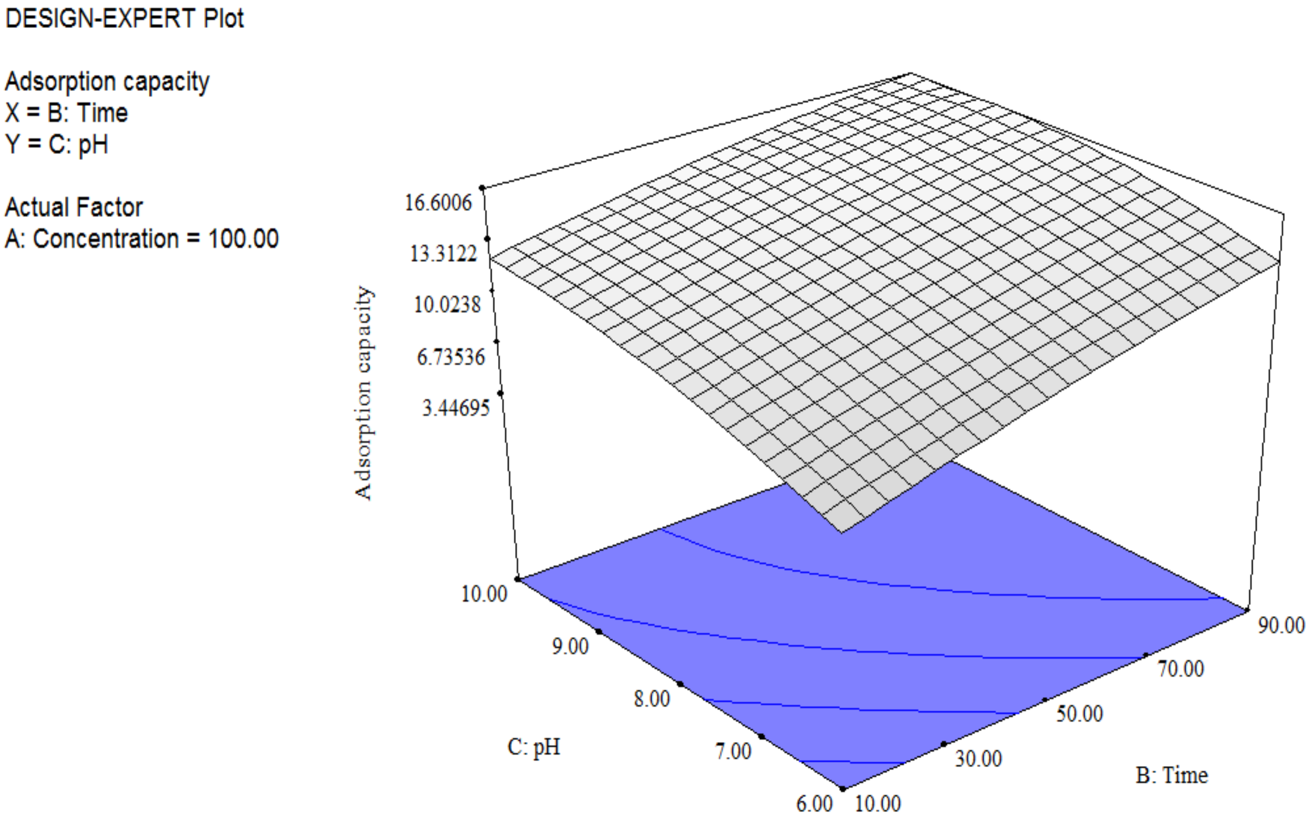
**a)**

The interaction effect of concentration and pH was shown in Fig. 4.6(b) at constant contact time of 90 min. The maximum adsorption capacity of 16.60 mg/g was found when solution concentration is 100 ppm and pH is 10. The minimum absorption capacity of 3.16 mg/g was observed at 50 ppm concentration and pH 6. The result indicates that increasing both concentration and pH improves the adsorption capacity but the contribution of concentration is more significant than pH similar to MG.



**b)**

At constant 100 ppm concentration, interaction effect of pH and time was also shown in Fig. 4.6(c). The result can be explained as increasing both time and pH improves the adsorption capacity but the contribution of time is more significant as compared to pH. The maximum adsorption capacity is observed at contact time of 90 min and pH of 10, it has a value of 16.60 mg/g while the minimum is at pH 6 and smallest time (10 min) with a value of 5.68 mg/g.



**c)**

**Figure 4.6** Interaction effects of process variables on adsorption capacity (3D surface plot) for MB

a) Interaction effect of concentration and time b) Interaction effect of concentration and pH and c) Interaction effect of time and pH

*Model adequacy test using ANOVA*

The adequacy of the model was also justified by the analysis of variance (ANOVA). The fitting of the experimental data to the regression model was checked and suitably explained by the value of the adjusted determination coefficient ($R^2$Adj-MG= 0.9759 and $R^2$Adj-MB= 0.9460). This result means that 0.0241% and 0.054% of the total variation on MG and MB adsorption data can be explained by the selected model. The adequate precision ratio of 51.63 and 42.26 for MG and MB, respectively indicates an appropriated signal to noise ratio. The ratio determined was greater than 4, representing that the quadratic model can be used to navigate the design space of this process.

Furthermore, as shown in Fig. 4.7 and 4.8 for MG and MB respectively, the relationship between actual values and predicted values showed that the actual values are distributed relatively near to the straight line, indicating good fitness of the model for both dyes.

Again in Fig. 4.9 and 4.10, the plot of studentized residuals versus run order was tested and the residuals were scattered randomly around ±3.00. This was an indication of better fitment of the model with the experimental data.

