JIMMA UNIVERSITY
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THESIS ON:

ADSORPTION STUDIES ON REMOVAL OF METHYLENE BLUE DYE USING DRINKING WATER TRANSPORT SLUDGE FROM WATER

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JIMMA, ETHIOPIA

ADSORPTION STUDIES ON REMOVAL OF METHYLENE BLUE DYE USING DRINKING WATER TREATMENT SLUDGE FROM WATER

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THIS THESIS SUBMITTED TO JIMMA UNIVERSITY COLLEGE OF NATURAL SCIENCES DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENTS OF THE REQUIREMENT FOR THE DEGREEOF MASTER OF SCIENCE IN CHEMISTRY

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DECLARATION

This thesis entitled **adsorption studies on removal of Methylene blue dye using drinking water treatment sludge from water,** submitted to College of Natural Sciences, Department of Chemistry in partial fulfillment of the requirements for the Degree of Master of science in chemistry. Shambel Yeshitila hereby I declare that this M.Sc. thesis is my original work and has not been presented for a degree in any other University and that all source of materials used for the thesis have been properly acknowledged.

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ABSTRACT

Wastewater generated by textile plants is linked to one of the major problems of water pollution. It contains a mixture of different dyes, auxiliaries, additives and additional chemicals that were added during textile production processes, causing serious environmental concerns. Focusing the environmental issue and economic point of view, the use of low cost and eco-friendly adsorbents has been investigated as an alternative to the current expensive method of removing dyes from wastewater. Drinking water treatment sludge (DWTS) was produced together with processed drinking water in a typical water treatment plant. A large amount of Alum derived DWTS was generated in Jimma city, such that disposal of the sludge and its beneficial reuse was concerned. In this study, Drinking Water Treatment Sludge (DWTS) particularly, Alum Sludge adsorbent (ASA) was used for the removal of Methylene blue (MB) dye from aqueous solution using batch adsorption process. Some Physico-chemical properties of the adsorbent were determined, such as surface area, surface functional group, surface crystal & point of zero charge. For optimization of the adsorption, the effect of contact time, effect of initial solution pH, adsorbent dosage & initial Methylene blue concentration were investigated. The surface area measured by Sear method was $43.8m^2/g$ & point of zero charge was 6.23, for adsorbent. Untreated alum sludge adsorbent was characterized using by Fourier Transform Infrared (FTIR) & X-ray Diffraction (XRD). The equilibrium was achieved within an adsorption time of 60 min at the optimum pH of 7 & adsorbent dose of 5 g/L. In order to describe the relationship between the concentration of MB dye in the solution and the amount of MB dye adsorbed to adsorbent, Langmuir & Freundlich isotherm models were used for the equilibrium tests. The equilibrium data were best fitted to the Langmuir isotherm model ($R^2 = 0.942$), the adsorption capacity (q_{max}) and efficiency (%) calculated from the Langmuir isotherm value obtained was 21.63 mg/g and 96.5% respectively. Pseudo-first-order and pseudo-second-order models were used to evaluate adsorption kinetics and it was found that the pseudo-second-order model data ($R^2 = 0.859$) is the best described MB adsorption for adsorbent. From this study, DWTS could be reused, which is cost effective and environmentally friendly. Therefore, the application of DWTS could provide a solution for safe management of water treatment waste while providing a resource for water treatment.

Keyword: Batch adsorption, Drinking water treatment sludge, Methylene blue dye,
Isotherm and Kinetic models.

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ACRONYMS/ABREVIATIONS

ASA	Alum Sludge Adsorbent
CV	Crystal Violet
UV-VS	Ultra Violet Visible Spectrophotometer
FTIR	Fourier Transformer Infrared
MG	Malachite Green
MB	Methylene Blue
MO	Methyl Orange
pH	Power of Hydrogen
PFO	Pseudo-First-Order
PSO	Pseudo-Second-Order
PZC	Point of Zero Charge
WTPS	Water Treatment Plant Sludge
XRD	X-ray Diffraction

1. INTRODUCTION

1.1. Background of the study

Water is one of the most essential components of the environment which circulates among atmosphere, lithosphere and hydrosphere and it is required to fulfill different types of needs in every phase of the lifecycle[1].The rapid development of the industry such as textile, paper, printing, food, cosmetic industries are direct and indirect discharge of dyes to the environment from wastewater has been significantly augmented[2]. Industries produce wastewater containing organics with a strong color, where in the dyeing processes the percentage of dye lost wastewater is 50% of the dye because of the low levels of dye-fiber fixation[3]. Discharge of these dyes in to water bodies affects the people who may use these effluents polluted water for living purposes such as washing, bathing and drinking[4]. Dyes also prevent light penetration and thereby reduce photosynthetic activities of water streams and disturb the aquatic equilibrium[5]. The problems become high due to the fact that the complex aromatic structures of the dyes render them ineffective in the presence of heat, light, microbes, and even oxidizing agents and degradation of the dyes become difficult[6].

Methylene Blue (MB) dye is an organic cationic dye and aromatic heterocyclic compound with chemical formula $C_{16}H_{18}N_3SCl$ and yields a blue solution when dissolved in water[7]. MB has a characteristic deep blue colour in the oxidized state and is colorless in the reduced form [8, 9]. The chemical structure of MB is complex; it is difficult to fade away from exposed light and water; therefore, it is difficult to remove it from wastewater using commonly used techniques[10, 11]. MB is toxic, carcinogenic and non-biodegradable and can cause a serious threat to human health and destructive effects on the environment[12]. MB causes several risks to human health such as respiratory distress, abdominal disorders, blindness and digestive and mental disorders[13, 14]. MB also affects the photosynthetic activity of aquatic life, decreases the diversity and aesthetics of the biological community[15]. As the results, MB dye is stable to light and not biologically degradable; it is resistant to aerobic digestion and signify one of the difficult groups to removed from the industrial wastewater[16, 17].

Wastewater effluents contain synthetic MB dyes which may cause a potential hazard to the environment and human health[18]. Due to the environment and health concerns associated with the wastewater effluents, different conventional methods have been used in the removal of Methylene blue (MB) dyes; such as chemical-precipitation[19], adsorption[20], ion-exchange[21], membrane-separation[22], electrodialysis[23] and Electro-coagulation[24]. However, these methods have some shortcoming such as low efficiency, high operating and maintenance cost, generate sludge causing disposal problems, or produce a secondary pollutant, which limits their applicability in the real situation[25]. In contrast adsorption method is simple to operate, solves the challenge of sludge disposal, high efficiency and an effective method for the removal of MB dye from aqueous solutions[26]. This Physico-chemical technique has been found to be most simple and economical for the removal of dyes from textile effluents[27]. A number of low cost materials including industrial waste material, agricultural waste material and naturally found material have been tried out for the removal of dyes[28]. Even though, the adsorption capacity with these adsorbents were not found much large but still they are widely needed as they are found to be cost effective, eco-friendly and fairly efficient[29]. Different adsorbent like natural diatomite, alumina, chitosan, clays, orange and banana peels, fly ash, Red mud, activated and modified sludge have been used to remove MB dye from wastewater[7, 14, 20, 30].

Aluminum salts are one of the most commonly used coagulants in the water treatment plant (WTP) industry. In drinking WTP; where aluminum salts are used as the primary coagulating-flocculating agents, immense amounts of alum sludge (AS) was generated every day[31]. The proper collection, transport and disposal cost to land filling of the sludge is one of the most meaningful problems for the drinking WTP[32]. Therefore, attention has been focused on research towards its reuse. Up to now, several researchers have investigated the suitability of alum sludge taken from drinking water treatment plant works for the removal of heavy metals, phosphorus, reactive dyes, azo-dyes using activated and/or modified from aqueous solution[3, 33]. The focus of this study is the approach where untreated alum sludge is used, and feasibility of using low cost adsorbent for MB dye removal[31, 34]. The effects on adsorption of contact time, initial pH of solution, initial concentration of MB and adsorbent dose were investigated. At different initial concentrations and contact times; the isotherm models were tested for their applicability and kinetic models were applied to the rates of adsorption process.

1.2. Statement of the problems

Textile effluents are considered very complex since they contain salt, surfactants, metal ions and their metal complexes, toxic organic chemicals and toxic anions[33, 34]. Dyes and their precursors are well known for high toxicity and supposed to be human carcinogens as they form toxic aromatic amines[12]. These dyes are difficult to break down biologically due to the complex nature of their chemical structures[10]. Removing the colour of wastewater is an issue of concern for both aesthetics and health [7, 37]. The textile industries are required to treat waste matter containing dyes before they are discharged to water bodies[38].

There are several promising techniques for removal of dyes from wastewater such as: physical, chemical and biological methods which were widely used to treat wastewater[39]. However, in developing countries, such methods remain difficult and tend to produce secondary pollutant. Among these technologies adsorption is frequently used as an effective technique to remove water soluble contaminants and an attractive method for the removal of dyes such as MB in terms of its low cost, simplicity of design and operation[40]. Since the removal of MB from aqueous solutions and wastewater using alum sludge (AS) as adsorbent was not been investigated, it could be used to remove MB dye from water bodies. Therefore, this application can be a stepping stone for providing a solution for safe management of industrial waste while providing a resource for water and waste water treatment.

1.3. Objective of the study

1.3.1. General objective:

- ✓ To evaluate Methylene Blue (MB) dye removal from aqueous solutions using Alum Sludge adsorbent (ASA).

1.3. 2. Specific objectives:

- ✓ To investigate the adsorption efficiencies of ASA for the removal of Methylene blue (MB) from aqueous solutions.
- ✓ To determine the effects of parameters such as contact time, initial solution pH, adsorbent dose and initial concentrations of MB on the adsorption efficiencies of ASA.
- ✓ To characterize the surface functional group and structure of crystals of ASA.
- ✓ To assess the kinetic and isotherm models for the adsorption of MB dye onto the ASA.
- ✓ To evaluate the regeneration capacity of ASA.

1.4. Significance of the study

It is known that Methylene blue dye is used in various industries such as textile, cosmetic, pharmaceutical, paper, printing, food industries etc. However, an intensive and uncontrolled uses of this dye result in the contamination of the water. Therefore, the development of efficient and effective method for the removal of Methylene blue is crucial. In general, the finding of this study will have the following significances:

- ✓ The obtained results could be used as background information regarding the removal techniques for Methylene blue from aqueous solutions and wastewater samples.
- ✓ It could help concerned bodies to put attention on the source of Methylene blue contamination to avoid pollutions of environment.
- ✓ The investigated method could provide data to explore low-cost technology and the use of an aluminum sludge waste to solve problem related to Methylene blue removal from various water sources.
- ✓ The finding could also serve as resource materials to carry out future research on similar method.

2. LITERATURE REVIEW

2.1. Dyes

Dyes are chemical compounds that have a complex aromatic molecular structure that attach to fabrics or surface shells to create colour. These structures are present in stable dyes, are very difficult to treat, and have low biodegradability. The depolarization of waste water from the textile and manufacturing industries is a major challenge for environmental managers because dyes are soluble in water and produce very bright colors in water with acidic properties[5, 10, 14]. Dyes as colorful substances have been utilized by humans since 3500 BC in various applications using natural extracts of flowers, fruits and certain insects[6]. Synthetic dyes are developed and have replaced natural dyes gradually in different industries because their molecules are stable and can resist degradation upon contact with water, detergents, or any other washing agents[41]. They are widely used in textiles, printing, rubber, cosmetics, plastics, leather industries to color their products leads to the production of a large quantity of colored manure[36]. They constitute a significant group of pollutants as several industries discharge a huge amount of wastewater containing various dyes into natural water bodies[35].The removal of colour from wastewater is often more important than the removal of other organic colorless chemicals[42]. Due to high concentration of organics in the effluents and higher stability of modern synthetic dyes, their discharges into rivers are harmful to aquatic life[35, 43].Therefore, decolorization of effluents from textile dyeing, paper, ceramics, cosmetics, printing, food industries were regarded important, because of aesthetic and environmental concerns[43–45].Thus there is an urgency of finding a potential advanced treatment process, which could be an economic and effective process of treating colored wastewater completely[46, 47].