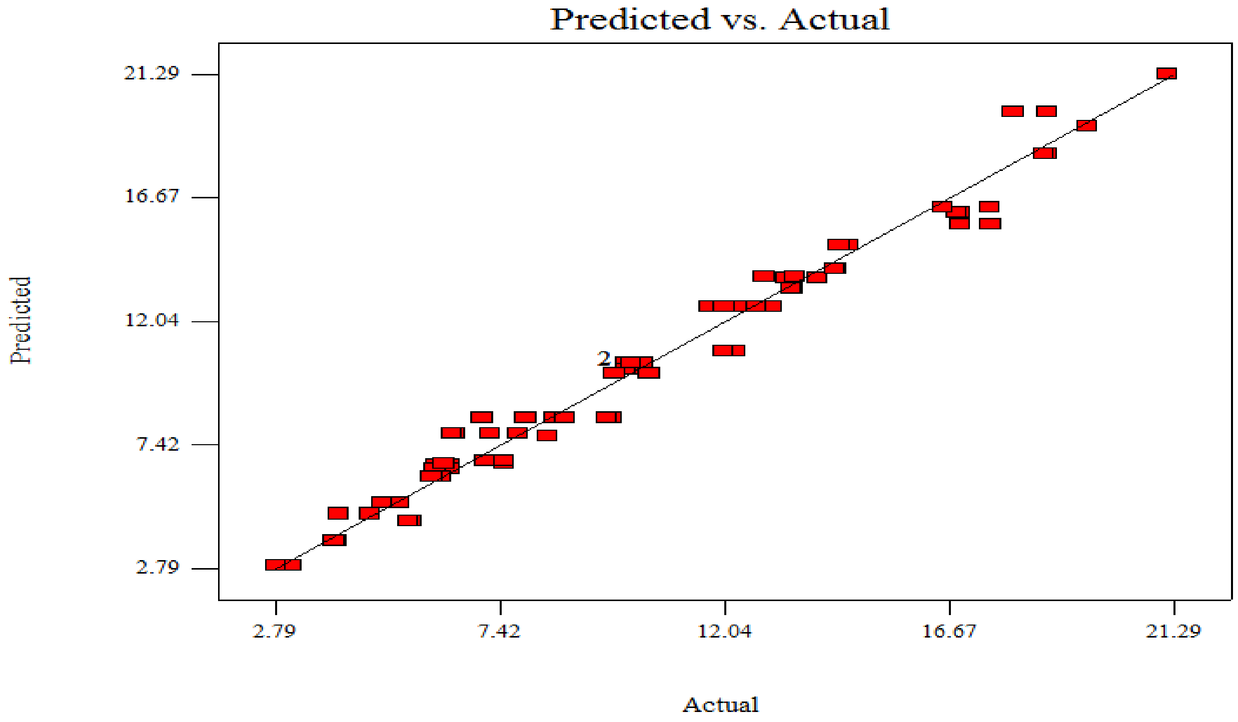


**Figure 4.7** Predicted vs. Actual values for MG.

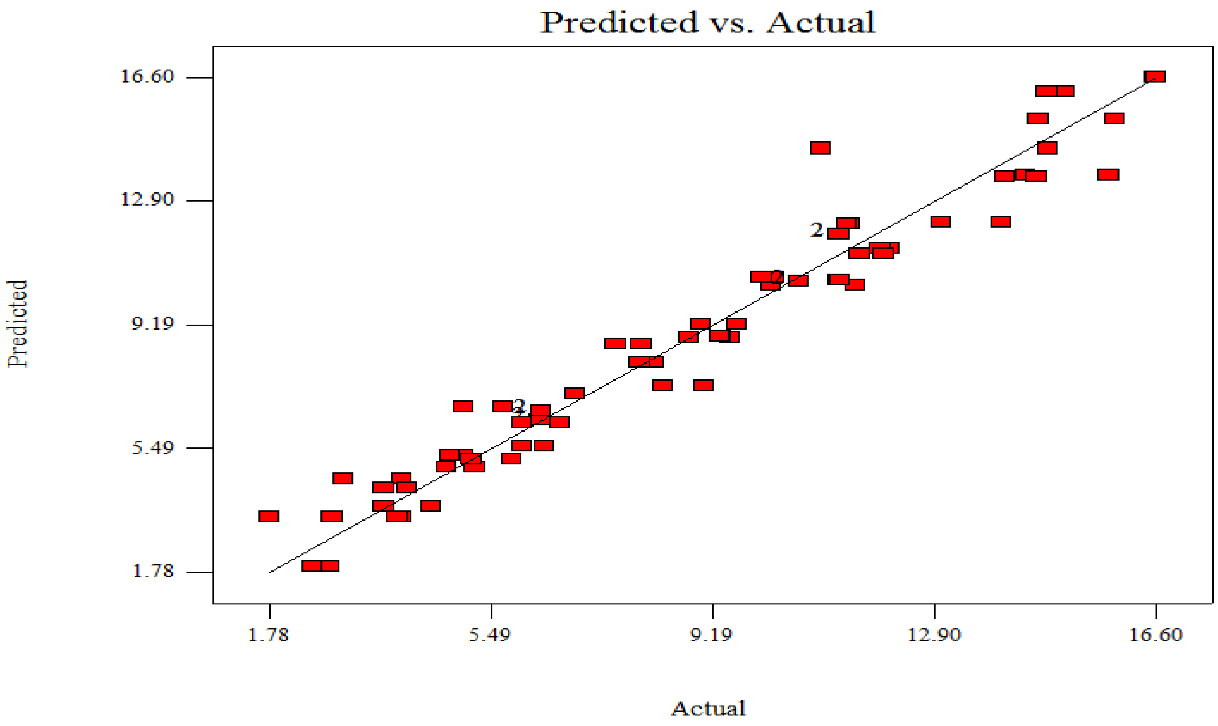


**Figure 4.8** Predicted vs. Actual values for MB.

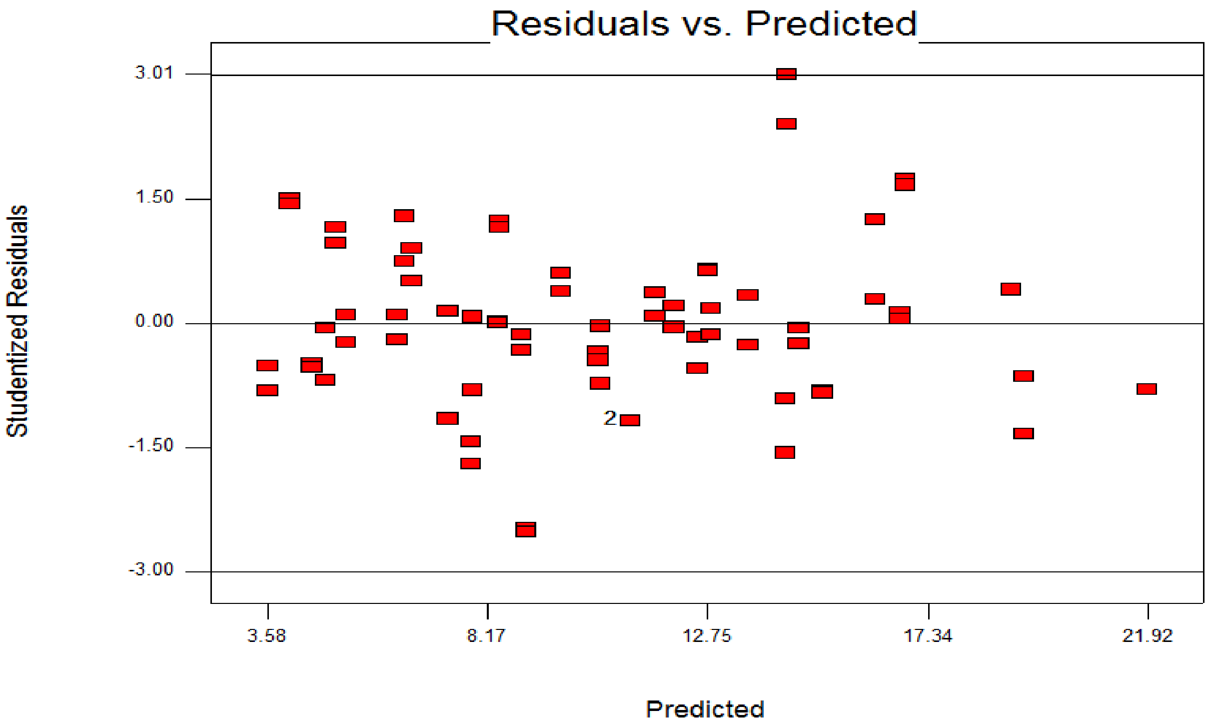


**Figure 4.9** Residuals vs. Predicted values for MG.

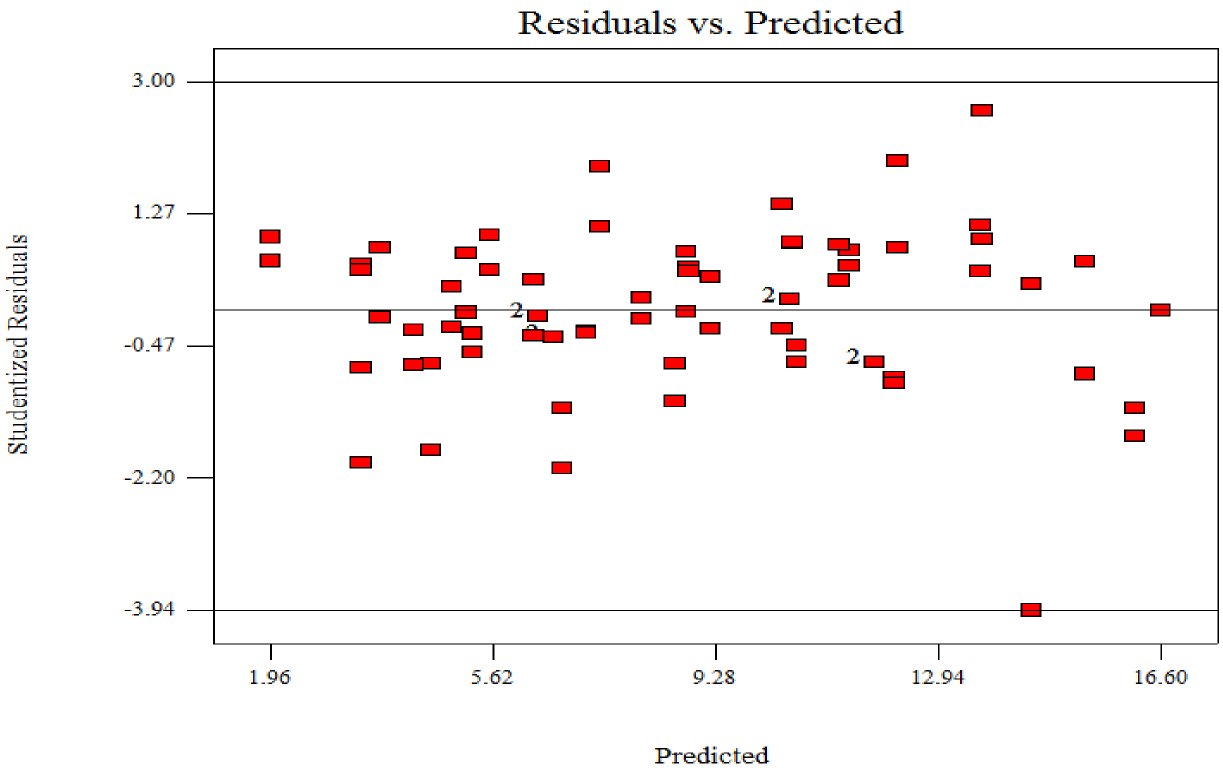


**Figure 4.10** Residuals vs. Predicted values of for MB.

### 4.2.2.4. Determination of equilibrium time

The equilibrium time is the time at which the process reaches equilibrium. The rate of adsorption of molecules on to the surface becomes similar to the rate of desorption from the surface. The equilibrium time should be known because it can help us in determining the residence time for an adsorption process.

Determination of equilibrium time for the adsorption process was done by carrying the process for longer periods of time i.e. 10 min, 30 min, 1, 2, 3, 4 and 24 hrs at concentration of 100 ppm, with 0.5g adsorbent dose and pH of 10. As shown in Fig. 4.11 the adsorption capacity of MG and MB dyes increased from 13.48 mg/g to 21.39 mg/g and from 11.48 mg/g to 18.55 mg/g respectively up to 3 hrs and remain constant 20 hrs later with maximum removal efficiency of 80.27 % and 79.41% for MG and MB respectively. Therefore, equilibrium time of 3 hrs was selected for the adsorption of both dyes for further studies. Equilibrium contact time from other researchers showed a contact time of 3, 4 and 5 hrs (Gong et al., 2013; Indra D. et al., 2006) while in this study also an equilibrium time of 3 hrs was observed.

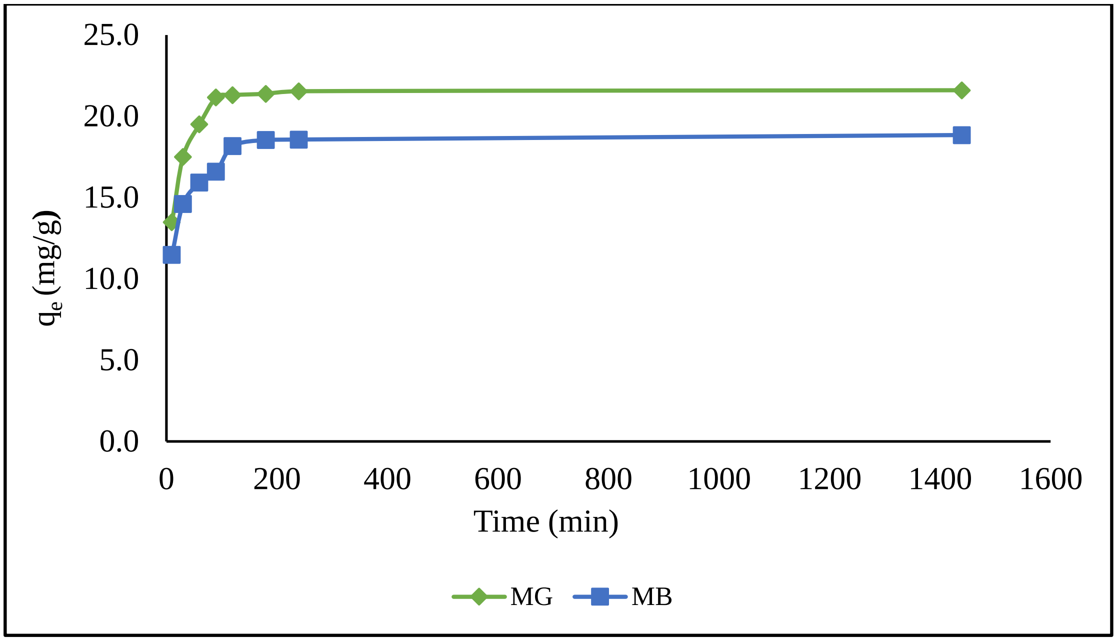


**Figure 4.11** Equilibrium time for MG and MB.

#### 4.2.2.5. Effect of adsorbent dose

In order to study the effect of adsorbent dose on the adsorption of the malachite green and methylene blue aqueous mixed dye solution, a series of adsorption experiments were carried out with different adsorbent dosages at constant initial dye concentration of 100 ppm and pH 10. The result of the study is plotted in Fig. 4.12 and 4.13. The graph shows stable values for the adsorption capacity of higher doses than 0.5 g per 250 ml. The adsorption capacity decrease as the dose increases probably due to unused adsorption sites on the surface of the adsorbent. Different adsorbent dose for bagasse fly ash adsorbent were reported, most of them obtained an increasing trend initially and then a constant regime, which is comparable with this study but some use large dosage (50 g/L) when the removal contains competitive dyes (Indra D. et al., 2006) and small dosage(1 g/L) for removal of single dye (Indra D et al., 2005).

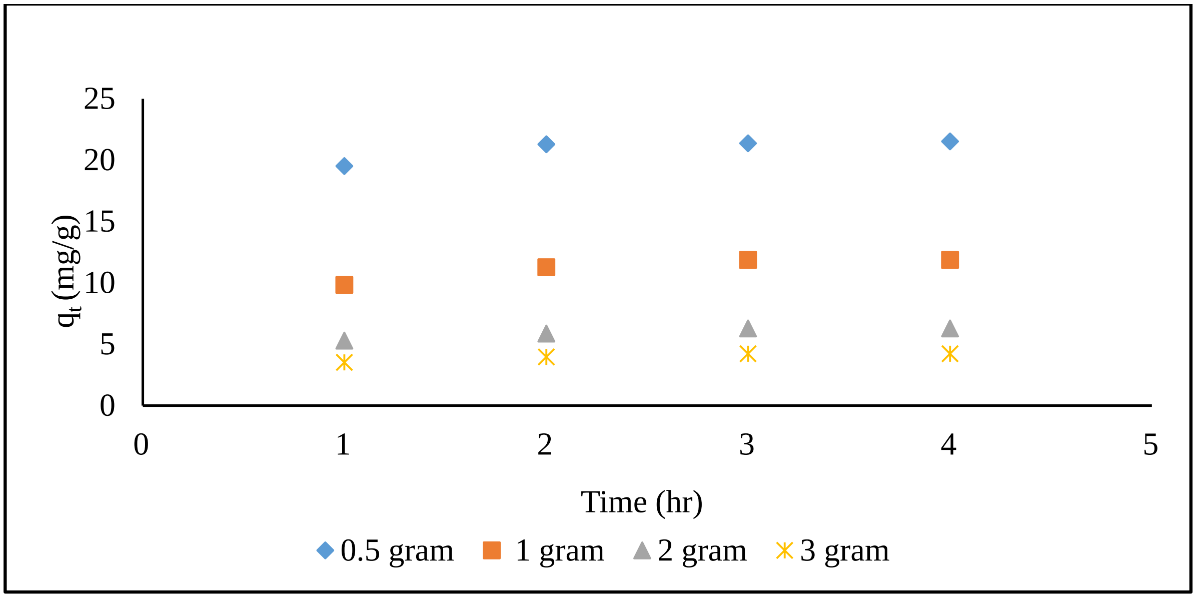


**Figure 4.12** Effect of adsorbent dose on adsorption capacity for MG.

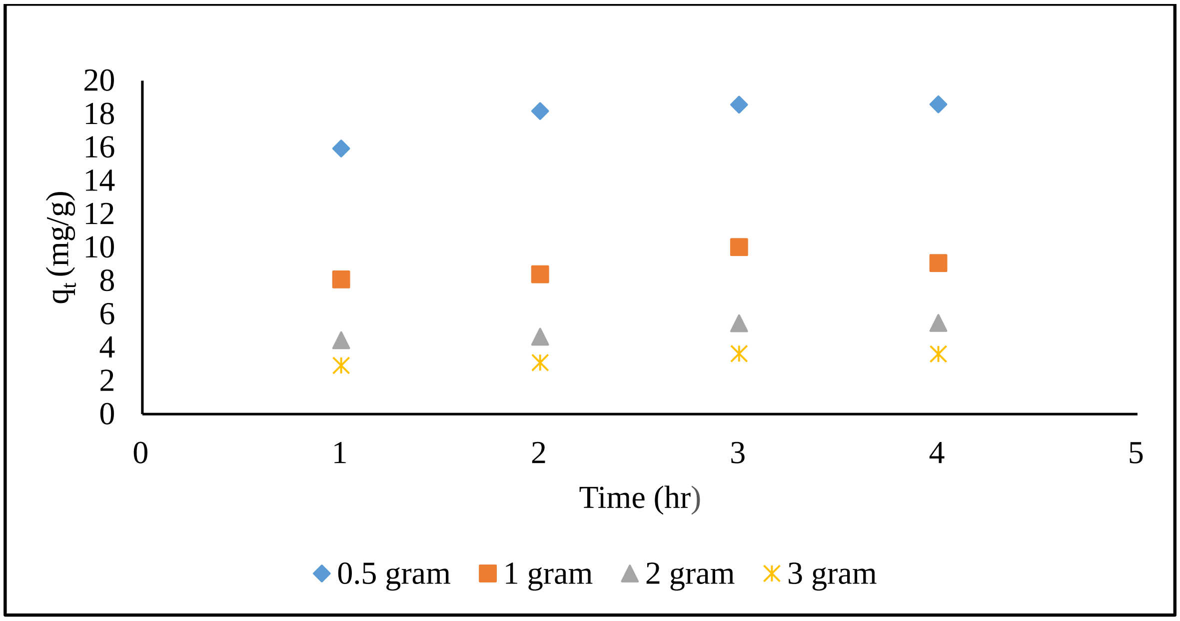


**Figure 4.13** Effect of adsorbent dose on adsorption capacity for MB.

When the adsorbent dosage increase from 0.5 to 3 g, the adsorption capacity ($q_e$, mg/g) decreased from 21.387 to 4.22 and 18.546 to 3.61 for malachite green and methylene blue dyes respectively. This could be the result of disproportionation of the added amount of the fly ash and the existing concentration, that is most of the added fly ash are not used. But the removal efficiency improved with increased amount of adsorbent dose for malachite green up to a maximum efficiency of 94.51% at a dose of 2 g and 93.29 % for methylene blue dye also at 2 g dose (Fig 4.14).

Increasing the dose more than 2 g does not improve the removal efficiency of the dye for the solution with a concentration of 100 ppm.

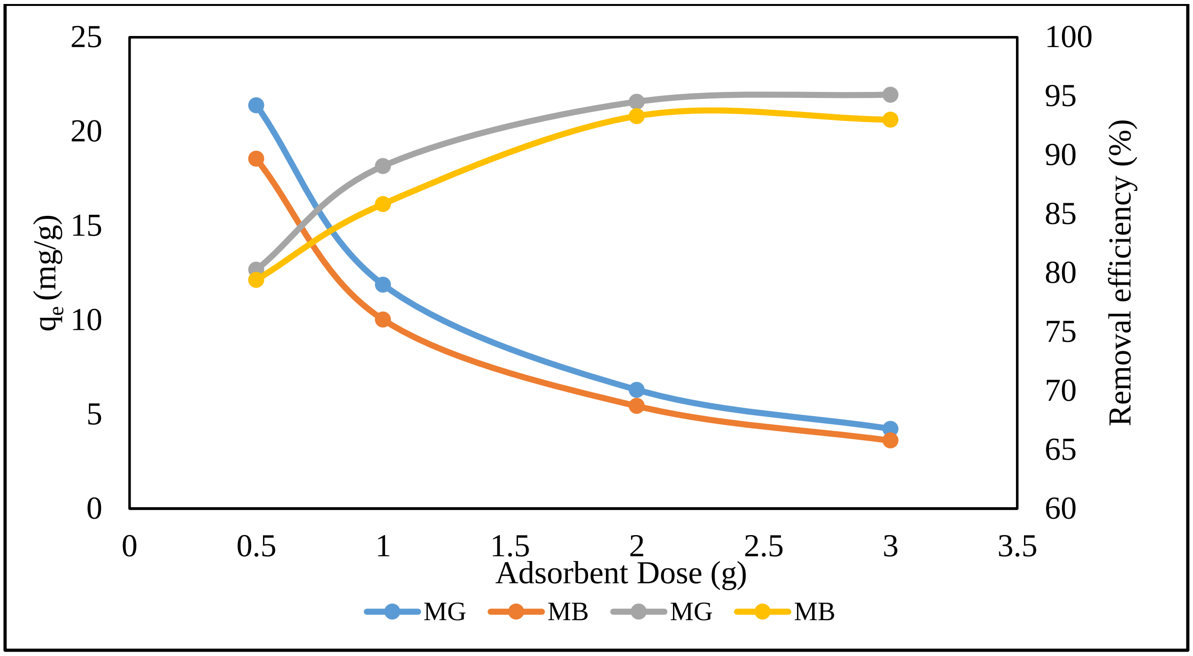


**Figure 4.14** Effect of adsorbent dose on adsorption capacity and removal efficiency at equilibrium time for MG and MB

### 4.2.2.6. Effect of process variables at optimum BFA dose

The influence of using the appropriate adsorbent dose on the adsorption capacity of the adsorbent was investigated using this set of experiments. The result of this experiments show similar trend as those in the preliminary tests, that is higher pH, time and concentration gave better results. The maximum adsorption capacity and removal efficiency observed was the same as the value obtained for the 2 g dose at 100 ppm, 3 hrs and a pH of 10. The table result of the experiment is presented in appendix B6 for MG and B7 for MB.

### 4.2.2.7. Effect of higher dye concentration

Further study of the adsorption capacity was carried out for larger concentration of solution (200, 300, 400, 500 ppm) at an adsorbent dose of 2 g and time of 3 hrs. Figure 4.15 presents the result of the experiment for higher concentration of the dye solution. The result show that about 300 ppm is the maximum amount of concentration that could be adsorbed using the 2 g adsorbent dose. Many researchers have shown the effect of increasing the initial concentration of the dye solution result in an increasing adsorption capacity trend followed by a constant adsorption capacity region (Gong et al., 2013; Indra D. Mall et al., 2006; Indra Deo et al., 2005). Indra D. used BFA to adsorb Orange G and Methyl violet dyes and obtained at 5 ppm with 50 g/L, 91% removal and about 35% removal at 30 ppm (Indra D. et al., 2006). While in this paper, 94.51% and 93.29% removal was achieved for 100 ppm of MG and MB adsorbed on BFA with an adsorbent dose of 8 g/L.

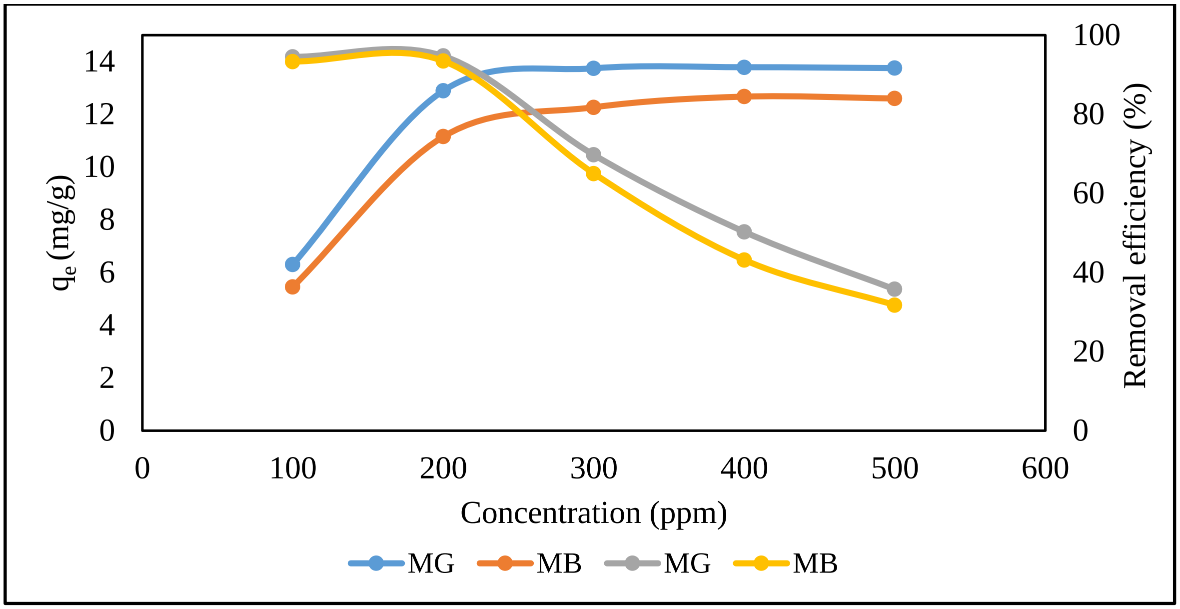


**Figure 4.15** Study of adsorption capacity for higher concentration solution at optimum conditions.

## 4.3. Adsorption isotherm models

In order to understand mechanism of the process better and to optimize the design of an adsorption process, experimental data were analyzed to see if the process behaves similarly with the common adsorption models. In this study, Langmuir and Freundlich isotherm models have been tried to see if they could describe the adsorption process. These models are simple, well established and have physical meaning and are easily interpretable.

### 4.3.1. Langmuir isotherm model

In the Langmuir model is based on the simplest model of adsorption with the basic assumptions including 1) molecules are adsorbed at discrete active sites on the surface, 2) energetically uniform adsorbing surface, 3) each active site adsorbs one molecule only, 4) no interaction among the adsorbed molecules. The Langmuir isotherm model can be represented by equation 4.1.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad \text{..........................................................4.1}$$

The values $K_L$ and $q_m$ were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$, respectively.

The Langmuir model constants obtained from both dyes are listed in Table 4.7. In Figure 4.16, the result shows good correlation with the Langmuir isotherm model evidenced by the $R^2$ values (0.9684 for MG and 0.9947 for MB) which is close to unity. This result works for both dyes meaning that the overall process can be modelled as monolayer coverage of dye molecules on the surface of the bagasse fly ash.

If the equilibrium parameter ($R_L$) is between 0 and 1, the adsorption process is favorable (equation 4.2). $R_L$ values for MG and MB are 0.11 and 0.14, respectively. Therefore, the adsorption process is favorable.

$$R_L = \frac{1}{1+(1+K_L C_o)} \quad \text{.........................................................................4.2}$$

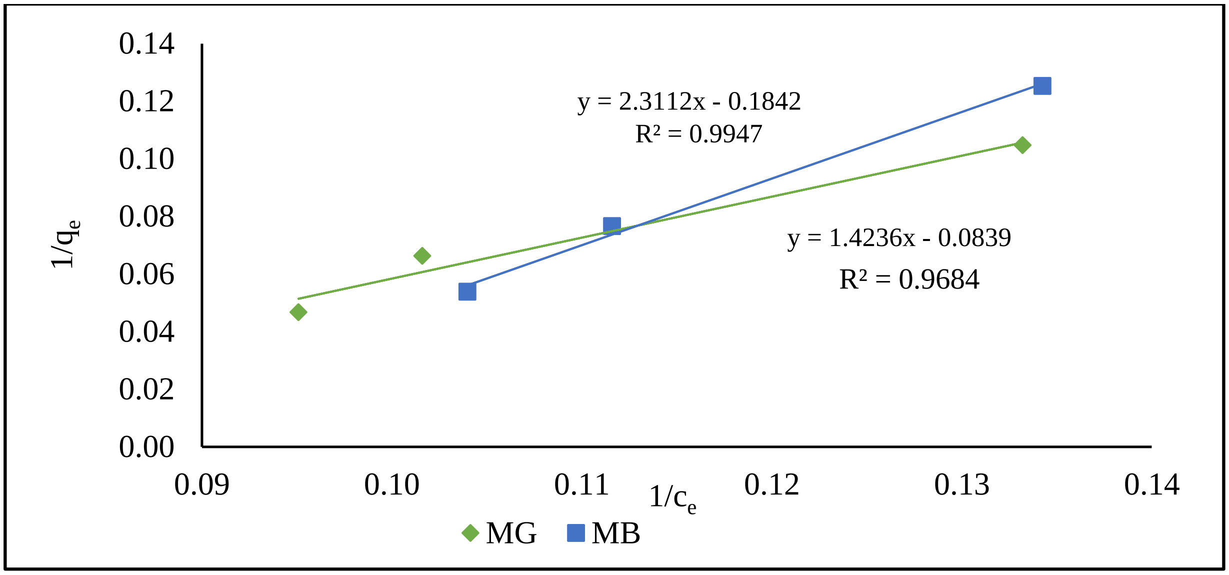


**Figure 4.16** Langmuir isotherm model for MG and MB.

### 4.3.2. Freundlich isotherm model

The Freundlich isotherm is one of the most popular isotherm which gives reasonable description of the adsorption of liquid molecules on solid surfaces. The Freundlich isotherm is derived by assuming that the amount of substance adsorbed at equilibrium has a power law dependence on the concentration of the solute. Freundlich Isotherm model can be formulated by equation 4.3.

$$\log q_e = \log K_f + \frac{1}{\mathrm{n}}\log C_e \ldots\ldots\ldots\ldots 4.3$$

The Freundlich isotherm model constants, $K_f$ and n, were computed from the slope and intercept of the equation for the graph (log $q_e$) versus (log $C_e$), respectively. The fit of the data to the Freundlich isotherm was also tested by the $R^2$ value of the plot, which gave satisfactory result. The list of constants and goodness of fit are all reported on Table 4.7 for both dyes.

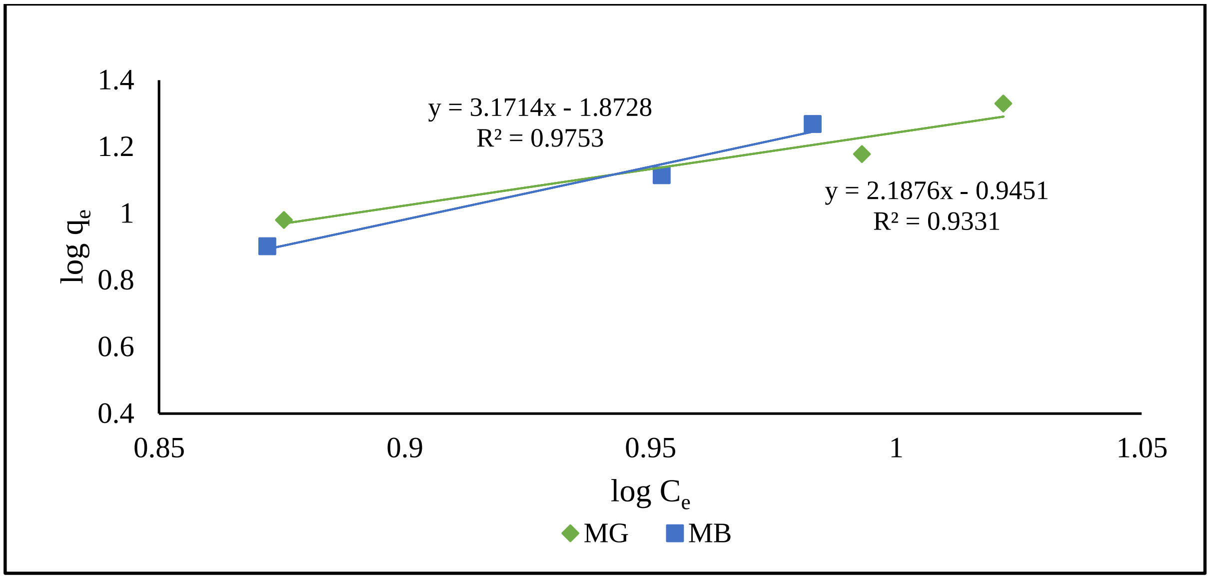


**Figure 4.17** Freundlich isotherm model for MG and MB.

**Table 4.7** Langmuir and Freundlich isotherm constants for MG and MB.

| **Isotherm** | **Langmuir model** | | | **Freundlich model** | | |
|---|---|---|---|---|---|---|
| **parameters** | **$q_m$ (mg/g)** | **$K_L$ (L/mg)** | **$R^2$** | **$K_f$ (mg/g)** | **1/n** | **$R^2$** |
| Malachite green | 11.92 | 0.06 | 0.97 | 8.81 | 2.19 | 0.933 |
| Methylene blue | 5.19 | 0.08 | 0.99 | 8.15 | 3.33 | 0.963 |

## 4.4. Adsorption kinetics models

Adsorption kinetics describes the rate of solute uptake, which is also responsible for the residence time needed for an adsorption study. Therefore, it is important characteristics in defining the efficiency of sorption processes. In this study, adsorption kinetics of MG and MB dyes has been carried out to understand the adsorption behavior of bagasse fly ash with respect to contact time. The initial dye concentration used are 50 ppm, 75 ppm and 100 ppm by monitoring the adsorption capacity of MG and MB dyes. Pseudo first-order and Pseudo second-order kinetics models were used to test the behavior of the batch adsorption experiment. The result for the Pseudo first and second-order kinetic constants are shown in Table 4.8.

### 4.4.1. Pseudo first-order kinetics model

The Pseudo first-order rate kinetics model based on adsorption capacity of adsorbent is generally expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \text{.............................................} 4.4$$

The plot of log ($q_e$ – $q_t$) versus t should give a linear relationship from which $K_1$ and $q_e$ can be determined from the slope and intercept of the plot, respectively.