2.2. Classification of dye

Commonly, the dyes used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, and azo dyes, mordant dyes, vat dyes, disperse dyes and sulfur dyes, where azo derivatives are the major class of dyes that are used in the industry today[30, 48, 49]. There are several ways for classification of marketable dyes. It can be classified based on their chemical structure into azo, anthraquinone, indigoid, nitroso, nitro, and triarylmethane dyes[44, 45]. Sometimes, they are classified by their application or by their solubility in water. However, the classification based on application is advantageous before considering chemical structures in detail because of the complexities of the dye nomenclature from this type of system[50]. Dyes are also usually classified based on their particle charge upon dissolution in aqueous application medium; such as cationic (all basic dyes) [42, 51], anionic (acid, reactive dyes)[5, 16]and non-ionic (dispersed dyes)[52].

2.2.1. Reactive dyes

They are anionic dyes which contain reactive groups such as vinyl sulphone, chlorotriazine, trichloropyrimidine, and difluorochloropyrimidine that covalently bonded with the fiber during the dyeing process[49]. Moreover, azo dyes represent the largest class of reactive dyes used in the textile industry followed by anthraquinone and phthalocyanine classes. Azo dyes have the largest variety of dyes and under anaerobic conditions; the dye's linkage can be reduced to form aromatic amines which are colorless but can be toxic and carcinogenic[26, 49].

2.2.2. Anionic dyes

They have negative ions due to the excess presence of the OH^- ions in aqueous solution. Anionic dyes are water soluble and they include acid dyes, azo dyes, direct dyes and reactive dyes[16]. Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of dye and that of the fiber [15]. Their removal is the most challenging task as they produce very bright colors in water and show acidic properties [10].

2.2.3. Cationic dyes

They are also called basic dyes due to the presence of positive ions in the molecule's structure. Basic dyes are water soluble and they are highly visible in water even at very low concentration Basic dyes consist of monobasic, diazoic and amine compounds[16, 53]. They are used to colour wool, silk, nylon, mod-acrylic and polyester materials. Cationic functionality is found in various types of dyes such as cationic azo dyes, methane dyes, anthraquinone, di- and tri-arylcarbenium, phthalocyanine dyes, polycarbocyclic and solvent dyes [34, 44].

2.3. Methylene blue (MB) dye

2.3.1. Chemistry of Methylene blue (MB)

MB is a solid, odorless, dark green powder at room temperature and yields a blue solution when dissolved in water[54, 55]. MB is one of the most commonly used dyes in the industry[52]. Its formula, $C_{16}H_{18}ClN_3S$ with a molecular weight of 319.85 g/mol[44]. MB has a characteristic deep blue colour in the oxidized state and is colorless in the reduced form[53]. The main components of MB dye molecule is: the chromophoric, which are responsible for producing the color, and the auxochrome, which can not only supplement the chromophoric but also render the molecule soluble in water and give enhanced affinity to attach toward the fibers [8, 22]. The colour of MB depends on its chromophoric and auxochrome groups. The chromophoric of MB is the N–S conjugated system on the central aromatic heterocyclic, while the auxochrome is N-containing groups with lone pair electrons on the benzene ring [38, 56].

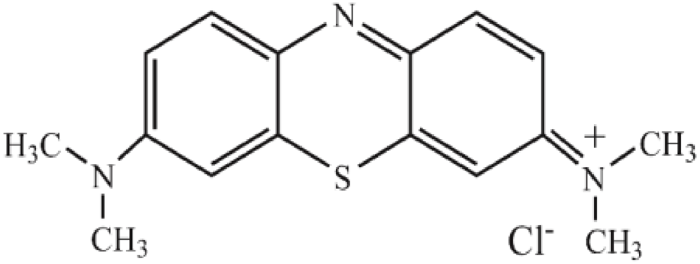


Fig.1 The structure of Methylene blue (MB) dye [21]

2.3.2. Toxicity of Methylene blue

Textile industries usually release a large amount of MB dyes in natural water sources, which becomes a health hazard to human beings and microorganisms[48]. MB dye is harmful to human health above a certain concentration due to its extensive toxicity[55]. MB is toxic, carcinogenic and non-biodegradable and can cause a serious hazard to human health and destructive effects on the environment[12, 57]. MB causes several risks to human health such as respiratory distress, abdominal disorders, blindness, digestive and mental disorders[58]. It also causes nausea, diarrhea, vomiting, shock, tissue necrosis, and increased heart rate and skin/eye irritations[17]. MB discharge into the environment is a significant threat for aesthetical and toxicological reasons[59]. It also reduces light penetration and a toxic supply to food chains for organisms and also even at a very low concentration, makes highly colored sub-products[1, 2, 41].

2.3.3. Uses and applications of Methylene blue

MB is an attractive molecule with various properties useful for biomedical application and is used as an effective therapeutic agent to treat anemia and malaria[36, 40]. MB has primarily been used in human and veterinary medicine for several diagnostic and therapeutic procedures[51]. MB was the first synthetic antimalarial used during the late 19th - early 20th centuries against all types of malaria and can also act as a chloroquine sensitize[50]. It can also use for the following purposes: Dyeing of fabric, staining in bacteriology, Oxidation-reduction indicator and Antiseptic[6, 13, 33]. MB dye is being used for the photodynamic treatment of cancer[12]. It is widely used as photosensitizing agent for photodynamic inactivation of RNA viruses (including HIV, hepatitis B and hepatitis C viruses) in plasma[57]. Presently, it is used clinically in a wide range of medications that treat conditions such as urinary tract infections, thyroid surgery, cancer chemotherapy[57]. MB dye has many potential applications in the textile, pharmaceutical, paper, dyeing, printing, paint, medicine, and food industries[16]. It is the most common dye in the textile industry; is considered one of the most popular clothing colorants[8]. MB dye is applicable as a photo sensitizer, an oxidation-reduction indicator, an optical redox indicator in analytical chemistry and in the trace analysis of anionic surfactant[27]. It is also applied as a potential material in dye-sensitized solar cells, capacitors, sensors, microbial fuel cells[60].

2.3.4. Methylene blue dye impacts on the environment

Due to its high solubility, mobility and reaction, MB harmfully affects the environment, Human health and the atmosphere[50, 61]. The accumulation of dyes in economically essential crops and vegetables watered with textile effluent has been analyzed[51]. While reduced MB is an essential human healthy treat, there is no question that both acute and incurable poisonous compounds are oxidized MB compounds[37]. The dose entry outcome for this portion has not yet been adequately tested to enable regulations to be specified but a few risk assessment analyses are currently being attempted. In recent days, the direct discharge of wastewater from textile, printing, ceramics etc to water bodies has become an emerging environmental issue[58]. Most of these effluents are highly complex mixtures containing inorganic and organic compounds that theoretically make a pollution-intensive sphere for the industry wastes[17, 59]

2.4. Methylene blue dye removal technologies

MB dye contamination is common all over the world; for water resources the impact of this contamination is severe[62, 63]. As a result, it is useful to remove MB from the contaminated water[1]. Many treatment processes have been developed to remove MB from wastewater. The most important of these technologies include: chemical-precipitation[11], adsorption[16], membrane process[18], ion-exchange[21], electrodialysis[23] and electro-coagulation[24]. However, all these technologies have their intrinsic advantages and limitations in application[23, 33, 64]. Most of the methods familiarity from some shortcoming such as incomplete removal, low selectivity, high reagent and energy requirement, high capital and operational cost and generation of toxic sludge or other waste product that require careful disposal has made it very important for a cost effective treatment method[35, 36, 45, 46]

2.4.1 Chemical precipitation

Chemical precipitation is the most widely used for MB removal from inorganic and organic effluent [65].It is regarded as one of the established technologies for MB dyes and other pollutants removal from wastewater due to its simplicity and low cost [33]. In this method, pollutants settle down as precipitates which then separated from the solution employing filtration, centrifugation or other suitable methods[4]. Coagulant as a precipitating agent causes the smaller particles suspended in solution to increase their particle size for settling down as sludge [66]. Flocculation is a slow gentle mixing of the water to encourage the flocs to form and grow to a size which will easily settle out[48]. In the conventional water treatment process coagulation using alum and ferric coagulants has been used for MB removal, in which the removal is due to precipitation as basic and acidic dyes [19, 34]. Usually, hydroxide precipitant is commonly used for its low cost, simplicity and the ease of pH control. In hydroxide precipitation process, addition of coagulants such as iron salts, alum and organic polymers can increase the removal quantity of MB dyes from wastewater [67, 68]. The disadvantage of this processes are requirement of working with corrosive chemicals which increase operator safety concerns and addition of treatment chemicals, especially lime, may increase the volume of waste sludge [31, 36]

2.4.2 Membrane filtration

The word membrane originated from the Latin word membrane which means a skin[45]. It can be defined as a discontinuous phase between two adjacent phases that permits the exchange of matter, energy and information [33]. It selectively passes the materials and used to separate single-celled organisms like bacteria to atom [18]. Between the phases with selective or nonselective properties; the main membrane separation processes used for wastewater treatment are Reverse osmosis (RO), Nano-filtration (NF), Ultra-filtration (UF), Micro-filtration (MF) etc [69, 70].

2.4.3. Reverse osmosis

Reverse osmosis is used to separate salts and small organic molecules from liquid streams, using membranes with dense active layers, where the preferred transport mechanisms are often attributed to solution/diffusion[24]. Due to the high density of the active layer, operating pressures have to be much higher than those used in micro-filtration and ultra-filtration[71]. The nanofiltration process is an intermediate separation process between reverse osmosis and ultra-filtration, commonly used in the separation of organic solutes with low molecular weight and in the partial demineralization (essentially polyvalent salts) of liquid streams[72].

2.4.4. Ion exchange

Ion exchange is a reversible chemical reaction through which ions in solution are exchanged for similar ions attached to a solid matrix[21,59,73]. It is very effective for reducing MB from wastewater as it is a cost-effective and convenient process in operations[74]. The solid matrix particles commonly used are synthetic organic ion exchange resins[75]. The exchange resins can take up positively or negatively charged ions from an electrolyte solution and discharge other ions with the same charges in an equivalent amount into the solution[53]. Ion exchange resins are water insoluble solid substances which can absorb positively or negatively charged ions from an electrolyte solution and release other ions with the same charges into the solution in an equivalent amount[18]. The positively charged ions in cationic resins such as hydrogen and sodium ions are exchanged with positively charged ions, such as nickel, copper and zinc ions, in the solutions. Similarly, the negative ions in the resins such as hydroxyl and chloride ions can be replaced by the negatively charged ions such as chromate, sulfate, nitrate, cyanide and dissolved organic carbon (DOC)[41]. Ion exchange is one of the “best available technologies” for the removal of MB dye[35]. It is a proven technology for small systems for the removal of low concentrations of MB dye. Cations exchangers are effective for chromophoric MB while anion exchangers are appropriate for axuchromic MB dye removal[51]. The disadvantage of this process includes high cost and selectivity of ions[26].

2.4.5. Adsorption process

Adsorption is the process of transferring the ions from solution phase to solid phase and in the process a film called adsorbent surface is created[21,75]. In the adsorption technique, the formation of bonds between dissolved or tiny particles and the surface of a solid is adsorption process[38].