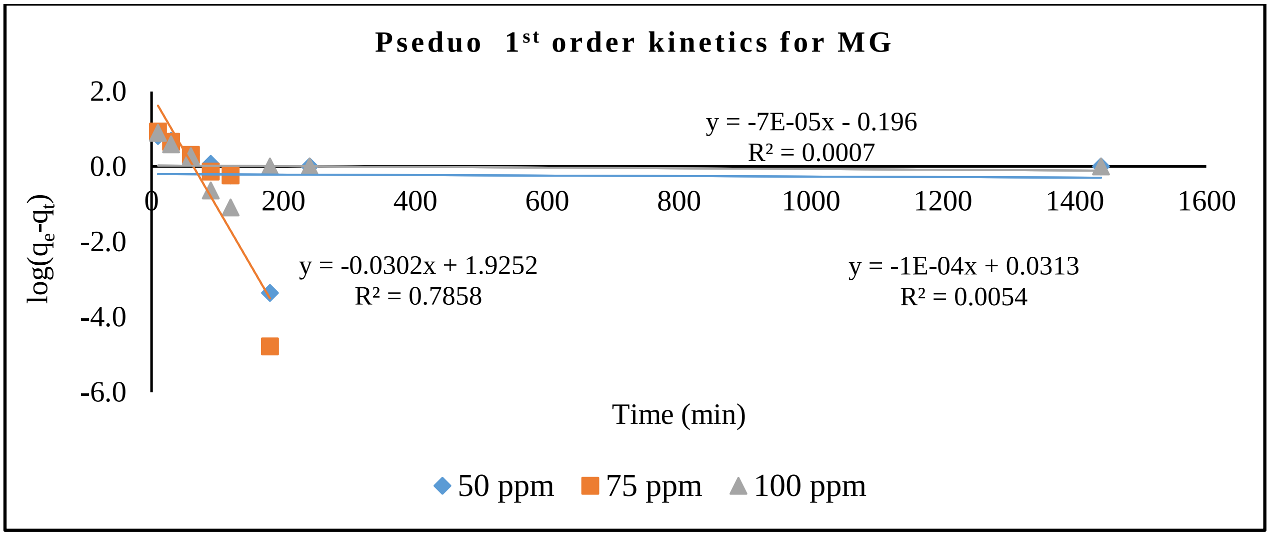


**Figure 4.18** Pseudo first-order kinetics for MG.

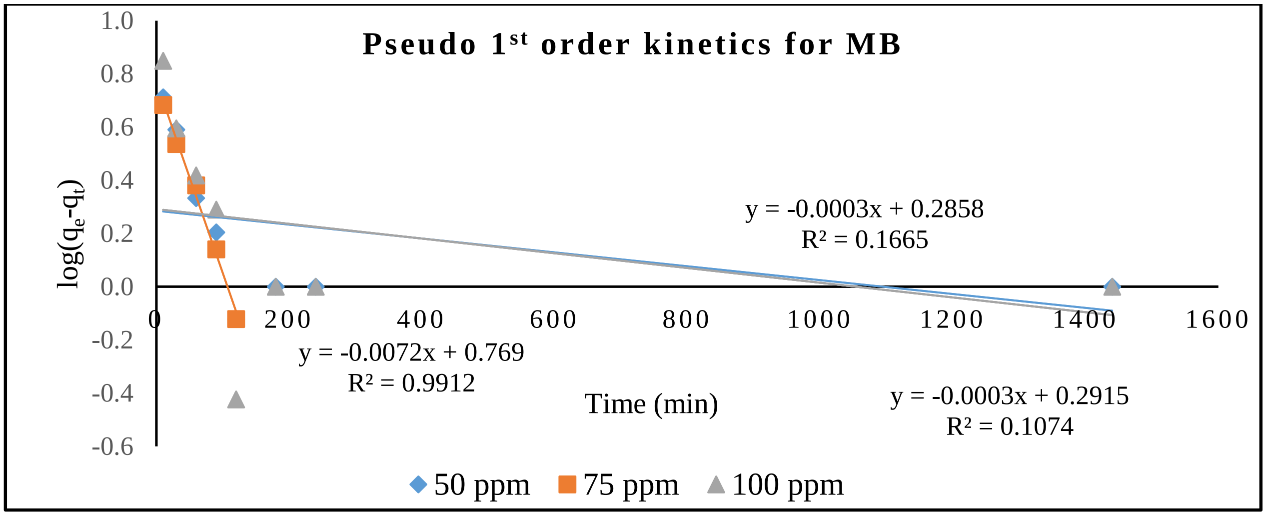


**Figure 4.19** Pseudo first-order kinetics for MB.

### 4.4.2. Pseudo second-order kinetics model

The Pseudo-second order kinetics model was tested in the same way by rewriting the equation in its linear form and plotting the appropriate variables. The equation that describes the pseudo-second order model is given in the following linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad \text{……} \quad 4.5$$

The constants, $q_e$ and $K_2$, were computed from the slop and intercept of $t/q_t$ versus t linear plot, respectively.

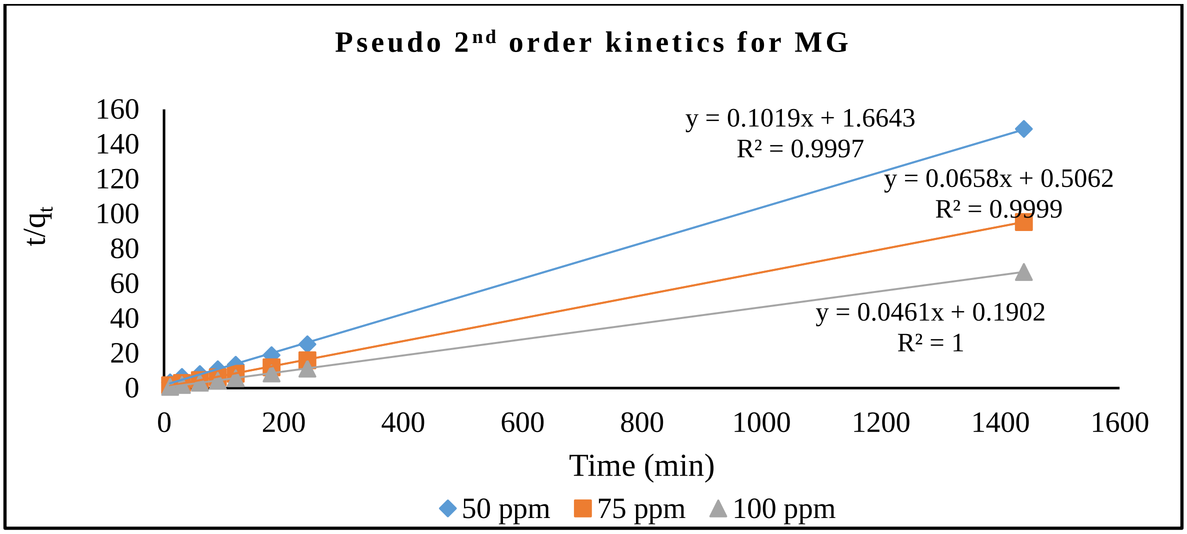


**Figure 4.20** Pseudo second-order kinetics for MG.

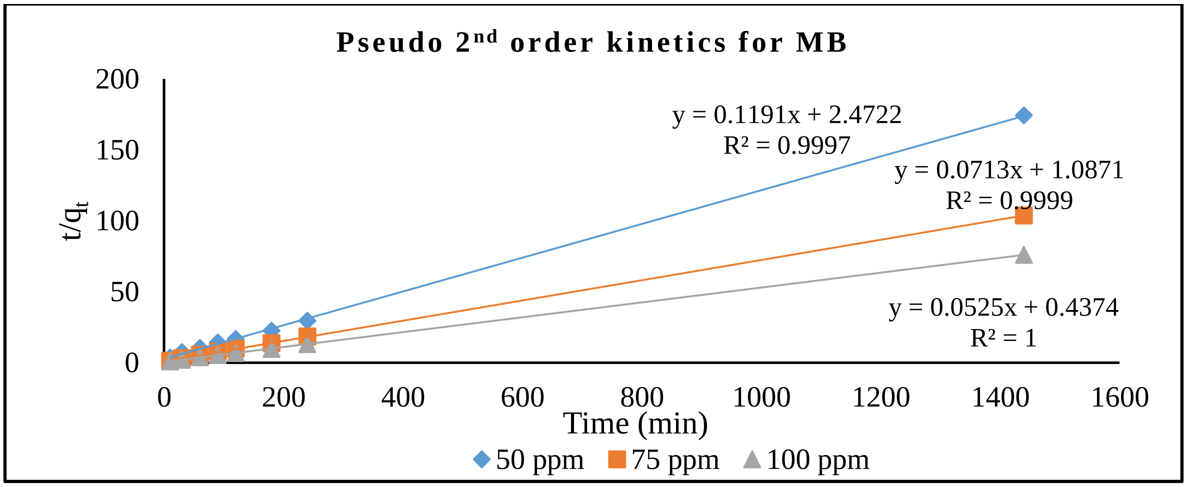


**Figure 4.21** Pseudo second-order kinetics for MB.

The graph for both dyes gave unsatisfactory fit with the Pseudo first order kinetic model implying the process of adsorption has no first order kinetics for both dye (Fig. 4.18 and 4.19). While the graph for the Pseudo second order gives excellent fit for the experimental data for each dye (Fig. 4.20 and 4.21). Therefore, the adsorption of the two dyes on the bagasse fly ash follows a pseduo second order kinetics which is a better since it would result in a fast adsorption reaction.

**Table 4.8** The Pseudo first and second-order constants for MG and MB.

| | | | **Pseudo 1st order constants** | | | **Pseudo 2nd order constants** | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Dye type** | **Concentration (mg/l)** | **$q_e$, exp (mg/g)** | **$q_e$,cal (mg/g)** | **$K_1$ (g/mg.min)** | **$R^2$** | **$q_e$, cal (mg/g)** | **$K_2$ (g/mg.min)** | **h (mg/g.min)** | **$R^2$** |
| MG | 50 | 9.547 | 0.636 | $1.61*10^{-4}$ | 0.0007 | 9.814 | 0.006 | 0.578 | 0.9997 |
| | 75 | 15.064 | 84.18 | 0.069 | 0.7858 | 15.197 | 0.0086 | 1.986 | 0.9999 |
| | 100 | 21.387 | 1.07 | 0.0023 | 0.0054 | 21.69 | 0.011 | 5.175 | 1 |
| MB | 50 | 7.98 | 1.93 | $6.9*10^{-4}$ | 0.1665 | 8.396 | 0.0057 | 0.402 | 0.9997 |
| | 75 | 13.035 | 5.87 | 0.017 | 0.9912 | 14.025 | 0.0046 | 0.905 | 0.9999 |
| | 100 | 18.55 | 1.96 | $6.9*10^{-3}$ | 0.1074 | 19.05 | 0.0063 | 2.286 | 1 |

## 4.5. FTIR analysis

The adsorption capacity of BFA can be influenced by the chemical structure of the surface. The FTIR technique is an important tool to identify some of the characteristic functional groups, which are capable of adsorbing dye ions. The infrared spectrum of BFA includes strong and weak peaks in the region of 4000-400 cm$^{-1}$ as shown in Fig. 4.22.

Absorption bands in the region between 3100 and 3400 cm$^{-1}$ indicates the presence of both free and hydrogen bonded OH groups on the adsorbent surface. This stretching is due to both the silanol (Si–OH) groups and adsorbed water (peak at 3436 cm$^{-1}$) on the surface. The stretching of the OH groups bound to methyl radicals presented a very light signal 2925 cm$^{-1}$. The band at 1593 cm$^{-1}$ may be due to conjugated hydrocarbon bonded carbonyl groups and the peak at 1102 cm$^{-1}$ is due to –C–O–H stretching. As can be seen from the large change in the absorption band for the silanol group and compared to the C-O group, the silanol groups are more responsible for the adsorption process than the carbonyl group.

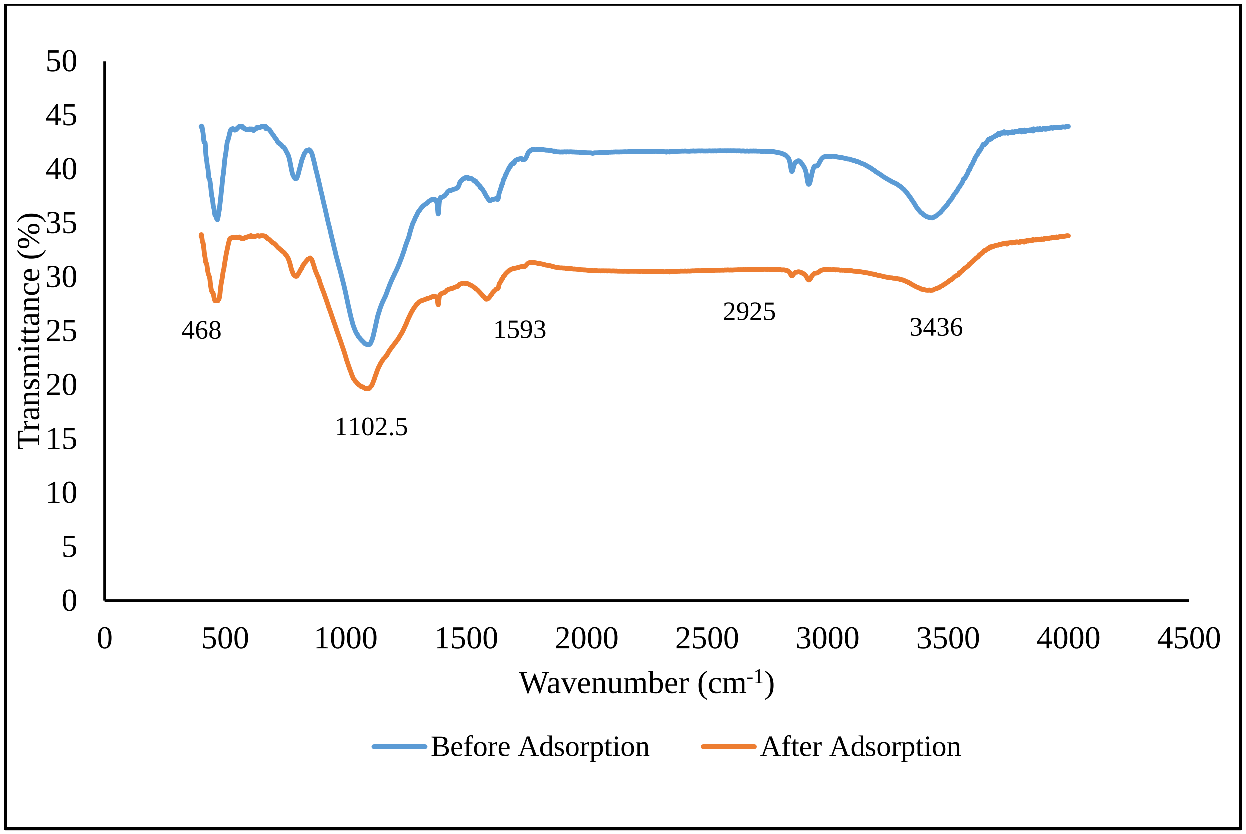


**Figure 4.22** FTIR analysis for BFA before and after adsorption.

# 5. CONCLUSION AND RECOMMENDATION

## 5.1. Conclusion

In this study, the adsorption efficiency of bagasse fly ash was investigated in detail by considering various factors that affect the adsorption process such as initial dye concentration, time, pH and adsorbent dose by starting from the proximate analysis of the BFA. The proximate analysis allowed the selection of the particle size that is expected to give good adsorptive behavior based on the ash content of material. The BFA with a particle size of <250 μm gave the maximum ash content than the bigger sizes of BFA and hence the BFA with particle size <250 μm was used for the rest of the study. The availability of this material was also estimated using the production capacity of the currently operating sugar factory.

The raw bagasse fly ash was treated with $H_2O_2$ to improve the efficiency of the material by removal of heterogeneously distributed organic matter and unwanted inorganic dirt materials. The performance of these materials (treated and untreated BFA) was analyzed by testing the materials on a single and binary aqueous dye solution. The result showed that the single dye adsorption with the treated BFA gave the highest result, then the binary mixture dye solution with the treated BFA also gave a good result while the untreated BFA gave relatively lower results for the adsorption capacity. Hence, the treated BFA was used for further analysis.

The effect of operating parameters was studied for concentration, time, pH and adsorbent dose. Increasing the concentration of the initial aqueous solution for the specified amount of 0.5 g adsorbent dose at different pH and time, also increased the adsorption capacity for an increase in concentration from 50 ppm to 100 ppm. This could be because the change in concentration is small enough for the used amount of adsorbent. While a time of 3 hrs was obtained as optimum for the adsorption process after test for all used concentrations. The result of the experiment for the influence of the pH at values of 6, 8 and 10, showed a maximum result at a pH 10, decreased for a pH 8 and lowest value was observed at a pH 6. The result was explained by the deprotonation of the dyes at higher pH and protonation at lower pH leading to an electrostatic repulsion and attraction effect with the surface of the adsorbent.

Finally, adsorbent dose was also investigated thoroughly to determine the optimum dose for a certain concentration. The removal efficiency improved with increased amount of adsorbent dose for malachite green up to a maximum efficiency of 94.51% at a dose of 2 g and 93.29 % for methylene blue dye also at 2 g dose.