This Physico-chemical technique has been found to be most simple and economical for the removal of MB dyes from textile effluents[39]. A number of low cost materials including agricultural waste material, naturally found material and industrial waste material have been tried out for the removal of MB dyes[38, 77]. Even though, the adsorption capacity with these adsorbents were not found much large but still they are widely needed as they are found to be cost effective, eco-friendly and somewhat efficient[59, 78].

2.4.5.1. Mechanism of Adsorption

Adsorption is one of the unit operations in waste water treatment which occupies an important position due to its cost, economic feasibility and its efficiency process for treatment of wastewater containing dissolved organic pollutants[59, 79]. In the adsorption process, molecules are extracted from one phase (liquid phase) and concentrated at the surface of a second phase (solid phase) which occurs due to an attractive force existing between the adsorbent surface and the adsorbate molecules[39]. Therefore, it is a removal process where certain molecules are bound to an adsorbent particle surface by either chemical or physical attraction[56]. The adsorption process consists of three consecutive steps are Substances adsorb to the exterior of the adsorbent, move into the adsorbent pores and adsorb to the interior walls of the adsorbent[16, 22]

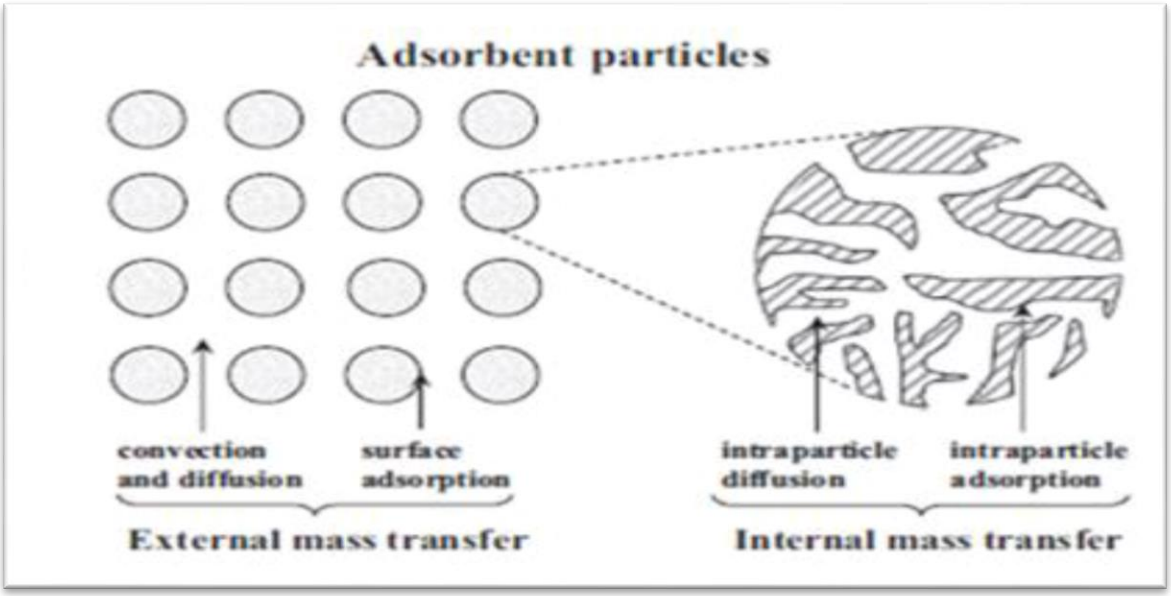


Fig.2 Schematic expression for the three steps of adsorption process

2.4.5.2. Types of Adsorption

The adsorption of molecules to a substrate is often described as Physisorption or chemisorptions depending on the strength of the interaction between the substrate and adsorbate[33]. The two types are schematically shown below in Fig.3.

➢**Physisorption**

Physisorption or physical adsorption occurs as a result of energy difference or electrical attractive forces, adsorbate molecules become physically fastened to the adsorbent surface[39]. Physisorption takes place with the formation of single or multiple layers of adsorbate on the adsorbent surface and is characterized by low activation energy (enthalpy) of adsorption[37].

➢**Chemisorptions**

Chemisorptions or chemical adsorption occurs when a chemical reaction occurs between the adsorbed molecules and the adsorbent[39]. Chemisorptions takes place with the formation of a single layer of adsorbate attached to the adsorbent surface by chemical bonds. This type of interaction is strong with covalent bond between adsorbate and the surface of the adsorbent is characterized by a high enthalpy of adsorption[40][80].

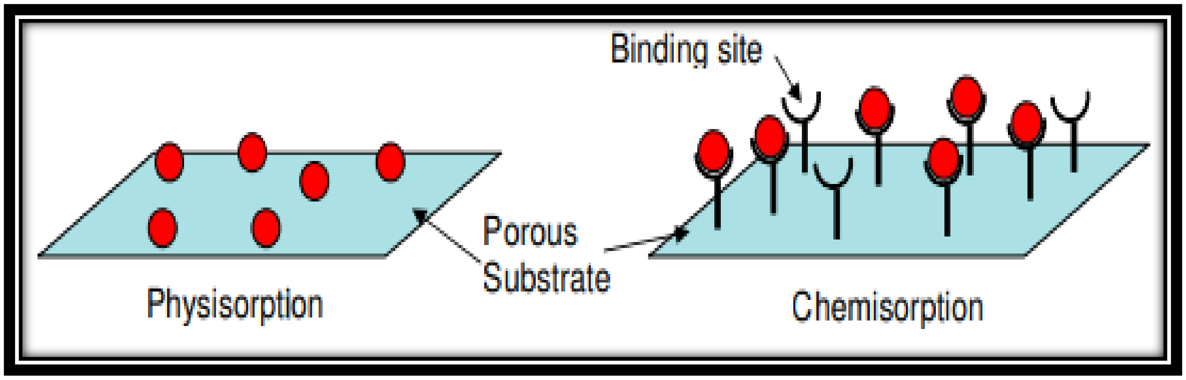


Fig.3 Schematic expression for the two types of adsorption

2.4.6. Industrial waste materials as adsorbent for MB dye removal

Industrial waste materials such as metal hydroxide sludge, fly ash, red mud, activated carbon, coal ash have been examined as low cost adsorbents to carry out decolorization process.

2.4.6.1. Activated Carbon

Activated carbon is one of the commonly adopted adsorbent materials for the removal of organic and inorganic pollutants from textile effluents[37]. Dyes which are less soluble in water shows slow rate of adsorption on carbon content while water soluble dyes like acidic, basic dyes and reactive dyes do not get readily adsorbed on carbon[61,79]. The reason behind their poor adsorption is the polar nature of these dyes and non polar nature of carbon. Hence, adsorption on carbon would be less efficient when used alone. But, it becomes more efficient adsorbent when used along with coagulants. Although, Activated carbon has been found to be quite effective in removal of dyes but due to its high cost and loss of adsorbent during the deactivation; the forces of the researchers in seek of replacing it with some low cost adsorbents[17, 74].

2.4.6.2. Alum Sludge

Sludge is semi-solid slurry of waste or residue that accumulates at the bottom of industrial processes, water treatment or wastewater treatment plants[66]. Alum sludge is a by-product from the processing of drinking water in drinking water treatment plants. Alum sludge produced when alum (aluminum sulfate) is used as coagulant[81]. The disposal of this sludge to a landfill causes environmental problems; since alum sludge contains a high level of aluminum, which has been shown to be toxic to aquatic life and relatively inert, providing marginal benefits to soil fertility. Moreover, the reuse of alum will be economically and environmentally beneficial[82]. Previous studies have shown that drinking water treatment sludge (Alum sludge) can be used as an effective adsorbent for phosphate, some heavy metals and dyes removal[70, 82]. Metal hydroxide sludge is one of the industrial waste materials that have been used as adsorbent the separation of dyes from textile effluents[49, 68]. Metal hydroxides generally have an amphoteric nature. Therefore, the adsorption capacity may decrease because of the increasing solubility of the metal hydroxides in the strong acidic or basic medium. The existence of excessive acid or base in the solution decreases the adsorption effectiveness of metal hydroxide sludge [46, 70].

2.4.6.3. Red Mud

Red mud is other industrial waste material that has been tried out as adsorbent. Red mud has been discharged as bauxite (Al_2O_3) processing residue during Alumina production[20]. Nearly about 34% removal efficiency has been reported with red mud for Malachite Green dye[42]. It has been also investigated as most effective adsorbent for the removal of Safranin-O dye with 93.2% removal efficiency using Red mud[8].

2.4.6.4. Fly Ash

Fly ash is one of the industrial byproduct that has been used for the removal of dyes. Baggase fly ash is one of the byproduct of sugar industry which is cheaply available in abundance[30]. It has been examined as suitable adsorbent as fly ash of sugarcane. Baggase does not contain any toxic metal. Baggase fly ash has been tried out as adsorbent for the removal of Malachite Green dye form aqueous solution with 17% adsorption.

2.5. Factors affecting adsorption process

Many physicochemical factors influence the amount of adsorption of an adsorbate onto an adsorbent these include surface area, surface functional groups and morphology of adsorbents[69], initial concentration, temperature, pH and contact time between adsorbate and adsorbent[80, 83]. Apart from the physicochemical factors such as agitation speed, the presence of other anions and cations, metal speciation, pollutant solubility are may also have an influence[68, 84].

2.5.1. Effect of contact time

In adsorption systems, contact time plays a vital role irrespective of other experimental parameters affecting the adsorption kinetics[85]. Adsorption is also affected by contact time between surface of adsorbent and the solution containing adsorbate[86]. In earlier works reported that adsorption proceeds fast and most MB is adsorbed at the very beginning of the process. The determination of the optimum contact time needed to achieve the highest removal of MB is very important in batch adsorption experiments[56, 76].

2.5.2. Effect of pH

The pH factor is very important in the adsorption process of dyes in aqueous solutions. The pH of solution affects the solubility of the adsorbates, concentration of the counter ions on the adsorbent surface and the degree of ionization of the adsorbate during the process [37, 38]. As a result, the rate of adsorption will vary with the pH of an aqueous solution. At low pH values, surface of the adsorbent becomes positively charged because of protonation of the functional groups on adsorbent surface sites[79]. So adsorption of cationic (MB) adsorbate decreases because of electrostatic repulsion between adsorbate and protonated adsorbent sites[51]. As the pH of the dye solution increases, deprotonation of positively charged groups on the adsorbent happen. Thus electrostatic attraction between negatively charged sites on the adsorbent and adsorbate cations cause increase in adsorption process[36]. As a result, at low pH solution, the percentage of adsorbate removal will increase for anionic species adsorption, while for cationic species percentage removal will decrease[74]. In contrast, at a high solution pH, the percentage removal will increase for cationic adsorption and decrease for anionic species adsorption process[42]. Adsorption of MB is highly influenced by the pH of the solution according to others studies on MB removal efficiency which increased with an increase in pH for basic MB dye[55, 87]

2.5.3. Effect initial concentration

The initial concentration is important in adsorption, since a given mass of adsorbent material can only adsorb a fixed amount of adsorbate[55]. Normally, for a given mass of adsorbent material; the amount of adsorbate, MB dye that can be adsorbed is fixed. But the actual amount of MB dye adsorbed per unit mass of adsorbent increased with increase in concentration[83]. The higher the concentration of the adsorbate, the smaller the volume it can remove; This may be due to the high driving force for mass transfer at a high initial MB concentration[88]. Other researchers indicate at a low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial MB concentration increases, the active sites of the adsorbent surface should be occupied for adsorption molecules will be lacking[54, 67].

3. MATERIALS AND METHODS

3.1. Chemicals

The chemicals used for this study were: Powder Methylene Blue, MB (99.5%, FINKEM, England), Hydrochloric acid, HCl (37%, Riedel-deHaën, Germany) & Sodium hydroxide, NaOH (98%, BDH, England) were used for pH adjustment, Sodium Chloride; NaCl (s.d fine-CHEM LimiTEd) was used for determination of pH_{pzc} & surface area of adsorbent. Potassium Bromide, KBr (fine-CHEM LimiTEd) was used to fine the adsorbent. Distilled water was used for preparation of all solutions and dilutions, during the laboratory work. All chemicals in this study were used without further purification.

3.2. Instruments

Double Beam UV-Vis Spectrophotometer (ModelSPECORD200/PLUS, analytikjena, Germany) was used to evaluate the final MB concentration and measure the absorbance of the samples after the reaction was carried out, pH meter (Bante instruments, pH 902P, USA) used to adjust the solution in acidic /basic media, thermostat water bath (Model GrantGLS400, England) used to carry out the batch adsorption process at 25 ℃ (200 rpm), Oven (Model GENLAB, England) was used for drying purpose, Centrifuge (Model 800, China) was used for separate of supernatants and solid matters at 3000 rpm. Fournier Transformer Infrared Spectrophotometer, FTIR (Model: Perkin Elmer Spectrum two) used to identify functional groups and X-ray Diffractometer, XRD (XRD-7000) used to determine the structure of crystals of sample.

3.3. Adsorbent collection and preparation

3.3.1. Preparation of different adsorbents for selection

Before the selection of the utilized adsorbent, a number of locally available water treatment plant (WTP) by-product and agricultural wastes namely Alum Sludge (AS), Orange Peel (OP), Saw Dust (SD), Bean shell (BS) were collected from Jimma city. Then, each was washed with tap water followed by distilled water, dried at open air & oven at 105 ℃ crushed with pestle & mortar, sieved with 250 μm particle size mesh and stored in plastic container for further screening study.

3.3.2. Preparation of alum sludge

In this study, alum sludge was collected from Jimma water treatment plant (JWTP) of Jimma city. The collected alum sludge (AS) was washed using tap water frequently; followed by distilled water and dried using open air and oven at 105 ℃ for overnight. Then, it was grounded by mortar and pestle, sieved to the mesh size of 250 μm to have fine powder and the homogeneous size particles. Finally, it was stored in air tight container for MB dye batch adsorption study.

3.4. Adsorbent characterization

The surface functional group of alum sludge adsorbent (ASA) was characterized by FTIR (Model: Perkin Elmer Spectrum two)[31, 69] in the scanning range of 400 – 4000 cm^{-1} and Surface crystal was characterized by XRD (XRD- 7000)[72] in the scanning range of 10° – 90°. The pH of the adsorbent was measured using pH meter and the surface area of adsorbent was also determined by using the Sear's method[72].

3.4.1. The study of adsorbent pH

1.0 g of alum sludge adsorbent (ASA) was weighed and transferred into a 500 mL beaker and then 100 mL of distilled water was added and stirred for 1 hr using magnetic stirrer. The mixture was allowed to stabilize and then the pH was measured using pH meter[72].

3.4.2. Surface area determination

Sears' method was used for the determination of surface area of the adsorbent[77]. 1.0 g of the ASA was weighed, then 20 g of NaCl was added and the volume was made up to 50 mL with distilled water and the mixture was shaken for five min. Its final pH was adjusted to 4 with 0.1 M HCl. It was then titrated against 0.1 M NaOH to raise the pH from 4 to 9 and the volume of 0.1 M NaOH used was measured in duplicate and the average value was taken for the surface area calculation by Sears' method [64]. Then, the surface area (S) was calculated from eqn. (1).

$$\mathrm{S} = 32\mathrm{V} - 25 \qquad (1)$$

where, S is surface area of adsorbent per gram (m^2/g), V is volume (mL) of 0.1M NaOH required to raise the pH of the sample from 4 to 9. The numbers 32 and 25 are physical constants[72].

3.4.3. pH point of zero charge (pH_{PZC}) determination

The point of zero charge of the ASA was determined by the solid addition method[89]. A 40 mL of 0.1 M and 0.01 M NaCl solution was transferred into 50 mL of plastic bottles which contains 5 g/L of ASA dose in duplicated. The initial pH (pH 0) values of the solution were adjusted in the range of 3 to 12 by adding either 0.1 M HCl or 0.1 M NaOH and the values of pH initial was recorded. Then, the plastic bottles were placed into a constant temperature water bath shaker at speed of shaking (200 rpm) for 24 hrs. The pH values of the supernatant liquid were centrifuged after 24 hrs and the values of pH final solution were measured by pH meter. The difference between final pH-initial pH values in y-axis was plotted against the initial pHi (x-axis).

3.4.4. Surface functional group determination

The surface functional groups of the ASA before and after adsorption were characterized by FTIR[86]. The prepared ASA Samples powder was mixed with KBr particles to make it suitable to Infrared analysis. The mixture was then pressed to a small thickness to make the sample a pellet that required for FTIR study. The transmission spectra of the samples were recorded within range of 400 – 4000 cm^{-1} using the KBr pellet[69].

3.4.5. Structure of the crystals and particle size determination

The structure of the crystals and particle size determination of alum sludge adsorbent (ASA) was characterized by using X-Ray Diffractometer (XRD – 7000)[69]. The powder samples were packed and loaded into the diffractometer. The powder was packed into the holder then pressed down and flattened in order to present a smooth diffraction surface[72]. Then, the diffractometer was run over a 2θ range of 10° to 90°.

3.5. Preparation of stock solution

A stock solution of MB with a concentration of 1000 mg/L was prepared by dissolving 1 g of Powder Methylene Blue dye solid (MB, 99.5%) in 1000 mL distilled water. Then standard solution containing 100 mg/L of MB was prepared in 500 mL volumetric flask by diluting 50 mL of stock solution with distilled water and filled up to the mark. The working solution (10 mg/L of MB solution) was prepared by diluting 10 mL from 1000 mg/L standard solution with distilled water in 1000 mL volumetric flask.

3.6. Preliminary experiments

The preliminary experiments were performed to select adsorbents with better adsorption capacity for MB dye removal. For this purpose, five (5) different adsorbents namely Alum Sludge (AS), Orange Peel (OP), Saw Dust (SD), Blended Orange Sawdust (BOS), Bean shell (BS) were tested for the adsorption of MB dye removal from aqueous solutions. The experiments were carried out under similar situation in duplicate, where the plastic bottle containers labeled with the name of each adsorbent with 40 mL of 10 mg/L of MB solution and each containing 0.2 g of the adsorbent was agitated on shaker for 12 hrs. Then the supernatant of each sample was analyzed by using double beam UV-Visible spectrophotometer. Accordingly, after selection of the AS adsorbent, it uptake to anionic dye; Methyl orange (MO) & cationic dye; Malachite green (MG), Crystal Violet (CV) & Methylene blue (MB) at λ_{max} of 591, 619, 466 & 665 nm respectively was checked on their initial pH of dyes (5.68, 5.54, 4.85 & 5.67) respectively & contact time 12 hrs using the same concentration of dyes, (10 mg/L) for each of them in a duplicate.

3.7. Batch adsorption study

The batch adsorption experiment was carried out by shaking 40 mL 10 mg/L of MB dye solutions having trial 0.1, 0.3 & 0.5 g of ASA in plastic bottles were shaken on a shaker ready with thermostat at 200 rpm speed and 25 ℃ for 24 hrs [47] . After a predetermined contact time the bottles were removed from the shaker and the supernatant was centrifuged (3000 rpm) and analyzed using double beam UV-Visible Spectrophotometer. From reading trial 5 g/L ASA dose was taken as optimum dose for batch process. The effects of contact time, initial MB concentration, pH and adsorbent dose on adsorption were evaluated by batch adsorption experiment[20, 22]. To determine the calibration curve of MB, absorbance of solutions with predetermined MB concentrations at λ_{max} of 665 nm was detected by Double beam UV-Vis spectrophotometer. In the following adsorption experiment, the concentration of the MB solution after absorption was determined by using this calibration curve; removal (%) eqn. (2), the equilibrium adsorption capacity, q_e or q_t (mg/g) are expressed as eqn.(3) and (4) respectively.

$$\text{Adsorption}, \% = \frac{C_o - C_e}{C_o} X\, 100 \qquad (2)$$

$$\text{Adsorption Capacity, } q_e = \frac{C_o - C_e}{m} \text{ X V} \qquad (3)$$

$$\text{Adsorption Capacity, } q_t = \frac{C_o - C_t}{m} \text{ X V} \qquad (4)$$

where, C_o, C_t and C_e are the initial MB concentration in solution before mixing with adsorbent (mg/L), the concentration of MB at time t (min), and the concentration of MB at equilibrium (mg/L), respectively; V is the volume of MB solution (L) and m (g) is the mass of adsorbent. All adsorption experiments were conducted in duplicates and the results were reported as average.

3.7.1. Effect of contact time

The effect of contact time is one of the important parameters on the percentage removal of MB dye by the adsorption of ASA to establish adsorption kinetics[20, 90]. The adsorption of MB dye by the adsorbent was studied at range of adsorption periods 1–180 min for (ASA)[38, 60]. This was done by weighing 0.2 g of the ASA in plastic bottles containing 40 mL of 10 mg/L of MB solutions in duplicate at initial pH of MB dye (5.67), then shaking the plastic bottles at 200 rpm (25 ℃) for each time interval in the thermostatic water bath shaker. At each interval the solution was centrifuged at 3000 rpm for 10 min; then, the supernatant of MB solutions in the plastic bottles were analyzed at 665 nm by Double beam UV-Visible spectrophotometer. The equilibrium time was determined at a time with the highest adsorption capacity using eqn (4).

3.7.2. Effect of solution pH

Experiments were performed for each adsorbent at initial solution pH 3 - 12 to study the effects of pH on the adsorption mechanism. The optimum pH was established when 0.2 g of ASA was mixed with 40 mL of 10 mg/L of MB working solution in plastic bottles [38, 84]. The solution's pH was adjusted by the drop wise addition of 0.1 M HCl or 0.1 M NaOH. The plastic bottles containing the mixture were left in a shaker in a thermostatic water bath and shaken for 60 min at 200 rpm (25 ℃). The bottles were removed from the thermostatic water bath shaker when the equilibrium time for adsorption was done then centrifuged at 3000 rpm for 10 min. The supernatant of MB was analyzed by Double beam UV-Visible Spectrophotometer at 665 nm. The optimal pH with the highest adsorption efficiency of MB was calculated using eqn (2).

4.7.3. Effect of adsorbent dosage

To investigate the effect of adsorbent dose, experiments were conducted by mixing 40 mL of 10 mg/L of MB dyes with adsorbent dose ranging from 2–12.5 g/L and agitated for 60 min. at 200 rpm, 25 ℃ by keeping the pH of the solution 7 [38, 60]. After the equilibrium time of adsorption has been completed, the adsorbent was extracted from each solution then centrifuged (3000 rpm) for 10 min. The adsorption equilibrium time of concentration of the MB dyes in each solution was analyzed by Double beam UV-Visible spectrophotometer at 665 nm.

3.7.4. Effect of initial concentration

The initial MB concentration provided the necessary driving force to overcome the mass transfer resistance of MB between the aqueous and solid phases[91]. The effect of initial MB concentrations on the adsorption efficiency was tested at 40 mL of MB with different initial MB concentrations of 10 - 200 mg/L for ASA at contact time (60 min), pH of solution (7), adsorbent dose (5 g/L), at shaking speed 200 rpm, 25 ℃ in duplicate [55, 83]. After the equilibrium time of adsorption has been completed, the adsorbent was extracted from each solution then centrifuged (3000 rpm) for 10 min. The adsorption equilibrium time of concentration of the MB dyes in each solution was analyzed by Double beam UV-Visible spectrophotometer at 665 nm.