The kinetic and isotherm study was also carried out in order to understand the mechanism of the adsorption process. Langmuir and Freundlich isotherm was used and the experimental data were fitted with the equations for the model. The result indicated that the adsorption process followed both the Langmuir and Freundlich isotherm models. The kinetics was also investigated to determine the rate of adsorption using pseudo-first order and pseudo-second order kinetics models. The data followed the Pseudo-second order kinetics almost perfectly than the Pseudo-first order kinetics. Finally, the data was also analyzed using the design expert 6.0.8 software and the result shows the model and interaction effects are significant.

## 5.2. Recommendation

This paper is only an initial work on the study of the efficiency of bagasse fly ash for use on the treatment of waste water from some industries. It only entails the removal efficiency of BFA to remove a binary mixture of cationic dyes. BFA has a promising potential for the removal of this mixture of dyes from aqueous solution. But as most wastewater from industry contain a lot of different species than just water and two different dyes, there is a need to undertake further research on the material. The most important further research works are identified below.

- Characterization of the BFA using advanced techniques such as SEM; to determine the surface morphology of the adsorbent, BET; to visualize the pore structure of the material.
- The regeneration potential of the used BFA should be studied before the commercial application of the material.
- The efficiency of this material should also be investigated for the removal of heavy metals, BOD and COD from aqueous solution and also the application of the material on real wastewater containing all sorts of pollutants.
- Finally, column performance of BFA should be investigated and the possibility of designing a fixed packed bed adsorber that removes significant amount of pollutants including COD, BOD, heavy metal, and dye pollutants.

# REFERENCES

Ahmad, A., Mohd-setapar, S. H., Chuong, S., & Khatoon, A. (2015). RSC Advances Recent advances in new generation dye removal technologies : novel search for approaches to reprocess wastewater. *RSC Advances*, *5*, 30801–30818.

Ahmaruzzaman, M. (2010). A review on the utilization of fly ash. *Progress in Energy and Combustion Science*, *36*(3), 327–363.

Albanis, T. A., Hela, D. G., Sakellarides, T. M., & Danis, T. G. (2000). Removal of dyes from aqueous solutions by adsorption on mixtures of fly ash and soil in batch and column techniques. *Global Nest: The Int.J*, *2*(3), 237–244.

American Society for Testing and Materials, ASTM, (1989). Standard methods for Chemical analysis of wood charcoal, Philadelphia, USA.

Amin, N. K. (2008). Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. *Desalination*, *223*, 152–161.

Amran, M., Salleh, M., Khalid, D., Azlina, W., Abdul, W., & Idris, A. (2011). Cationic and anionic dye adsorption by agricultural solid wastes : A comprehensive review. *DES, 280*(1-3), 1–13.

Anbia, M. (2011). Removal of Malachite Green from Dye Wastewater Using Mesoporous Carbon Adsorbent. *Journal of the Iranian Chemistry Society*, *8*(February), 67–76.

Ayeche, R. (2012). Treatment by coagulation-flocculation of dairy wastewater with the residual lime of National Algerian Industrial Gases Company ( NIGC-Annaba ). *Energy Procedia*, *18*, 147–156.

Babel, S., & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water : a review. *Journal of Hazardous Materials*, *97*, 219–243.

Babu, B. R., Parande, a K., Raghu, S., & Kumar, T. P. (2007). Cotton Textile Processing : Waste Generation and Effluent Treatment. *Journal of Cotton Science*, *153*(11:141), 141–153.

Banerjee, S., & Sharma, Y. C. (2013). Journal of Industrial and Engineering Chemistry Equilibrium and kinetic studies for removal of malachite green from aqueous solution by a low cost activated carbon. *Journal of Industrial and Engineering Chemistry*, *19*(4), 1099–1105.

Beyene, H. D. (2014). The potential of dyes removal from textile wastewater by using different treatment technology , a Review. *International Journal of Environmental Monitoring and Analysis*, *2*(6), 347–353.

Bhatnagar, A., & Sillanpää, M. (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment-A review. *Chemical Engineering Journal*, *157*, 277–296.

C.K. Jain. Arvind Kumar, M. H. I. (2008). Color removal from paper mill effluent through adsorption technology. *Envron Monit Assess*, 343–348.

Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal : A review. *Bioresource Technology*, *97*, 1061–1085.

Dalai, C., Jha, R., & Desai, V. R. (2015). Rice Husk and Sugarcane Baggase Based Activated Carbon for Iron and Manganese Removal. *Aquatic Procedia*, *4*(Icwrcoe), 1126–1133.

Deokar, R., & Sabale, A. (2014). Original Research Article Biosorption of Methylene Blue and Malachite Green From Binary Solution onto Ulva lactuca. *International Journal of Current Microbiology and Applied Sciences*, *3*(5), 295–304.

Elgeundi, M. (1991). Colour removal from textile effluents by adsorption techniques. *Water Research*, *25*(3), 271–273.

Ghaly, A. E., Ananthashankar, R., Alhattab, M., & Ramakrishnan, V. V. (2014). Chemical Engineering & Process Technology Production , Characterization and Treatment of Textile Effluents : A Critical Review. *Chemical Engineering and Process Technology*, *5*(1), 1–19.

Gong, L., Sun, W., & Kong, L. (2013). Adsorption of Methylene Blue by NaOH-modified Dead Leaves of Plane Trees. *Computational Water, Energy, and Environmental Engineering*, *2013*(April), 13–19.

Gupta, N., Kushwaha, A. K., & Chattopadhyaya, M. C. (2011). Application of potato ( Solanum tuberosum ) plant wastes for the removal of methylene blue and malachite green dye from aqueous solution. *Arabian Journal of Chemistry*, 1–10.

Gupta, V. K., & Ali, I. (2000). Utilisation of bagasse fly ash ( a sugar industry waste ) for the removal of copper and zinc from wastewater. *Separation and Purification Technology*, *18*, 131–140.

Gupta, V. K., & Ali, I. (2004). Removal of lead and chromium from wastewater using bagasse fly ash - a sugar industry waste. *Journal of Colloid and Interface Science*, *271*, 321–328.

Gupta, V. K., Jain, C. K., Ali, I., Chandra, S., & Agarwal, S. (2002). Removal of lindane and malathion from wastewater using bagasse fly ash - A sugar industry waste. *Water Research*, *36*(10), 2483–2490.

Gupta, V. K., & Sharma, S. (2003). Removal of Zinc from Aqueous Solutions Using Bagasse Fly Ash - a Low Cost Adsorbent. *Separation and Purification Technology*, (Cl), 6619–6624.

Hameed, B. H., & El-khaiary, M. I. (2008). Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre : Equilibrium isotherms and kinetic studies. *Journal of Hazardous Materials*, *154*, 237–244.

Isa, M. H., Siew, L., Asaari, F. A. H., Aziz, H. A., Ramli, N. A., Paul, J., & Dhas, A. (2007). Low cost removal of disperse dyes from aqueous solution using palm ash. *Dyes and Pigments*, *74*, 446–453.

Kalderis, D., Koutoulakis, D., Paraskeva, P., Diamadopoulos, E., Otal, E., Valle, J. O. D., & Fernández-Pereira, C. (2008). Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse. *Chemical Engineering Journal*, *144*(1), 42–50.

Kanawade, S. M. (2010). Low cost Sugarcane Bagasse Ash as an Adsorbent for Dye Removal from Dye Effluent. *International Journal of Chemical Engineering and Applications*, *1*(4), 309–318.

Kanawade, S. M., Gaikwad, R. W., Blue, A. M., & Hyacinth, C. W. (2011). Removal of Methylene Blue from Effluent by Using Activated Carbon and Water Hyacinth as Adsorbent. *International Journal of Chemical Engineering and Applications*, *2*(5), 317–319.

Kandasamy, J., Vigneswaran, S., Hoang, T. T. L., & Chaudhary, D. N. S. (2011). Adsorption and biological filtration. *Water and Wastewater Treatment Technology*, 456–462.

Karnitz, O., Gurgel, L. V. A., de Melo, J. C. P., Botaro, V. R., Melo, T. M. S., de Freitas Gil, R. P., & Gil, L. F. (2007). Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresource Technology*, *98*(6), 1291–1297.

Karthik, V., Saravanan, K., & Nadu, T. (2014). An overview of treatments for the removal of textile dyes. *Journal of Chemical and Pharmaceutical Sciences*, *7*(4), 301–307.

Kharade, A. S., Suryavanshi, V. V, Gujar, B. S., & Deshmukh, R. R. (2014). Waste product " bagasse ash " from sugar industry can be used as stabilizing material for expansive soils. *International Journal of Research in Engineering and Technology*, 506–512.

Kharub, M. (2012). Use of various technologies , Methods and adsorbents for the removal of dye. *Journal of Environmental Research and Development*, *6*(3), 879–883.

Kumar, D. (2004). Removal of some basic dyes from artificial textile wastewater by adsorption on Akash Kinari coal. *Journal of Scientific and Industrial Research*, *63*(April), 355–364.

Lakdawala, M. M., Patel, Y. S., Appl, A., & Res, S. (2012). The effect of low cost material Bagasse Fly ash to the removal of COD Contributing component of combined waste water of Sugar Industry Scholars Research Library. *Archives of Applied Science Research*, *4*(2), 852–857.

Lokeshwari, N., & Joshi, K. (2014). Low cost adsorbent for reducing organic components. *Journal of Industrial Pollution Control*, *30*(1), 53–58.

Madurwar, M. V, Mandavgane, S. A., & Ralegaonkar, R. V. (2014). Use of sugarcane bagasse ash as brick material. *Journal of Water Resource and Protection*, *107*(6), 1044–1051.

Makeswari, M., & Santhi, T. (2013). Removal of Malachite Green Dye from Aqueous Solutions onto Microwave Assisted Zinc Chloride Chemical Activated Epicarp of Ricinus communis. *Journal of Water Resource and Protection*, *2013*(February), 222–238.

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 and Pigments*, *56*, 239–249.

Malik, P. K. (2004). Dye removal from wastewater using activated carbon developed from sawdust : adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, *113*, 81–88.

Mall, I. D., Srivastava, V. C., & Agarwal, N. K. (2006). Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash d kinetic study and equilibrium isotherm analyses. *Dyes and Pigments*, *69*, 210–223.

Mall, I. D., Srivastava, V. C., Agarwal, N. K., & Mishra, I. M. (2005). Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses. *Colloids and Surfaces*, *264*, 17–28.

Mane, V. S., Indra Deo Mall, & Srivastava, V. C. (2007). Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. *Journal of Environmental Management*, *84*, 390–400.

Mane, V. S., Mall, I. D., & Srivastava, V. C. (2007). Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution. *Dyes and Pigments*, *73*, 269–278.

Miclescu, A., & Wiklund, L. (2010). Methylene blue , an old drug with new indications ? *Journal of Roman de Anestezie Terapie Intensiva*, *17*(1), 35–41.

Mohan, D., Singh, G., & Kumar, K. (2002). Removal of Dyes from Wastewater using Flyash, a Low-Cost Adsorbent. *Ind. Eng Chem Res*, *41*, 3688–3695.

Ozsoy, H. D., & Leeuwen, J. H. Van. (2010). Removal of color from fruit candy waste by activated carbon adsorption. *Journal of Food Engineering*, *101*(1), 106–112.

Pedro, J., Sousa, S., Gonçalves, I., Porter, J. J., & Ferreira-dias, S. (2004). Modelling adsorption of acid orange 7 dye in aqueous solutions to spent brewery grains. *Separation and Purification Technology*, *40*, 163–170.

Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials*, *177*(1-3), 70–80.

Ramachandran, P., Vairamuthu, R., & Ponnusamy, S. (2011). Adsorption isotherms , kinetics , thermodynamics and desorption studies of reactive orange16 on activated carbon derived from. *Biochemical Pharmacology*, *6*(11), 15–26.

Ramesh, K. S. B. S. T. (2013). Removal of dyes using agricultural waste as low-cost adsorbents : a review. *Applied Water Science*, 773–790.

Rastogi, K., Sahu, J. N., Meikap, B. C., & Biswas, M. N. (2008). Removal of methylene blue from wastewater using fly ash as an adsorbent by hydrocyclone. *Journal of Hazardous Materials*, *158*, 531–540.

Sartape, A. S., Mandhare, A. M., Jadhav, V. V, Raut, P. D., Anuse, M. A., & Kolekar, S. S. (2014). Removal of malachite green dye from aqueous solution with adsorption technique using Limonia acidissima ( wood apple ) shell as low cost adsorbent. *Arabian Journal of Chemistry*, 1–10.

Seey, T. A. N. L., Jain, M., & Mohd, N. (2012). Characterization of mangrove bark adsorbent and its application in the removal of textile dyes from aqueous solutions. *Journal of Applied Hypotechnology in Environmental Sanitation*, *1*(3), 121–130.

Shahryari, Z., Goharrizi, A. S., & Azadi, M. (2010). Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. *International Journal of Water Resources and Environmental Environmental Engineering*, *2*(2), 16–28.

Sharma, S., Saxena, R., & Gaur, G. (2014). Study of Removal Techniques for Azo Dyes by Biosorption : A Review. *Journal of Applied Chemistry*, *7*(10), 6–21.

Singh, L., Kumar, B., Kumar, A., & Karar, K. (2014). Journal of Environmental Chemical Engineering Arsenic removal using bagasse fl y ash-iron coated and sponge iron char. *Biochemical Pharmacology*, *2*(3), 1467–1473.

Sun, D., Zhang, Z., Wang, M., & Wu, Y. (2013). Adsorption of Reactive Dyes on Activated Carbon Developed from Enteromorpha prolifera. *American Journal of Analytical Chemistry*, *2013*(July), 17–26.

Taha, G. M. (2006). Utilization of Low-Cost Waste Material Bagasse Cr 3 1 from Industrial Waste Water. *Ground Water Monitoring and Remediation*, (4), 137–141.

V. K. Gupta; . Khamparia; .Tyagi; . Jaspal;, & Malviya, . (2015). Decolorization of mixture of dyes : A critical review, *1*(1), 71–94.

Wahyu, C., Salim, C., & Hinode, H. (2011). Journal of Analytical and Applied Pyrolysis Preparation and characterization of activated carbon from bagasse fly ash. *Journal of Analytical and Applied Pyrolysis*, *91*(1), 257–262.

Wong, Y. C., Senan, M. S. R., & Atiqah, N. A. (2013). Removal of Methylene Blue and Malachite Green Dye Using Different Form of Coconut Fibre as Absorbent. *Journal of Basics and Applied Sciences*, 172–177.

Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption : A review. *Advances in Colloid and Interface Science*, *209*, 172–184.

Zheng, L., Wang, X., & Wang, X. (2015). Reuse of reverse osmosis concentrate in textile and dyeing industry by combined process of persulfate oxidation and lime-soda softening. *Journal of Cleaner Production*, *108*, 525–533.