3.8. Data analysis

3.8.1. Adsorption kinetics

It is very important to know the rate at which the process takes place and the factors that control the rate of the process, for this purpose kinetics of the process were evaluated [85]. Pseudo-first-order (PFO) and Pseudo-second-order (PSO) adsorption kinetics model were employed to evaluate the kinetics of the adsorption of MB dye using constant adsorbent dosage of 5 g/L and 20 mg/L of initial MB concentration [92, 93]. MB concentration was measured at different time intervals (1 - 180 min) for ASA by taking samples solution periodically. Then, the supernatants were analyzed for MB concentrations using the Double Beam UV-Visible Spectrophotometric method. The experimental data was evaluated using non-linear form of pseudo-first-order and pseudo-second-order kinetics[90] is given in eqns. (5) and (6), respectively. The adsorption affinity of the adsorbent was assessed to have the information about the adsorption rate of the adsorbent using the eqn. (7).

$$q_t = q_e(1 - \exp^{-K_1 t}) \quad (5)$$

$$q_t = \frac{K_2 {q_e}^2 t}{1 + K_2 t} \quad (6)$$

$$V_o = K_2 {q_e}^2 \quad (7)$$

where, V_o is Adsorption affinity, K_1 (min^{-1}) is pseudo-first-order rate constant, K_2 (g/mg.min^{-1}) is pseudo-second-order rate constant, q_t, q_e are the adsorption capacity (mg/g) at any time, t(min) and at equilibrium, respectively.

To predict the potential rate-limiting steps in the adsorption processes, intra-particle diffusion models (Weber- Morris) [94], was also used in eqn. (8) to analyze adsorption kinetics data:

$$q_t = K_p t^{0.5} + C \quad (8)$$

where, q_t is the amount of MB adsorbed on the adsorbents (mg/g) at time t, K_p (mg/(g.min$^{0.5}$) is the intra-particle diffusion rate constant; and C (mg/g) is the intercept of the intra-particle diffusion model. If the rate-limiting step of MB removal is the intra-particle diffusion, the plot of q_t vs. $t^{0.5}$ should be a straight line and pass through the origin [83].

3.8.2. Adsorption isotherms

The interaction between the adsorbate and adsorbent can be clearly understood with the adsorption isotherms [83]. The relationship between the amount of substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm[84]. The adsorption isotherms are important from both a theoretical and practical point of views; because the application of adsorption isotherms facilitates to describing the interaction between the adsorbate (MB) and the adsorbent of any system[85]. Experimental data were obtained by mixing a constant adsorbent dosage (5 g/L) with a series of increasing MB initial concentration from 10 - 200 mg/L at room temperature. The mixtures were agitated for 2 hrs to ensure that equilibrium is reached for adsorbent and then, the residual MB dye was determined.

The most widely accepted surface adsorption models for single-solute systems (Langmuir and Freundlich) models were selected in this study [95]. The equilibrium experimental data of MB adsorption was modeled using the non-linear forms of the Langmuir and Freundlich isotherm models [86]. The Langmuir isotherm assumes monolayer coverage of adsorbate on homogeneous sites of the adsorbent, uniform energy of adsorption and no interaction between molecules adsorbed on neighboring sites [95]. The non-linear form of Langmuir isotherm eqn.(9) and the important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor (R_L) [70], which is defined as in eqn.(10).

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (9)$$

$$R_L = \frac{1}{1 + K_L C_o} \qquad (10)$$

where, C_e (mg/L) is equilibrium concentration in solution or unadsorbed MB concentration in solution (mg/L), q_{max} (mg/g) is the maximum adsorption capacity based on the Langmuir equation; and K_L (L/mg) is the Langmuir constant. C_o (mg/L) is the initial MB concentration; The R_L values indicate the type of adsorption as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$)[70].

Freundlich isotherm is based on adsorption to heterogeneous surface or surfaces supporting sites of varied affinities and it is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation[15, 44]. The nonlinear form of Freundlich adsorption isotherm[53] eqn. (11) written as:

$$q_e = K_F C_e^{1/n} \qquad (11)$$

where, q_e (mg/g) is the equilibrium adsorption capacity; K_F (mg/g(L/mg)$^{1/n}$) is the adsorption coefficient based on the Freundlich constant and 1/n is the adsorption intensity based on the

Freundlich eqn.(11). In the Freundlich equation, the heterogeneity factor (1/n) is related to the capacity and intensity of the adsorption n is a measure of the deviation from linearity of adsorption [75]. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n =1, the adsorption is linear; $n < 1$ implies that adsorption process is chemical and $n > 1$ indicates physical process is a favorable in which the equilibrium concentration in mg/L. The value of 1/n ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface [74].

3.8.3. Statistic test

The chi-squared test is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models [86]. Moreover the coefficient of determination, the nonlinear chi-square, x^2 and statistic test was used to identify the best model fit to the observed experimental data [9]. The x^2 is computed using eqn. (12).

$$x^2 = \sum \frac{(q_e.\mathrm{exp} - q_e.\mathrm{cal})^2}{q_e.\mathrm{cal}} \qquad (12)$$

where q_e.cal is the equilibrium adsorption capacity calculated from the model and q_e is the experimental equilibrium adsorption capacity. A small value indicates similarity of data between the modeled and the experimental data, whereas a larger value implies variation between the modeled and experimental data [96].

3.9. Quality control

All polyethylene bottles and lab materials were washed with detergent, followed by repeated rinse with distilled water and soaked overnight in 10% of HNO_3. Then rinsed three times with distilled water and dried. In order to determine the accuracy of the data collected all batch adsorption tests were recorded in duplicate by using control and dilution factor in each experiment. Experimental analyses were carried out using MB containing a working solution prepared from intermediate solution[96]. The experiments confirm that the initial MB concentration, pH and MB ratio changed during the experiment because of the interaction between adsorbent and adsorbate. Regression and chi-square analyses of experimental data were performed using Origin 8 software [92, 96]. The correlation coefficient, R^2 and standard error in the evaluation of parameters were studied to characterize the accuracy of the optimal analysis of the data fit [90].

3.10. Adsorption cycle experiment

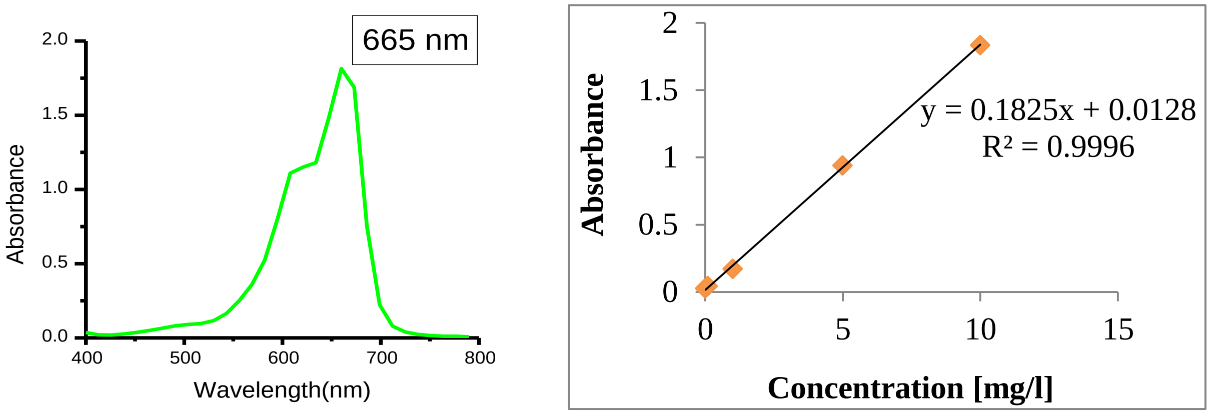
The capacity of ASA was evaluated by the adsorption experiment of MB dye with applying the optimum conditions of adsorption process. Accordingly, the adsorbent dose was 5 g/L, the MB dye concentration 10 mg/L, pH 7 and contact time 60 min at shaking of 200 rpm, 25℃. After adsorption of MB, the ASA was filtered from the solution by a Whatman paper No.4; then the residual MB dye concentration was measured by UV-visible spectrophotometer. Then the adsorbent was washed several times with distilled water and dried in oven at 105 ℃ till dryness. The experiment of adsorption was repeated with the same conditions for five cycles.

4. RESULTS AND DISCUSSIONS

In this batch adsorption study, a variety of parameters such as effect of contact time, initial solution pH, adsorbent dose and initial concentration of MB dye were investigated in duplicate and the results were reported as mean ± SD (Standard deviation) [76]. The obtained data was tested by the most common adsorption isotherm models and adsorption kinetics to assess whether the selected adsorbent is suitable for the adsorption of MB dye on ASA [84, 85] from aqueous solution or real wastewater sample.

4.1. Lambda max and calibration curve of MB

The selection of lambda max was obtained by scanning 10 mg/L of MB solution on Double Beam UV-Visible Spectrophotometer between the wavelengths 400–800 nm. The result of scanning the lambda max is shown in Fig.4 (A). From the spectra, it can be seen that the maximum peak (λ_{max}) wavelength for MB dye is at 665 nm. The absorbance of the samples was therefore read by adjusting at this wavelength. A standard calibration curve obtained from the Double Beam UV-Visible spectrophotometer used to measure the absorbance of MB at 665 nm[65] is shown in Fig.4 (B).



[A]

[B]

Fig.4 Lambda max [A] and standard calibration curve [B] for MB dye

4.2. Preliminary experiment

4.2.1. Preliminary experiment of locally available adsorbents

The preliminary experiment has been done to select adsorbents having high MB removal efficiency. For this purpose, five (5) different adsorbents namely Alum Sludge (AS), Orange Peel (OP), Sawdust (SD), Blended Orange Sawdust (BOS) & Bean shell (BS) have been tested for the adsorption of MB under similar situation. The adsorptive removal of MB is calculated and results are shown in Fig.5. As revealed in Fig.5, three of adsorbents (AS, SD, & OP) have more than 80% removal efficiency when compared to BOS & BS. Among these, AS was the better adsorbent resulting high removal efficiency of MB dye and selected for further studies. To the best of our knowledge, there is no any previous report on use of AS adsorbent for removal of MB dye from aqueous solution. Moreover, the AS adsorbent exhibit high MB removal efficiency, locally available, easy preparation & relatively low cost [91].