# APPENDICES

**APPENDIX A:** Proximate analysis of bagasse fly ash

### Ash content determination

- *For particle size < 250 µm*

weight of crucible =19.795 g

weight of crucible and sample before incineration ($W_1$) = 20.798 g

weight of crucible and sample after incineration ($W_2$) = 20.6113 g

$$\text{Ash content}(\%) = \frac{W_2}{W_1} * 100$$

$$= \frac{(20.6113 - 19.795)\text{ g}}{(20.798 - 19.795)\text{ g}} * 100$$

$$= 81.63\ \%$$

- *For particle size between 250 µm and 500 µm*

weight of crucible =19.9334 g

weight of crucible and sample before incineration ($W_1$) = 20.9228 g

weight of crucible and sample after incineration ($W_2$) = 20.2916 g

$$\text{Ash content}(\%) = \frac{W_2}{W_1} * 100$$

$$= \frac{(20.2916 - 19.9334)\text{ g}}{(20.9228 - 19.9334)\text{ g}} * 100$$

$$= 35.78\ \%$$

- *For particle size between 500 µm and 850 µm*

weight of crucible =36.8863 g

weight of crucible and sample before incineration ($W_1$) = 37.8867 g

weight of crucible and sample after incineration ($W_2$) = 37.0928 g

$$\text{Ash content}(\%) = \frac{W_2}{W_1} * 100$$

$$= \frac{(37.0928 - 36.8863)\text{ g}}{(37.8867 - 36.8863)\text{ g}} * 100$$

$$= 20.57\ \%$$

**Volatile matter determination**

- *For particle size < 250 µm*

weight of crucible =19.8022 g

weight of crucible and sample before incineration ($W_1$) = 20.8006 g

weight of crucible and sample after incineration ($W_2$) = 20.7516 g

$$\text{volatile matter}(\%) = \frac{\text{W1} - \text{W2}}{\text{W1}} * 100$$

$$= \frac{(20.8006 - 20.7516)\ \text{g}}{1\ \text{g}} * 100$$

= 4.9 %

- *For particle size between 250 µm and 500 µm*

weight of crucible =19.9394 g

weight of crucible and sample before incineration ($W_1$) = 20.9428 g

weight of crucible and sample after incineration ($W_2$) = 20.729 g

$$\text{volatile matter}(\%) = \frac{\text{W1} - \text{W2}}{\text{W1}} * 100$$

$$= \frac{(20.9428 - 20.729)\ \text{g}}{1\ \text{g}} * 100$$

= 21.38 %

- *For particle size between 500 µm and 850 µm*

weight of crucible =36.8903 g

weight of crucible and sample before incineration ($W_1$) = 37.8931 g

weight of crucible and sample after incineration ($W_2$) = 37.6354 g

$$\text{volatile matter}(\%) = \frac{\text{W1} - \text{W2}}{\text{W1}} * 100$$

$$= \frac{(37.8931 - 37.6354)\ \text{g}}{1\ \text{g}} * 100$$

= 25.77 %

### Moisture content determination

- *For particle size < 250 µm*

weight of crucible =20.32 g

weight of crucible and sample before incineration ($W_1$) = 21.32 g

weight of crucible and sample after incineration ($W_2$) = 21.26 g

$$\text{moisture content } (\%) = \frac{W_1 - W_2}{W_1} * 100$$

$$= \frac{(21.32 - 21.26)\text{ g}}{1\text{ g}} * 100$$

$$= 6\ \%$$

### Fixed Carbon Content determination

- *For particle size < 250 µm*

Fixed carbon (%) = 100 – [moisture (%) + ash (%) + volatile matter (%)]

= 100 – [6 + 81.63 + 4.9]

= 7.47 %

**APPENDIX B:** Adsorption study experiment results.

**APPENDIX B1:** Calibration Curve

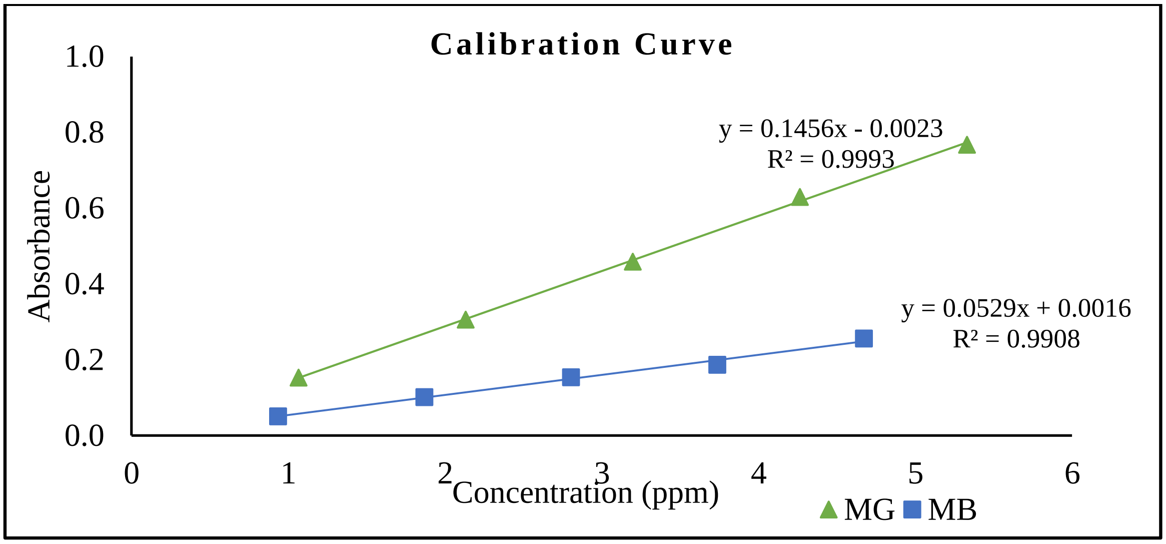


**Figure 1** Calibration curve for MG and MB

**APPENDIX B2:** Adsorption capacity and removal efficiency results for MG at constant adsorbent dose (0.5 g/250 ml).

| No. of experiments | A:Conc.(ppm) | B:Time (min) | C:pH | Response 1: qe(mg/g) | Response 2: Removal efficiency(%) |
|---|---|---|---|---|---|
| 1 | 50 | 10 | 6 | 4.03 | 30.28 |
| 2 | 75 | 10 | 6 | 6.37 | 31.88 |
| 3 | 100 | 10 | 6 | 10 | 37.54 |
| 4 | 50 | 30 | 6 | 5.31 | 39.91 |
| 5 | 75 | 30 | 6 | 8.54 | 42.74 |
| 6 | 100 | 30 | 6 | 12.38 | 46.45 |
| 7 | 50 | 60 | 6 | 6.38 | 48.01 |
| 8 | 75 | 60 | 6 | 10.11 | 50.58 |
| 9 | 100 | 60 | 6 | 14.6 | 54.8 |
| 10 | 50 | 90 | 6 | 7.48 | 56.27 |
| 11 | 75 | 90 | 6 | 12.26 | 61.37 |
| 12 | 100 | 90 | 6 | 16.88 | 63.36 |
| 13 | 50 | 10 | 8 | 5.57 | 41.911 |
| 14 | 75 | 10 | 8 | 9.69 | 48.48 |
| 15 | 100 | 10 | 8 | 13.42 | 50.38 |
| 16 | 50 | 30 | 8 | 6.19 | 46.55 |
| 17 | 75 | 30 | 8 | 10.33 | 51.69 |
| 18 | 100 | 30 | 8 | 16.89 | 63.41 |
| 19 | 50 | 60 | 8 | 7.77 | 58.74 |
| 20 | 75 | 60 | 8 | 11.74 | 58.74 |
| 21 | 100 | 60 | 8 | 18.69 | 70.13 |
| 22 | 50 | 90 | 8 | 7.93 | 59.62 |
| 23 | 75 | 90 | 8 | 13.32 | 66.64 |
| 24 | 100 | 90 | 8 | 18.69 | 70.16 |
| 25 | 50 | 10 | 10 | 3.09 | 23.21 |
| 26 | 75 | 10 | 10 | 6.46 | 32.32 |
| 27 | 100 | 10 | 10 | 13.48 | 50.59 |
| 28 | 50 | 30 | 10 | 4.72 | 35.76 |
| 29 | 75 | 30 | 10 | 10.48 | 52.42 |
| 30 | 100 | 30 | 10 | 17.51 | 65.71 |
| 31 | 50 | 60 | 10 | 7.49 | 56.35 |
| 32 | 75 | 60 | 10 | 13.02 | 65.17 |
| 33 | 100 | 60 | 10 | 19.51 | 73.23 |
| 34 | 50 | 90 | 10 | 8.38 | 62.98 |
| 35 | 75 | 90 | 10 | 14.33 | 71.69 |
| 36 | 100 | 90 | 10 | 21.16 | 79.96 |

**APPENDIX B3**: Adsorption capacity and removal efficiency results for MB at constant adsorbent dose (0.5 g/250 ml).

| No. of experiment | A:Conc.(ppm) | B:Time (min) | C:pH | Response 1: qe(mg/g) | Response 2: Removal efficiency(%) |
|---|---|---|---|---|---|
| 1 | 50 | 10 | 6 | 2.76 | 23.61 |
| 2 | 75 | 10 | 6 | 3.99 | 22.8 |
| 3 | 100 | 10 | 6 | 5.68 | 24.34 |
| 4 | 50 | 30 | 6 | 3.97 | 33.89 |
| 5 | 75 | 30 | 6 | 6.3 | 35.96 |
| 6 | 100 | 30 | 6 | 9.48 | 40.58 |
| 7 | 50 | 60 | 6 | 5.01 | 42.86 |
| 8 | 75 | 60 | 6 | 8 | 45.68 |
| 9 | 100 | 60 | 6 | 12.16 | 52.07 |
| 10 | 50 | 90 | 6 | 6.32 | 54 |
| 11 | 75 | 90 | 6 | 10.17 | 58.09 |
| 12 | 100 | 90 | 6 | 14.43 | 61.77 |
| 13 | 50 | 10 | 8 | 4.47 | 38.22 |
| 14 | 75 | 10 | 8 | 8.35 | 47.698 |
| 15 | 100 | 10 | 8 | 11.31 | 48.412 |
| 16 | 50 | 30 | 8 | 5.21 | 44.57 |
| 17 | 75 | 30 | 8 | 9.34 | 53.32 |
| 18 | 100 | 30 | 8 | 14.02 | 59.95 |
| 19 | 50 | 60 | 8 | 6.63 | 56.66 |
| 20 | 75 | 60 | 8 | 10.21 | 58.29 |
| 21 | 100 | 60 | 8 | 14.79 | 63.34 |
| 22 | 50 | 90 | 8 | 6.897 | 58.95 |
| 23 | 75 | 90 | 8 | 11.304 | 64.54 |
| 24 | 100 | 90 | 8 | 15.092 | 64.62 |
| 25 | 50 | 10 | 10 | 2.82 | 24.1 |
| 26 | 75 | 10 | 10 | 8.214 | 46.89 |
| 27 | 100 | 10 | 10 | 11.48 | 49.15 |
| 28 | 50 | 30 | 10 | 4.08 | 34.85 |
| 29 | 75 | 30 | 10 | 9.598 | 54.801 |
| 30 | 100 | 30 | 10 | 14.61 | 62.54 |
| 31 | 50 | 60 | 10 | 5.82 | 49.74 |
| 32 | 75 | 60 | 10 | 10.63 | 60.66 |
| 33 | 100 | 60 | 10 | 15.92 | 68.18 |
| 34 | 50 | 90 | 10 | 6.37 | 54.48 |
| 35 | 75 | 90 | 10 | 11.65 | 66.515 |
| 36 | 100 | 90 | 10 | 16.594 | 71.051 |

**APPENDIX B4:** Effect of adsorbent dose on adsorption capacity and removal efficiency for MG at constant concentration (100 ppm) and pH (10).

| No. of experiments | A:Dose (gram) | B:Time (hr) | Response 1: qe(mg/g) | Response 2: Removal efficiency(%) |
|---|---|---|---|---|
| 1 | 0.5 | 1 | 19.51 | 73.23 |
| 2 | 0.5 | 1 | 18.89 | 72.01 |
| 3 | 1 | 1 | 9.85 | 73.91 |
| 4 | 1 | 1 | 9.47 | 73.01 |
| 5 | 2 | 1 | 8.08 | 78.94 |
| 6 | 2 | 1 | 8.01 | 78.39 |
| 7 | 3 | 1 | 3.52 | 79.17 |
| 8 | 3 | 1 | 3.40 | 79.08 |
| 9 | 0.5 | 2 | 21.31 | 79.96 |
| 10 | 0.5 | 2 | 21.55 | 79.40 |
| 11 | 1 | 2 | 11.28 | 84.65 |
| 12 | 1 | 2 | 11.28 | 84.65 |
| 13 | 2 | 2 | 8.39 | 89.57 |
| 14 | 2 | 2 | 7.03 | 88.09 |
| 15 | 3 | 2 | 3.98 | 89.57 |
| 16 | 3 | 2 | 2.78 | 88.82 |
| 17 | 0.5 | 3 | 21.39 | 80.27 |
| 18 | 0.5 | 3 | 22.84 | 81.03 |
| 19 | 1 | 3 | 11.87 | 89.07 |
| 20 | 1 | 3 | 11.83 | 89.06 |
| 21 | 2 | 3 | 10.02 | 95.05 |
| 22 | 2 | 3 | 10.03 | 95.05 |
| 23 | 3 | 3 | 4.22 | 95.12 |
| 24 | 3 | 3 | 4.23 | 95.12 |
| 25 | 0.5 | 4 | 21.54 | 80.85 |
| 26 | 0.5 | 4 | 21.39 | 80.27 |
| 27 | 1 | 4 | 11.87 | 89.08 |
| 28 | 1 | 4 | 10.97 | 88.99 |
| 29 | 2 | 4 | 9.06 | 94.77 |
| 30 | 2 | 4 | 10.38 | 94.98 |
| 31 | 3 | 4 | 4.23 | 95.13 |
| 32 | 3 | 4 | 4.30 | 95.22 |

**APPENDIX B5:** Effect of adsorbent dose on adsorption capacity and removal efficiency for MB at constant concentration (100 ppm) and pH (10).