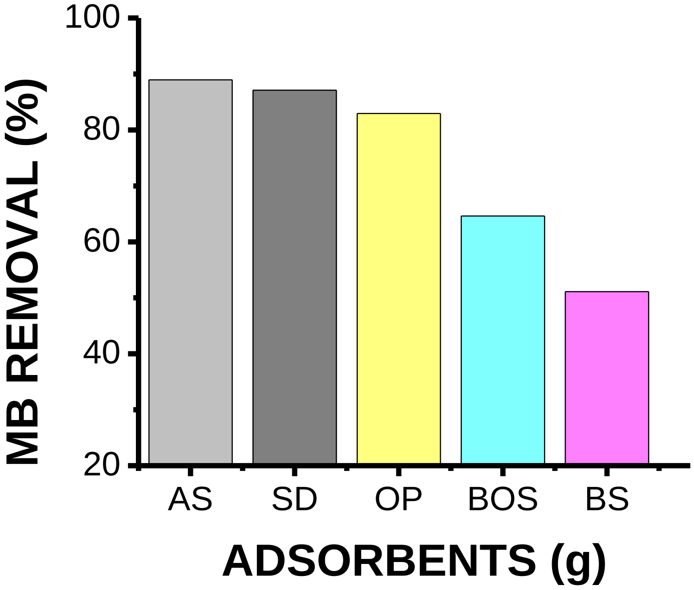


Fig.5 Selection of adsorptive removal of MB by different locally available adsorbents

4.2.2. Preliminary experiments for selecting different dyes

The preliminary experiments have been tested for the adsorption of Methylene blue (MB), Malachite green (MG), Crystal Violet (CV), Methyl orange (MO) dyes onto the selected adsorbent (ASA).The adsorptive capacity of adsorbent was assessed for an anionic dye; MO and cationic dyes; MG, CV and MB with the initial concentrations (10 mg/L) in their unadjusted pH 5.68, 5.54, 4.85 & 5.67, respectively. As revealed in Fig.6 the adsorption process of the adsorption capacity of the adsorbent, ASA was low for anionic dye & high for cationic dyes. This is because of the electrostatic interaction of adsorbent surface and adsorbate. The result shows were favorable for cationic dye and unfavorable for anionic dye [16]. These also provide additional information about the electrostatic interaction of adsorption processes between RAS adsorbent & adsorbate (dyes) used in this study. Consequently, the mechanism of dye removal was explained through the electrostatic interaction between the negatively charged surface of the RAS adsorbent and the positively charged adsorbate [76].

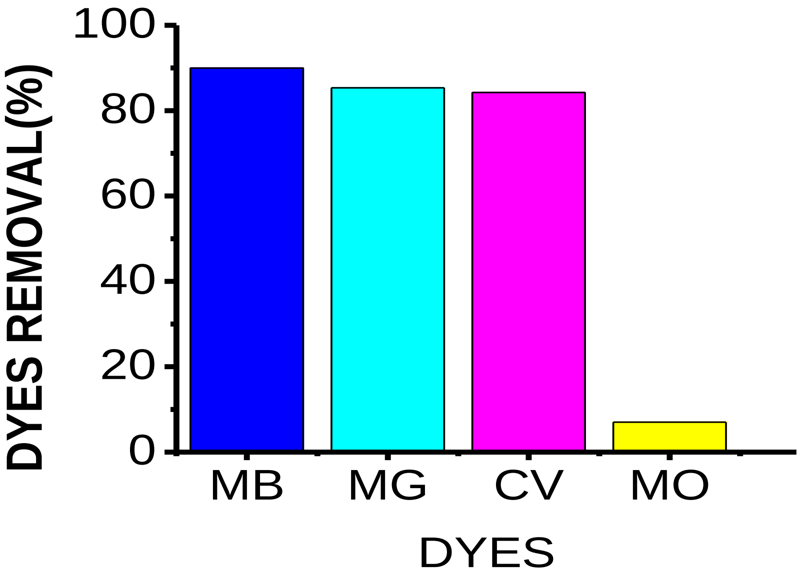


Fig.6 Test of adsorption efficiency of ASA for MB, MG, CV & MO dyes at initial concentration of 10 mg/L, 5 g/L of ASA for 12 hrs

4.3. Characterization of adsorbent

4.3.1. Surface area determination

The surface area of the prepared ASA was determined using the Sear Method of surface area determination[77].The specific surface area of ASA in various water treatment plants differ and characteristics are influenced by the quality of the drinking water source, coagulant type and treatment plant system[31, 72]. Specific surface area of ASA of obtained data was 43.8 m^2/g. The surface area for the prepared ASA is relatively higher compared to the surface area reported in literature[64]. which indicate that the adsorbent surface is good for adsorption process using ASA because of high surface area and porosity[89].

4.3.2. Determination of point of zero charge (pH_{PZC})

Adsorption of MB dye on the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the pH of the solution[89].To realize the adsorption mechanism, it is necessary to determine the point of zero charge (pH_{PZC}) of the adsorbent because the point of zero charge is the pH value at which the surface charge of adsorbent equals to zero[40]. The point zero charge (pHpzc) of ASA was found to be 6.23 shown in Fig.7. The surface of adsorbents becomes positively charged at pH < pHpzc favoring the adsorption of anionic dyes, whereas cationic dyes adsorption would be favorable at pH > pHpzc[40]. Change in the pH affects the adsorptive process through dissociation of functional groups as the active sites on the surface of the adsorbent[5]. Adsorption of the various anionic and cationic species on such adsorbents can be explained on the basis of the competitive adsorption of H^+ and OH^- ions with the adsorbate or dye[16]. The surface adsorbs anions favorably at lower pH due to the presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to assertion of OH^- ions. Therefore, the adsorption process of cationic (basic) dye MB is better at pH > pHpzc condition.

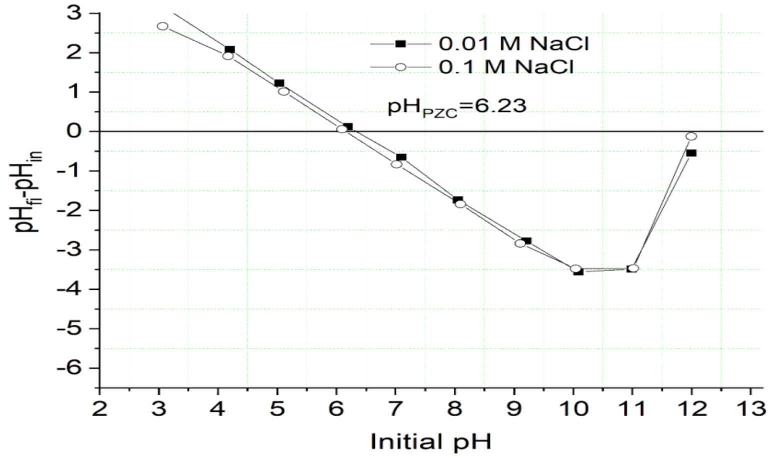


Fig.7 Determination of point of zero charge (pzc) of 0.2 g ASA mass in 0.01 M & 0.1 NaCl solutions speed of shaking at 200 rpm, 25 ℃ for 24 hrs

4.3.3. FTIR analysis of adsorbent

The possible functional groups on the surface of the ASA to the adsorption of MB were determined by FTIR spectroscopy was shown in Fig.8 below.

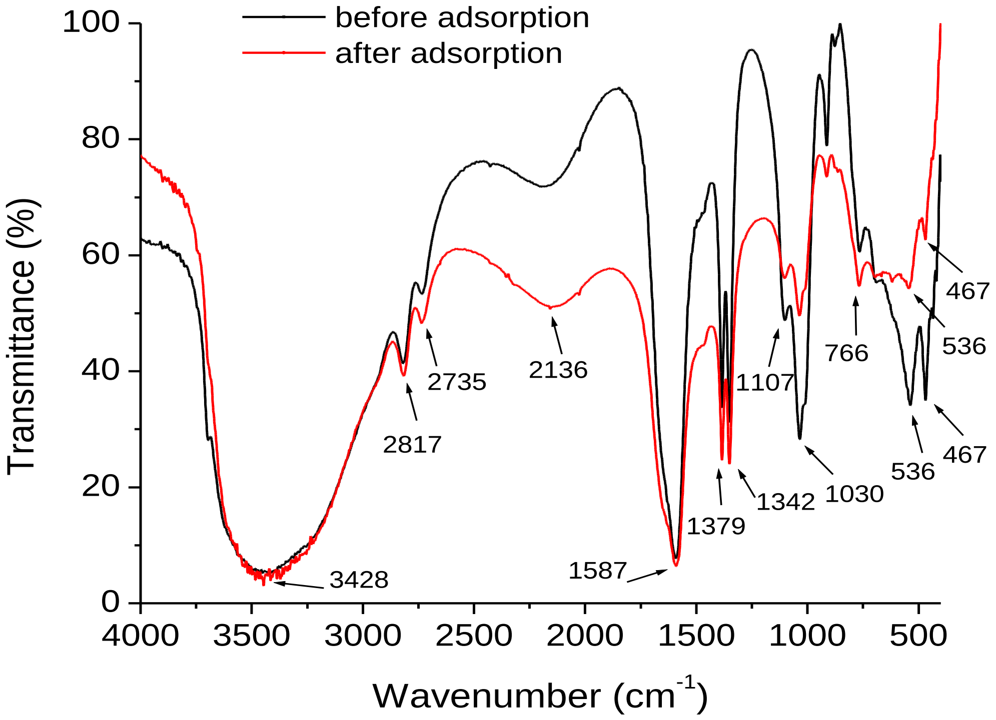


Fig.8 FTIR Spectra of ASA before and after Adsorption

The FTIR spectra were recorded before and after adsorption of MB to determine the vibrational frequency changes (if any) for the functional groups in the adsorbent. As revealed in Fig.8, the FTIR the spectrum showed the strong, broad peaks around 3428 cm^{-1} is due to stretching vibrations of hydroxyl group (HO-Al) on the surface of $Al(OH)_3$ molecules[78, 97]. The peaks around 2735 & 2817 cm^{-1} can be assigned to stretching vibrations of aliphatic, C-H (CH_3, CH_2) groups and thus, was change shapes of spectra when MB is adsorbed[40]. The peak value at 2136 cm^{-1} relates to the bending mode of acetylene group of C=C of alkenes [40]. The adsorption band at 1587 cm^{-1} corresponds to amine compound group frequencies of N-H secondary amine of NH bend [97].

The intense peaks around 1349 & 1386 cm^{-1} assigned the Al-O stretching vibration bending in different groups, thus shows the removal of MB dye was decreases in adsorption process[48]. The peaks at 1030 & 1107 cm^{-1} may be shift due to Al-N- stretching with MB dye[31]. Adsorption peak of aluminum oxy compounds of organic Al-O-Al occurs at 1030 cm^{-1}[89]. The peaks assigned at 766, 536 & 467 cm^{-1} for Al-O, Al-O-Al & O-Al-O stretching vibrations in $Al(OH)_3$ respectively with MB dye adsorption of good potential adsorbent for the treatment of wastewater[72]. Most of The band regions may be related the characteristic vibrations of metal oxides (Al_2O_3 or $Al(OH)_3$) which make it these functional groups are commonly found in water treatment plant sludge as organic and inorganic compounds. The FTIR Spectroscopy analyses were confirmed that the presence of O-H functional groups. The negatively charged groups of hydroxyl ions were attracting the positively charged MB dye molecules during the adsorption process[40]. The presence of other functional groups such as aliphatic, acetylene and amine group of frequencies were interacted with protons of the MB dye and form the covalent bond and electrostatic interaction between the ASA and MB dye[94]. In general, Fig.8 shows that changes in shape and shift in peak position were observed in the FT-IR spectra following adsorption of MB as a result of the functional group participating in the process of MB binding or adsorption and the adsorbent surface occupied by MB ions.

4.3.4. XRD Analysis of Adsorbent

In order to determine the crystals or minerals in the sample of adsorbents, XRD analysis was performed[68, 73]. The diffractograms indicate that the particles of ASA are semi-crystalline, as well as poorly ordered shown in Fig.9. The fitting of the diffractograms to data available in the XRD catalogue reflected the most presence of alumina (Al_2O_3) which is one of the major minerals in drinking water treatment plant[49]. As revealed in Fig.9 the peak positions at 25.5, 28.5, 37.4, 43.3, 57.5, and 68.5^0 2θ on the XRD patterns of AS matches the major peaks of Alumina (Al_2O_3)[97]. The matching of all major peaks on the XRD patterns of AS with pure alumina identified the prepared powder as being composed of Al_2O_3[89]. Some of the XRD patterns show the presence of an amorphous phase in the sample can lead to an irregular noise base line. Therefore, the XRD studies not only identified major peaks, it also provides information about the amorphous nature of ASA[97].