| No. of experiments | A:Dose (gram) | B:Time (hr) | Response 1: qe(mg/g) | Response 2: Removal efficiency(%) |
|---|---|---|---|---|
| 1 | 0.5 | 1 | 15.92 | 68.18 |
| 2 | 0.5 | 1 | 16.97 | 69.02 |
| 3 | 1 | 1 | 8.08 | 69.16 |
| 4 | 1 | 1 | 8.07 | 69.14 |
| 5 | 2 | 1 | 4.38 | 75.09 |
| 6 | 2 | 1 | 3.99 | 74.88 |
| 7 | 3 | 1 | 2.92 | 75.10 |
| 8 | 3 | 1 | 2.74 | 74.98 |
| 9 | 0.5 | 2 | 18.17 | 77.79 |
| 10 | 0.5 | 2 | 18.17 | 77.81 |
| 11 | 1 | 2 | 8.39 | 71.83 |
| 12 | 1 | 2 | 8.38 | 71.83 |
| 13 | 2 | 2 | 4.58 | 78.48 |
| 14 | 2 | 2 | 4.56 | 78.47 |
| 15 | 3 | 2 | 3.08 | 79.11 |
| 16 | 3 | 2 | 2.94 | 78.89 |
| 17 | 0.5 | 3 | 18.55 | 79.41 |
| 18 | 0.5 | 3 | 16.99 | 78.74 |
| 19 | 1 | 3 | 10.02 | 85.84 |
| 20 | 1 | 3 | 9.35 | 84.07 |
| 21 | 2 | 3 | 5.40 | 92.39 |
| 22 | 2 | 3 | 4.89 | 92.01 |
| 23 | 3 | 3 | 3.62 | 92.98 |
| 24 | 3 | 3 | 3.50 | 92.57 |
| 25 | 0.5 | 4 | 18.57 | 79.52 |
| 26 | 0.5 | 4 | 18.85 | 80.70 |
| 27 | 1 | 4 | 9.06 | 85.84 |
| 28 | 1 | 4 | 10.72 | 56.05 |
| 29 | 2 | 4 | 5.40 | 92.39 |
| 30 | 2 | 4 | 5.40 | 92.39 |
| 31 | 3 | 4 | 3.61 | 92.81 |
| 32 | 3 | 4 | 3.51 | 92.05 |

**APPENDIX B6:** Effect of process variables at optimum BFA dose for MG.

| No. of experiments | A:Conc.(ppm) | B:Time (hr) | C:pH | Response 1: qe(mg/g) | Response 2: Removal efficiency (%) |
|---|---|---|---|---|---|
| 1 | 50 | 1 | 6 | 1.60 | 48.17 |
| 2 | 75 | 1 | 6 | 3.28 | 65.71 |
| 3 | 100 | 1 | 6 | 4.92 | 73.79 |
| 4 | 50 | 2 | 6 | 1.88 | 56.40 |
| 5 | 75 | 2 | 6 | 3.41 | 68.26 |
| 6 | 100 | 2 | 6 | 4.93 | 74.05 |
| 7 | 50 | 3 | 6 | 1.99 | 59.79 |
| 8 | 75 | 3 | 6 | 3.52 | 70.44 |
| 9 | 100 | 3 | 6 | 5.02 | 75.30 |
| 10 | 50 | 4 | 6 | 2.07 | 62.18 |
| 11 | 75 | 4 | 6 | 3.63 | 72.73 |
| 12 | 100 | 4 | 6 | 5.04 | 75.59 |
| 13 | 50 | 1 | 8 | 2.03 | 61.08 |
| 14 | 75 | 1 | 8 | 3.52 | 70.44 |
| 15 | 100 | 1 | 8 | 5.00 | 75.07 |
| 16 | 50 | 2 | 8 | 2.24 | 67.48 |
| 17 | 75 | 2 | 8 | 3.71 | 74.31 |
| 18 | 100 | 2 | 8 | 5.11 | 76.76 |
| 19 | 50 | 3 | 8 | 2.38 | 73.02 |
| 20 | 75 | 3 | 8 | 3.95 | 79.03 |
| 21 | 100 | 3 | 8 | 5.27 | 79.17 |
| 22 | 50 | 4 | 8 | 2.43 | 73.02 |
| 23 | 75 | 4 | 8 | 4.03 | 80.73 |
| 24 | 100 | 4 | 8 | 5.55 | 83.32 |
| 25 | 50 | 1 | 10 | 2.17 | 65.21 |
| 26 | 75 | 1 | 10 | 3.88 | 77.74 |
| 27 | 100 | 1 | 10 | 5.31 | 79.71 |
| 28 | 50 | 2 | 10 | 2.51 | 75.48 |
| 29 | 75 | 2 | 10 | 4.10 | 82.02 |
| 30 | 100 | 2 | 10 | 5.87 | 88.06 |
| 31 | 50 | 3 | 10 | 2.67 | 80.19 |
| 32 | 75 | 3 | 10 | 4.38 | 87.62 |
| 33 | 100 | 3 | 10 | 6.30 | 94.51 |
| 34 | 50 | 4 | 10 | 2.85 | 85.67 |
| 35 | 75 | 4 | 10 | 4.49 | 89.91 |
| 36 | 100 | 4 | 10 | 6.29 | 94.40 |

**APPENDIX B7:** Effect of process variables at optimum BFA dosage for MG.

| No. of experiments | A:Conc.(ppm) | B:Time(hr) | C:PH | Response 1: qe(mg/g) | Response 2: Removal efficiency(%) |
|---|---|---|---|---|---|
| 1 | 50 | 1 | 6 | 1.09 | 37.38 |
| 2 | 75 | 1 | 6 | 2.12 | 48.36 |
| 3 | 100 | 1 | 6 | 3.63 | 62.16 |
| 4 | 50 | 2 | 6 | 1.12 | 38.15 |
| 5 | 75 | 2 | 6 | 2.38 | 54.28 |
| 6 | 100 | 2 | 6 | 3.71 | 63.59 |
| 7 | 50 | 3 | 6 | 1.24 | 42.35 |
| 8 | 75 | 3 | 6 | 2.57 | 58.79 |
| 9 | 100 | 3 | 6 | 3.89 | 66.59 |
| 10 | 50 | 4 | 6 | 1.69 | 57.71 |
| 11 | 75 | 4 | 6 | 2.87 | 65.52 |
| 12 | 100 | 4 | 6 | 3.94 | 67.53 |
| 13 | 50 | 1 | 8 | 1.35 | 46.28 |
| 14 | 75 | 1 | 8 | 3.06 | 69.95 |
| 15 | 100 | 1 | 8 | 3.87 | 66.20 |
| 16 | 50 | 2 | 8 | 1.83 | 62.39 |
| 17 | 75 | 2 | 8 | 3.32 | 75.86 |
| 18 | 100 | 2 | 8 | 4.01 | 68.61 |
| 19 | 50 | 3 | 8 | 2.03 | 69.26 |
| 20 | 75 | 3 | 8 | 3.43 | 78.31 |
| 21 | 100 | 3 | 8 | 4.72 | 80.75 |
| 22 | 50 | 4 | 8 | 2.07 | 70.64 |
| 23 | 75 | 4 | 8 | 3.47 | 79.19 |
| 24 | 100 | 4 | 8 | 4.79 | 81.96 |
| 25 | 50 | 1 | 10 | 1.80 | 61.62 |
| 26 | 75 | 1 | 10 | 3.17 | 72.32 |
| 27 | 100 | 1 | 10 | 4.43 | 75.91 |
| 28 | 50 | 2 | 10 | 2.06 | 70.47 |
| 29 | 75 | 2 | 10 | 3.63 | 82.88 |
| 30 | 100 | 2 | 10 | 4.64 | 79.38 |
| 31 | 50 | 3 | 10 | 2.31 | 78.96 |
| 32 | 75 | 3 | 10 | 3.76 | 85.77 |
| 33 | 100 | 3 | 10 | 5.45 | 93.30 |
| 34 | 50 | 4 | 10 | 2.40 | 81.95 |
| 35 | 75 | 4 | 10 | 3.83 | 87.39 |
| 36 | 100 | 4 | 10 | 5.47 | 93.64 |

**APPENDIX B8:** Effects of operating variables on removal efficiency at constant adsorbent dose (0.5 g/250 ml).

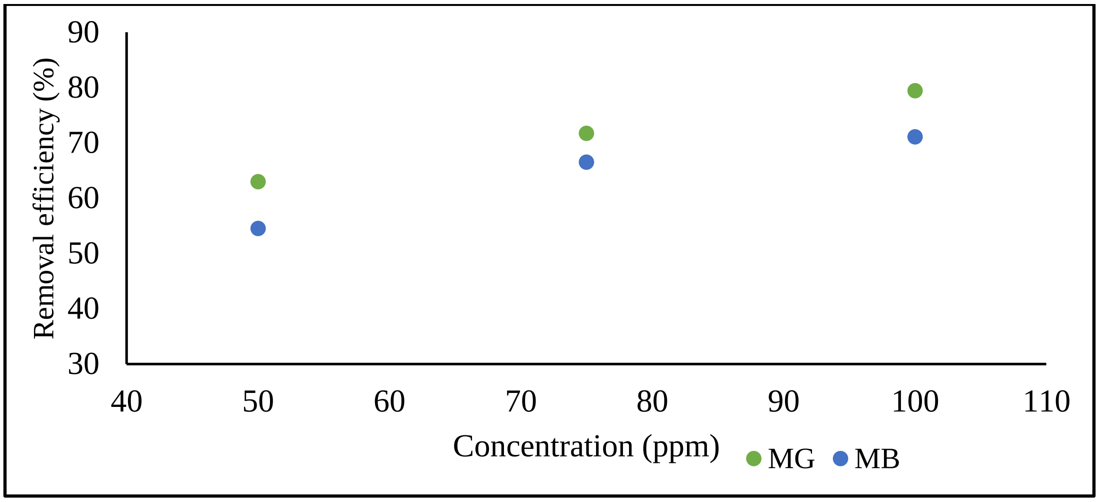


**Figure 2** Effect of initial dye concentration for both dyes [pH=10 and contact time =90 minute]

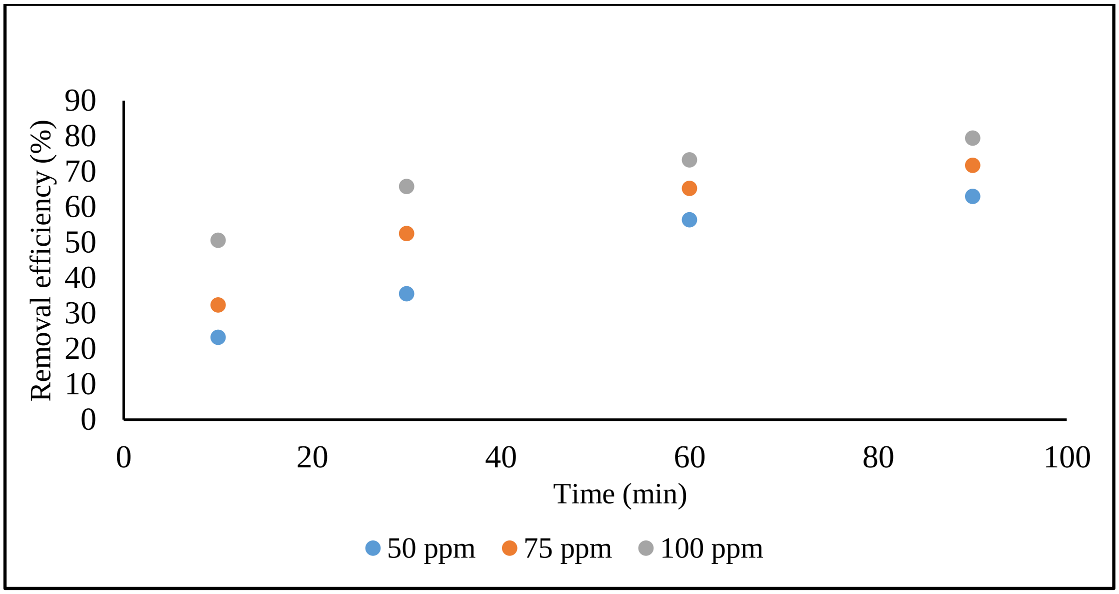


**Figure 3** Effect of time on removal efficiency for MG [pH=10]

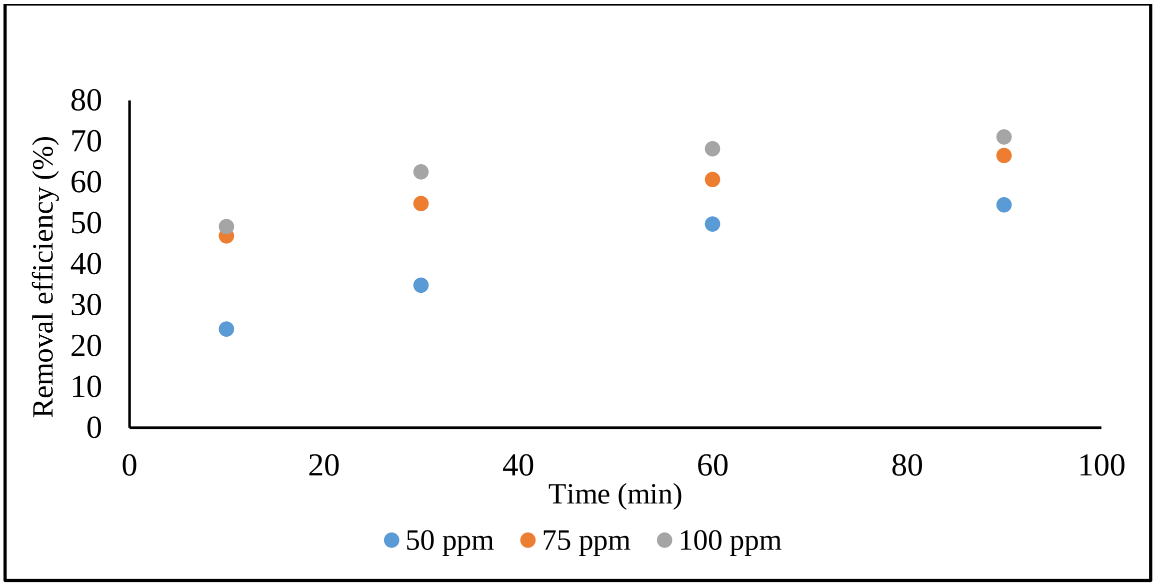


**Figure 4** Effect of time on removal efficiency for MB [pH=10]

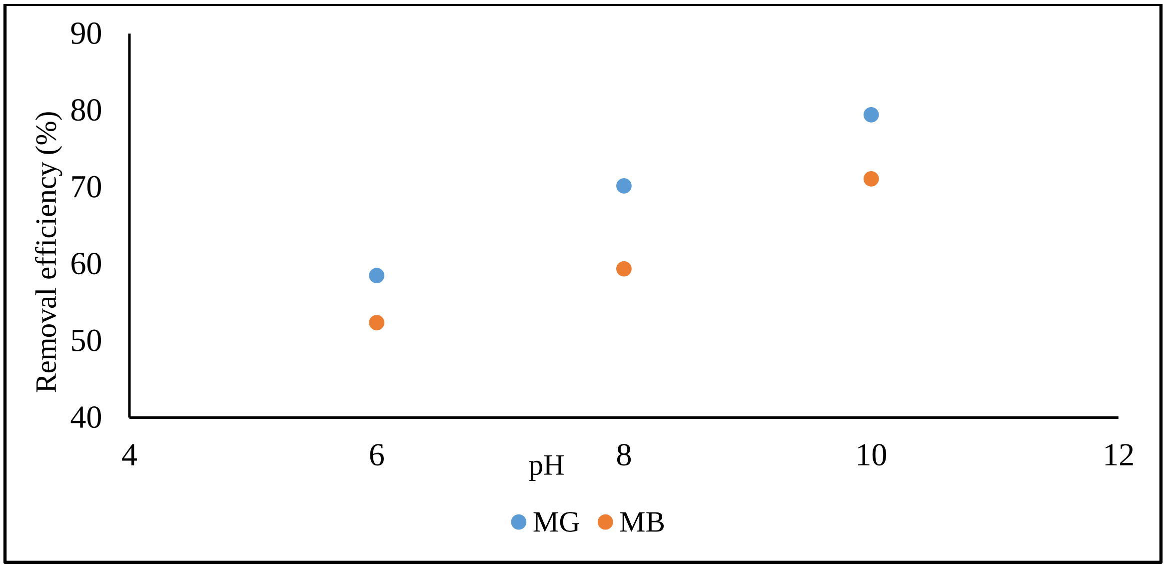


**Figure 5** Effect of pH on removal efficiency for both dyes [concentration =100 ppm and time =90 minute]

**APPENDIX C:** Adsorption isotherm and kinetics models results.

**APPENDIX C1:** Pseudo 1st order kinetics data.

| Concentration ( 50 ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|
| MG ($q_e$=9.547) | | | | MB($q_e$=7.976) | | | |
| t (min) | qt | $q_e$-$q_t$ | log ($q_e$-$q_t$) | t (min) | $q_t$ | $q_e$-$q_t$ | log ($q_e$-$q_t$) |
| 10 | 3.087 | 6.460 | 0.810 | 10 | 2.820 | 18.567 | 1.269 |
| 30 | 4.716 | 4.831 | 0.684 | 30 | 4.078 | 17.309 | 1.238 |
| 60 | 7.495 | 2.052 | 0.312 | 60 | 5.820 | 15.567 | 1.192 |
| 90 | 8.377 | 1.170 | 0.068 | 90 | 6.374 | 15.013 | 1.176 |
| 120 | 8.963 | 0.584 | -0.233 | 120 | 7.220 | 14.167 | 1.151 |
| 180 | 9.547 | 0.000 | -3.362 | 180 | 7.976 | 13.411 | 1.127 |
| 240 | 9.550 | -0.003 | #NUM! | 240 | 8.165 | 13.222 | 1.121 |
| 1440 | 9.684 | -0.137 | #NUM! | 1440 | 8.260 | 13.127 | 1.118 |

| Concentration (75 ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|
| MG ($q_e$= 15.064) | | | | MB ($q_e$=13.035) | | | |
| t(min) | $q_t$ | $q_e$-$q_t$ | log ($q_e$-$q_t$) | t(min) | $q_t$ | $q_e$-$q_t$ | log ($q_e$-$q_t$) |
| 10 | 6.459 | 8.605 | 0.935 | 10 | 8.214 | 4.821 | 0.683 |
| 30 | 10.477 | 4.587 | 0.662 | 30 | 9.598 | 3.436 | 0.536 |
| 60 | 13.023 | 2.041 | 0.310 | 60 | 10.625 | 2.410 | 0.382 |
| 90 | 14.328 | 0.736 | -0.133 | 90 | 11.650 | 1.385 | 0.141 |
| 120 | 14.480 | 0.584 | -0.234 | 120 | 12.279 | 0.756 | -0.121 |
| 180 | 15.064 | 0.000 | -4.783 | 180 | 13.035 | 0.000 | #NUM! |
| 240 | 15.067 | -0.003 | #NUM! | 240 | 13.035 | 0.000 | #NUM! |
| 1440 | 15.098 | -0.034 | #NUM! | 1440 | 13.886 | -0.851 | #NUM! |

| Concentration (100 ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|
| MG ($q_e$=21.387) | | | | MB ($q_e$=18.546) | | | |
| t(min) | $q_t$ | $q_e$-$q_t$ | log ($q_e$-$q_t$) | t(min) | $q_t$ | $q_e$-$q_t$ | log (qe-qt) |
| 10 | 13.480 | 7.907 | 0.898 | 10 | 11.478 | 7.068 | 0.849 |
| 30 | 17.509 | 3.878 | 0.589 | 30 | 14.606 | 3.941 | 0.596 |
| 60 | 19.513 | 1.874 | 0.273 | 60 | 15.923 | 2.624 | 0.419 |
| 90 | 21.155 | 0.232 | -0.635 | 90 | 16.594 | 1.952 | 0.291 |
| 120 | 21.305 | 0.082 | -1.084 | 120 | 18.168 | 0.378 | -0.422 |
| 180 | 21.387 | 0.000 | #NUM! | 180 | 18.546 | 0.000 | #NUM! |
| 240 | 21.542 | -0.155 | #NUM! | 240 | 18.572 | -0.026 | #NUM! |
| 1440 | 21.603 | -0.216 | #NUM! | 1440 | 18.847 | -0.301 | #NUM! |

**APPENDIX C2:** Pseudo 2nd order kinetics data.

| Concentration ( 50 ppm) | | | | | |
|---|---|---|---|---|---|
| MG | | | MB | | |
| t(min) | $q_t$ | $t/q_t$ | t(min) | $q_t$ | $t/q_t$ |
| 10 | 3.087 | 3.239 | 10 | 2.820 | 3.546 |
| 30 | 4.716 | 6.361 | 30 | 4.078 | 7.357 |
| 60 | 7.495 | 8.005 | 60 | 5.820 | 10.309 |
| 90 | 8.377 | 10.744 | 90 | 6.374 | 14.121 |
| 120 | 8.963 | 13.389 | 120 | 7.220 | 16.621 |
| 180 | 9.547 | 18.855 | 180 | 7.976 | 22.568 |
| 240 | 9.550 | 25.131 | 240 | 8.165 | 29.394 |
| 1440 | 9.684 | 148.700 | 1440 | 8.260 | 174.344 |

| Concentration (75 ppm) | | | | | |
|---|---|---|---|---|---|
| MG | | | MB | | |
| t(min) | $q_t$ | $t/q_t$ | t(min) | $q_t$ | $t/q_t$ |
| 10 | 6.459 | 1.548 | 10 | 8.214 | 1.217 |
| 30 | 10.477 | 2.864 | 30 | 9.598 | 3.126 |
| 60 | 13.023 | 4.607 | 60 | 10.625 | 5.647 |
| 90 | 14.328 | 6.281 | 90 | 11.650 | 7.725 |
| 120 | 14.480 | 8.287 | 120 | 12.279 | 9.773 |
| 180 | 15.064 | 11.949 | 180 | 13.035 | 13.809 |
| 240 | 15.067 | 15.928 | 240 | 13.035 | 18.412 |
| 1440 | 15.098 | 95.375 | 1440 | 13.886 | 103.705 |

| Concentration (100 ppm) | | | | | |
|---|---|---|---|---|---|
| MG | | | MB | | |
| t (min) | $q_t$ | $t/q_t$ | t (min) | $q_t$ | $t/q_t$ |
| 10 | 13.480 | 0.742 | 10 | 11.478 | 0.871 |
| 30 | 17.509 | 1.713 | 30 | 14.606 | 2.054 |
| 60 | 19.513 | 3.075 | 60 | 15.923 | 3.768 |
| 90 | 21.155 | 4.254 | 90 | 16.594 | 5.424 |
| 120 | 21.305 | 5.633 | 120 | 18.168 | 6.605 |
| 180 | 21.387 | 8.416 | 180 | 18.553 | 9.702 |
| 240 | 21.542 | 11.141 | 240 | 18.553 | 12.936 |
| 1440 | 21.603 | 66.658 | 1440 | 18.932 | 76.063 |

## **APPENDIX D:** Analysis of variance (ANOVA) for removal efficiency.

### **APPENDIX D1:** Analysis of variance (ANOVA) for removal efficiency for MG.

Response: Removal efficiency
ANOVA for response surface: Quadratic model
Analysis of variance table [Partial sum of squares]

| Source | Sum of Squares | DF | Mean Square | F-Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 12199.59 | 9 | 1355.51 | 116.98 | < 0.0001 | significant |
| A | 2227.05 | 1 | 2227.05 | 192.19 | < 0.0001 | |
| B | 7527.04 | 1 | 7527.04 | 649.56 | < 0.0001 | |
| C | 980.09 | 1 | 980.09 | 84.58 | < 0.0001 | |
| $A^2$ | 7.01 | 1 | 7.01 | 0.61 | 0.4395 | |
| $B^2$ | 276.55 | 1 | 276.55 | 23.87 | < 0.0001 | |
| $C^2$ | 552.69 | 1 | 552.69 | 47.70 | < 0.0001 | |
| AB | 33.26 | 1 | 33.26 | 2.87 | 0.0952 | |
| AC | 495.18 | 1 | 495.18 | 42.73 | < 0.0001 | |
| BC | 173.33 | 1 | 173.33 | 14.96 | 0.0003 | |
| Residual | 718.45 | 62 | 11.59 | | | |
| Lack of Fit | 709.50 | 26 | 27.29 | 109.77 | < 0.0001 | significant |
| Pure Error | 8.95 | 36 | 0.25 | | | |
| Cor Total | 12918.05 | 71 | | | | |

### **APPENDIX D2:** Analysis of variance (ANOVA) for removal efficiency for MB.

Response: removal efficiency
ANOVA for response surface: Quadratic model
Analysis of variance table [Partial sum of squares]

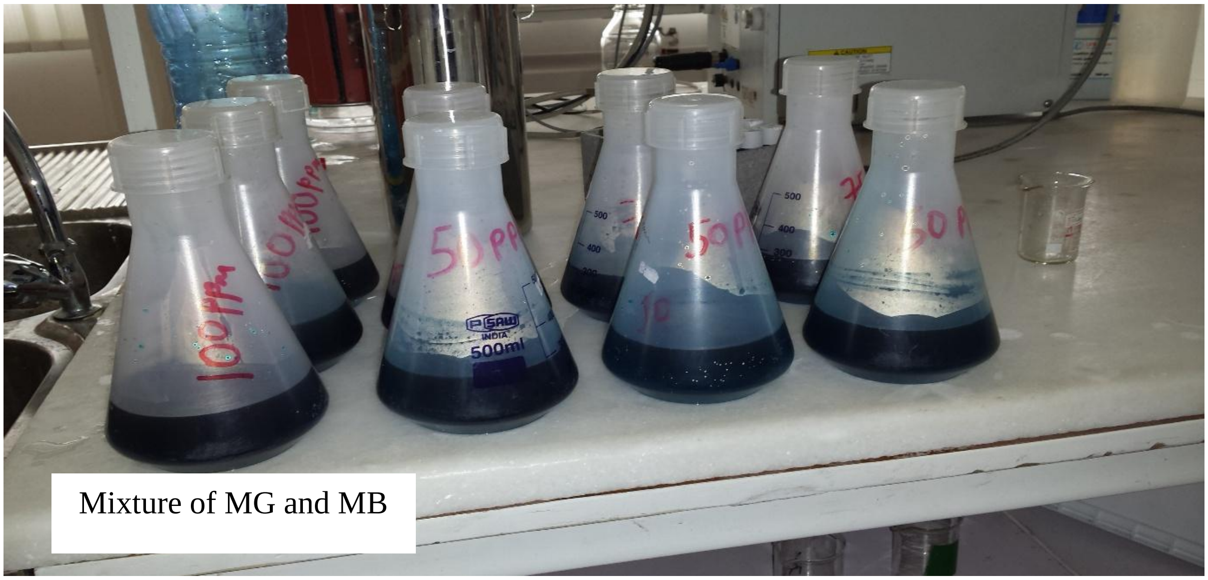
| Source | Sum of Squares | DF | Mean Square | F-Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 11996.07 | 9 | 1332.90 | 104.92 | < 0.0001 | significant |
| A | 1865.19 | 1 | 1865.19 | 146.81 | < 0.0001 | |
| B | 6564.22 | 1 | 6564.22 | 516.69 | < 0.0001 | |
| C | 1638.22 | 1 | 1638.22 | 128.95 | < 0.0001 | |
| $A^2$ | 83.84 | 1 | 83.84 | 6.60 | 0.0126 | |
| $B^2$ | 190.78 | 1 | 190.78 | 15.02 | 0.0003 | |
| $C^2$ | 865.85 | 1 | 865.85 | 68.15 | < 0.0001 | |
| AB | 27.99 | 1 | 27.99 | 2.20 | 0.1428 | |
| AC | 506.03 | 1 | 506.03 | 39.83 | < 0.0001 | |
| BC | 161.69 | 1 | 161.69 | 12.73 | 0.0007 | |
| Residual | 787.67 | 62 | 12.70 | | | |
| Lack of Fit | 766.65 | 26 | 29.49 | 50.48 | < 0.0001 | significant |
| Pure Error | 21.03 | 36 | 0.58 | | | |
| Cor Total | 12783.74 | 71 | | | | |

**APPENDIX E:** Fourier Transform Infrared Spectroscopy (FTIR) correlation table.

| Functional Group Names | Absorption Ranges($cm^{-1}$) | Type of Vibration causing IR absorption |
|---|---|---|
| Alkanes | 3000-2800 | H-C-H asymmetric & symmetric stretch |
| | 1500-1440 | H-C-H bend |
| Alkenes | 3100-3000 | C=C-H asymmetric stretch |
| | 1675-1600 | C-C=C symmetric stretch |
| Alkynes | 3300-3200 | ≡C H stretch |
| | 2200-2100 | C¯ C stretch |
| Aromatic Rings | 3100-3000 | C=C-H asymmetric Stretch |
| | 1600-1580 | C-C=C symmetric stretch |
| | 1500-1450 | C-C=C asymmetric stretch |
| Phenols & Alcohols | 3600-3100 | Hydrogen-bonded O-H stretch |
| Carboxylic Acids | 3400-2400 | Hydrogen-bonded O-H stretch |
| | 1730-1650 | C=O stretch |
| Ketones | 1750-1625 | C=O stretch |
| Aldehydes | 1750-1625 | C=O stretch |
| | 2850-2800 | C-H stretch off C=O |
| | 2750-2700 | C-H stretch off C=O |

| | | |
|---|---|---|
| Esters | 1755-1650 | C=O stretch |
| | (1300-1000) | (C-O stretch) |
| Ethers | (1300-1000) | (C-O stretch) |
| Amines—Primary | 3500-3100 | N-H stretch |
| | 1640-1560 | N-H bend |
| Amines—Secondary | 3500-3100 | N-H stretch |
| | 1550-1450 | N-H bend |
| Nitriles | 2300-2200 | C N stretch |
| Nitro Groups | 1600-1500 | N=O stretch |
| | 1400-1300 | N=O bend |
| Amides | 3500-3100 | N-H stretch |
| | 1670-1600 | C=O stretch |
| | 1640-1550 | N-H bend |

## **APPENDIX F:** Laboratory pictures



Mixture of MG and MB

Before adsorption

After adsorption