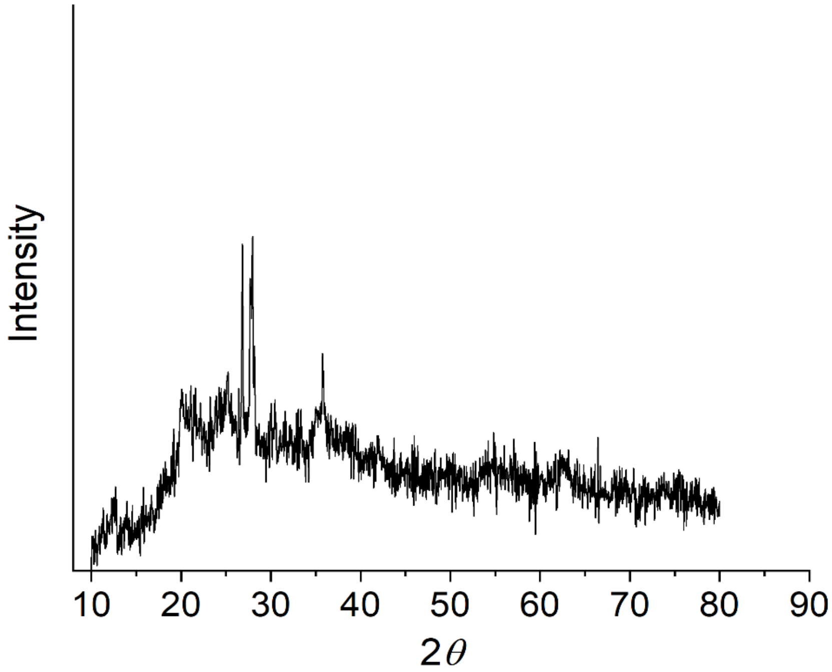


Fig.9 XRD Spectra of ASA before adsorption

4.4. Batch adsorption study

Optimization of Methylene blue adsorption; for optimization of the adsorption, the effect of contact time, effect of initial solution pH, adsorbent dose and initial Methylene blue concentration were investigated.

4.4.1. Effect of contact time

The effect of agitation time is one of the important parameters on the percentage removal of MB dye by the adsorption of ASA to establish adsorption kinetics. In other words, the percentage removal of MB depends on contact time. The time dependency of MB adsorption on alum sludge adsorbent was investigated by varying the contact time in the range of 1 min to 180 min; while the effect of other parameters, like unadjusted pH (5.68), adsorbent dose (5 g/L) and initial MB concentration (10 mg/L) were kept constant [54]. The effect of contact time on MB adsorption capacity is shown in Fig.10 below.

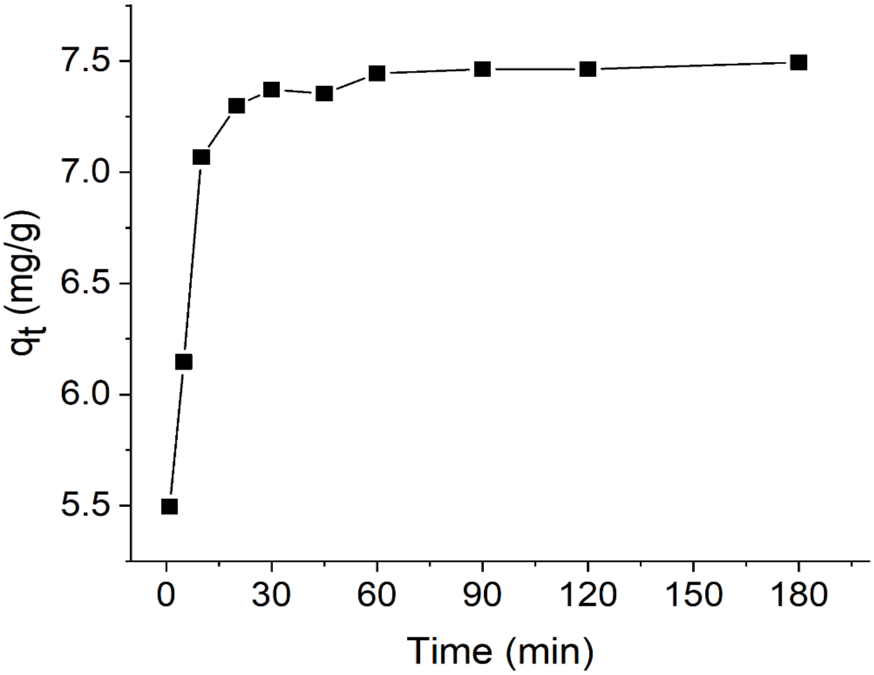


Fig.10 Effect of contact time on the MB removal by ASA, initial concentration (10mg/L), adsorbent dose (5 g/L) at 200 rpm, (25 ℃)

As revealed in Fig.10, the MB adsorption capacity of the adsorbent increased from 5.5 – 7.5 mg/g as the contact time increased from 1- 60 min. However, further increase in the contact time does not increase the MB uptake due to rate of MB adsorption equals the rate of MB deposition from the sites of ASA[21]. Initially, the adsorption rate increased rapidly by increasing the contact time due to the large number of vacancies on the adsorbent surface to adsorb MB dye. With rising contact time, MB adsorption has increased. This is due to prolonged interaction with the adsorbate (MB) between the adsorbent surfaces (ASA) and can be related to the increased intra-particle diffusion that occurred during longevity. This can be explained by the fact that a large number of vacant surface sites may initially have a high concentration gradient for MB adsorption, and the surface sites will become depleted by time. Upon depletion of active adsorbent sites, the rate of adsorption is controlled by the rate at which the adsorbate is transferred from the outside to the inside when equilibrium is achieved [83]. Therefore, 60 min was chosen as an optimum time for MB adsorption onto ASA for the study of other adsorption parameters.

4.4.2. Effect of pH on MB adsorption

The pH of the dye solution is majorly affects the adsorption process and predominantly on the adsorption capacity [68]. The adsorption process was greatly influenced by change in initial pH of the solution. The pH effect of the solution usually depends on the ions present in the reaction mixture and the electrostatic interactions with the adsorption surface. Thus the pH of the solution influences aqueous phase chemistry and binding surface chemistry of the adsorbent. The adsorption process was carried out with 40 mL of MB dye solution (10 mg/L) with different pH intervals (3 to 12) and adsorbent dose (5 g/L) with a contact time of 60 min. The effect of initial solution pH on the adsorption of MB using alum sludge adsorbent is depicted in Fig.11 below.

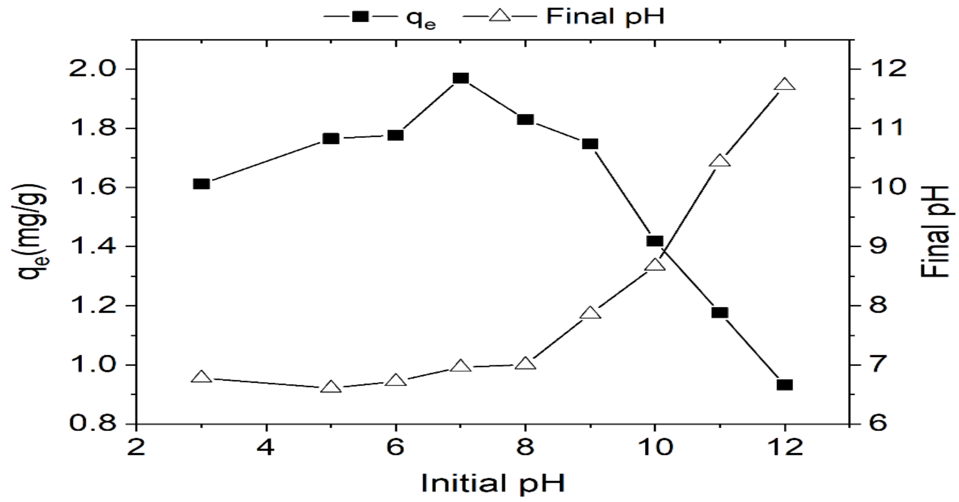


Fig.11 Effect of pH on the absorption of MB onto ASA, initial concentration (10 mg/L), adsorbent dose (5 g/L), contact time (60 min) at 200 rpm, (25℃)

As revealed in Fig.11, increasing initial solution pH range from 3 to 12 for adsorbent, the adsorption capacity increases from 1.65 mg/g to 2.06 mg/g for ASA. The maximum adsorption capacity (qe) was appeared at pHi (7), with no significant change above the value mentioned for ASA. In general, the increment of adsorption capacity and attaining maximum value at which the adsorbents have negative surface charge due to the electrostatic interaction of cationic MB dye and negatively charged surface functional group of adsorbent[64]. Thus, the electrostatic interaction strength between the two charges is high when the surface of adsorbent develops more negative surface charge. This phenomenon was responsible for the observed maximum adsorption capacity at initial solution pH 7 for ASA, the maximum amount of adsorbed was 2.06 mg/g [40]. In the beginning pH 3, the adsorption of MB dye was low; due to presence of an acidic medium or H^+ ions; the surface of the adsorbent may get positive charge which does not attract the positively charged MB dye in the solution [21, 68]. As the solution pH increases, the adsorbent surface attains the negative charge which enhances the adsorption capacity of ASA because of the formation of electrostatic interaction between the negatively charged ASA and positively charged MB dye[40].

However, further increasing the pH from 8 to 12, the adsorption capacity of decreased from 1.79 to 1.25 mg/g in the adsorption of MB dye on ASA[53]. This behavior can be explained by alkaline medium (pH > 7) repulsion takes place between the adsorbent material (ASA) and the base medium of the MB dye solution, for the reason that, at alkaline pH the MB dye in the solution also turns to negative charge and co-anions sites of MB dye make repulsion forces with the surface sites of ASA[68]. Furthermore, lower adsorption of MB at basic pH might also be explained by the competition of excess OH^- on the surface of adsorbent with the MB dye turn to negative charge such as Cl^{-1} were the result of electrostatic repulsion and desorption process occurred[86]. Therefore, the optimum pH for the removal of MB dye on ASA was found to be 7.

At high pH values, cations are adsorbed due to the negatively charged surface sites of adsorbent. Any metal oxide surface creates a charge (positive or negative) on its surface[40]. This charge is proportional to the pH of the solution which surrounds the metal oxide particles. A convenient index of the tendency of a surface to become either positively or negatively charged as a function of pH is the value of the pH required to give zero net surface charge (pzc) [53]. The pHpzc of alum sludge adsorbent was 6.23 shown in Fig.7. At pH values above pHpzc the adsorbent had net negative charge and would, therefore, be level to electrostatic attraction of cations dye. MB is cationic or basic dye as denoted by the presence of the positive nitrogen ions in its structure. Therefore, the effect of pH can be explained considering the surface charge on the adsorbent material[40]. At low pH values (pH < 6.23), the low adsorption was explained due to increase in positive charge (protons) density on the surface sites of ASA adsorbent and thus, electrostatic repulsion occurred between the MB^+ molecules and the boundary groups with positive charge on the surface as follows:

$$-AlOH + H^+ \rightarrow AlOH_2^+ + OH^-$$

At higher (pH > 6.23), the surface of ASA becomes negatively charged and electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the adsorption boundaries, thus resulting in an increase metal adsorption[40]. This mechanism can be shown as follows: $-AlOH + OH^- \rightarrow -AlO^- + H_2O$

$$-AlO^- + MB^+ \rightarrow AlO\text{-}MB$$

Generally, the possible modes of interaction of MB with the ASA surface have been gathered as electrostatic attraction, Lewis acid-base interaction and hydrogen bonding etc. Therefore, MB adsorption capacity is dependent upon the adsorbent type, the dyes species and the pH of solution[86].

4.4.3. Effect of adsorbent dose

The influence of ASA on the adsorption process was studied by performing with a series of adsorption experiments with different amount of ASA dose (2 to 12.5) g/L in a 40 mL of MB dye solution with the concentration of 10 mg/L and the solution pH of 7 with a contact time of 60 min [86]. The effect of adsorbent dose on the removal of MB dye was shown in Fig.12 below.

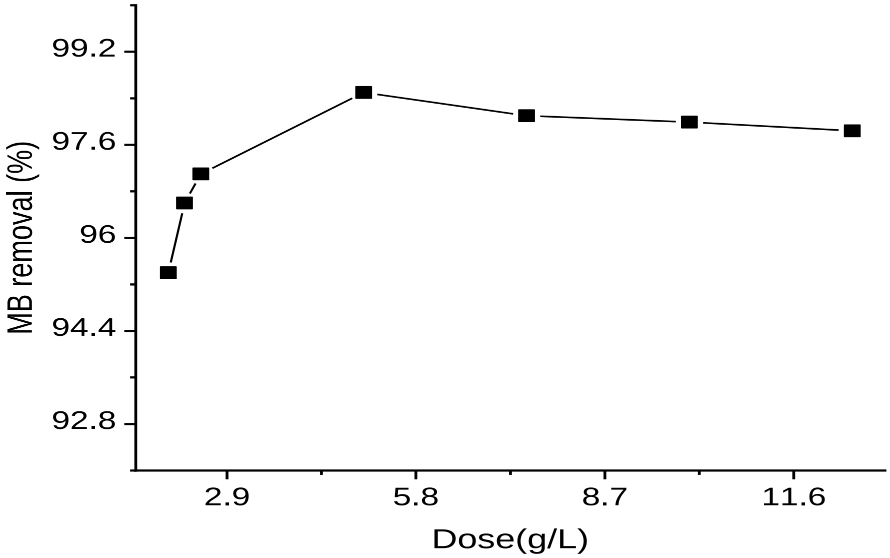


Fig.12 Effect of dose on MB adsorption onto ASA at initial concentration of (10 mg/L), pH of solution 7 for contact time of 60 min at 200 rpm, 25 ℃

The experimental results from the Fig.12 clearly stated that removal percentage of MB dye increased with increase the ASA dose from 2 to 5 g/L. This might be the more number of active sites available on the surface of ASA at higher dose and low diffusion resistance of MB dye onto the ASA[86]. The experimental results showed that MB dye was favorably adsorbed on the adsorbed surface which consists of enriched functional groups. The presences of functional groups on the ASA were confirmed by above mentioned FTIR studies [94]. Further increasing the adsorbent dose to 7.5 – 12.5 g/L, result no change in the adsorption of MB dye on ASA, because of the adsorption process reaches the equilibrium condition[68]. This might be due to that unavailability of adsorption sites and overlying of MB dye on the adsorption sites. Therefore, the optimum dose for the removal of MB on ASA was found to be 5 g/L [83].

4.4.4. Effect of initial MB concentration

The effect of initial concentration of MB adsorption onto ASA was investigated. The range of initial MB concentration solutions of 10 - 200 mg/L at constant contact time of 60 min, pH 7 and adsorbent dose (5 g/L) and shaking speed 200 rpm at 25 ℃ [21] shown in Fig.13 below.

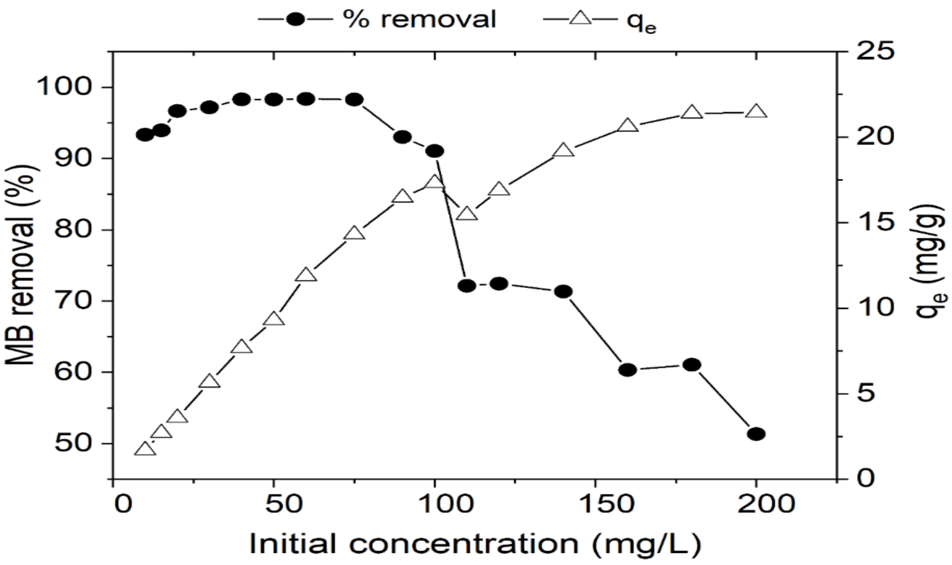


Fig.13 Effect of initial dye concentration by ASA, adsorbent dose (5 g/L), solution pH 7, speed of shaker (200 rpm) at 25 ℃ for 60 min

As revealed in Fig.13, the percent removal of MB from the solution increases with an increase in the initial MB concentration from 10 – 60 mg/L. This is due to the fact that at a lower concentration, there were enough active sites that adsorbent could easily take up MB dye. However, the removal efficiency of the pollutant decreased with an increase in the initial pollutant concentration. At the lower MB concentrations, enough high energy adsorption sites are available resulting in the high adsorption capacity, while with increasing initial MB concentrations the high energy adsorption sites became saturated and more MB left unadsorbed in the solution due to the saturation of binding sites[21]. This suggests that the less favorable binding sites are involved in the adsorption leading to a decrease in the removal efficiency with an increase in pollutant concentration. Furthermore, electrostatic repulsion between positive loads of adsorbed cationic MB leads to a decrease in adsorption percentages, which is consistent with other work. It also reported in the literature that the adsorption capacity of the adsorbent increases with an increase in the initial MB concentration due to the development of a concentration gradient and overcoming the mass transfer resistance. The adsorption capacity of MB on ASA increases from 1.74 – 21.63 mg/g when MB concentration is increased. This is due to high energetic force for mass transfer at higher initial concentration of MB dyes on ASA[83].

4.4.5. Adsorption kinetic studies

Kinetic models (pseudo-first-order, PFO and pseudo-second-order, PSO) were employed to study the adsorption kinetics of MB onto ASA[53, 92]. Both kinetic models were based on the assumption that the rate of occupation of adsorption sites is proportional to the number of vacant sites[50]. In this study, the extent of MB adsorption onto ASA is rapidly increased at the initial stage while remains constant after 45 min [9]. However, the equilibrium adsorption of MB on ASA was assumed to be 60 min in order to allow sufficient time for maximum adsorption of MB onto ASA. The fast adsorption at the initial stage can be associated with the presence abundance vacant active sites initially, which are responsible for the rapid adsorption of MB onto the adsorbent surface[56]. To study the mechanism involved in the adsorption process, the PFO and PSO kinetics models were used and non-linear regression method is more appropriate compared to linear method to determine the rate kinetic parameters[5], the obtained result is shown in Fig.14. The correlation coefficient (R^2) and the other parameters for the kinetic studies of MB adsorption onto ASA are shown in Table 1. As revealed in Fig.14 & Table 1, the PSO model better fit to the experimental data than the PFO model as the PSO model has higher correlation coefficient (R^2) and lower chi-square (x^2) values compared to the PFO kinetic model for MB adsorption onto ASA [92]. Thus, MB adsorption onto ASA is assumed to be a chemisorptions process [83]. Here, the observed rate constant (k_2) was considerably greater than with some reported value for MB adsorption on the variety of adsorbents [90], which indicate that the ASA was an efficient adsorbent for MB removal from aqueous solutions. Thus, the batch MB adsorption experiment using ASA follows pseudo-second-order kinetic model. Moreover, the values of q_e, cal (calculated) and qe, exp (experimental) are almost similar for MB adsorption onto ASA [89]. The overall high R^2 and low x^2 values (in Table 1) of PSO kinetic model are more appropriate to represent the adsorption kinetics of MB onto ASA[9].

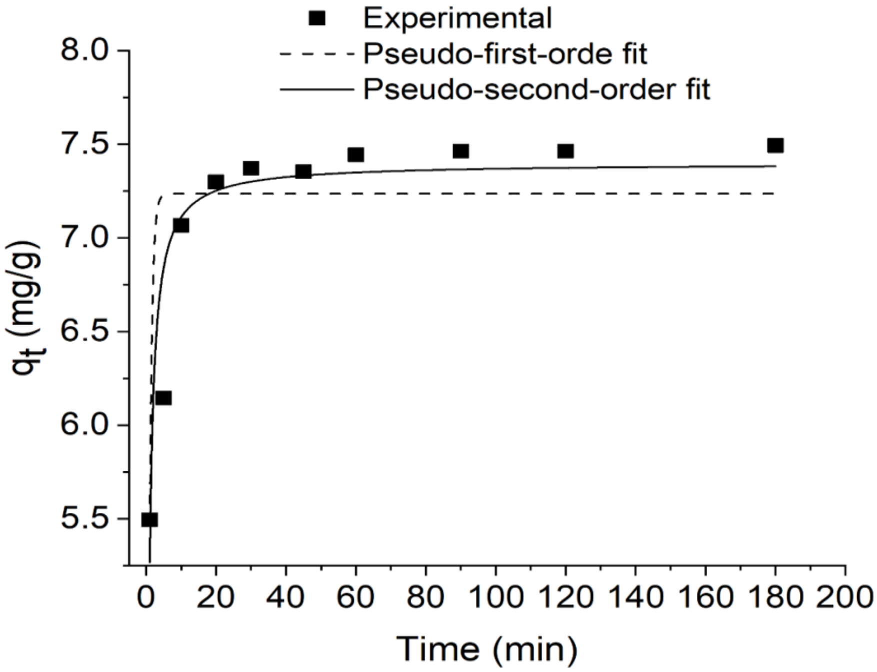


Fig.14 Pseudo second order and pseudo first order plot for adsorption of MB onto ASA.

Table 1 PFO & PSO model Parameters for MB adsorption onto ASA.

Parameter	PFO	PSO
C_o(mg/L)	20	20
$q_{e,Exp}$(mg/g)	7.494	7.494
$q_{e,Cal}$(mg/g)	7.236	7.399
k_1(min^{-1})	1.414	-
k_2(g/(mg.min))	-	0.334
V_0(mg/(g.min))	-	6.107
R^2	0.610	0.859
χ^2	0.610	0.074

Adsorption affinity (V_0) provides information on the adsorption rate at the beginning of the adsorption process [93]. Although the adsorption process proceeds in three steps specifically external surface diffusion, intra-particle diffusion, and finally adsorption [93]. Each of these steps could be rate-determining. In order to study the relevance of the intra-particle diffusion model, the amount adsorbed q_t vs. $t^{0.5}$, adsorption of dyes is mapped according to the theory proposed by Weber and Morris models [94] given by eqn.10. If the rate-limiting step is the intra-particle diffusion, the plot should be a straight line and pass through the origin[94]. However, in this work the plot does not pass through origin & show linearity of MB adsorption onto ASA (Fig.15) suggested that intra-particle diffusion was not the only controlling step in the adsorption process[64]. That is, the adsorption of MB and its kinetics could be the overall effect of the external diffusion transport of MB dye, the intra-particle diffusion of the MB dye, and the adsorption of MB by the active sites on the adsorbent surfaces, ASA[9, 10].

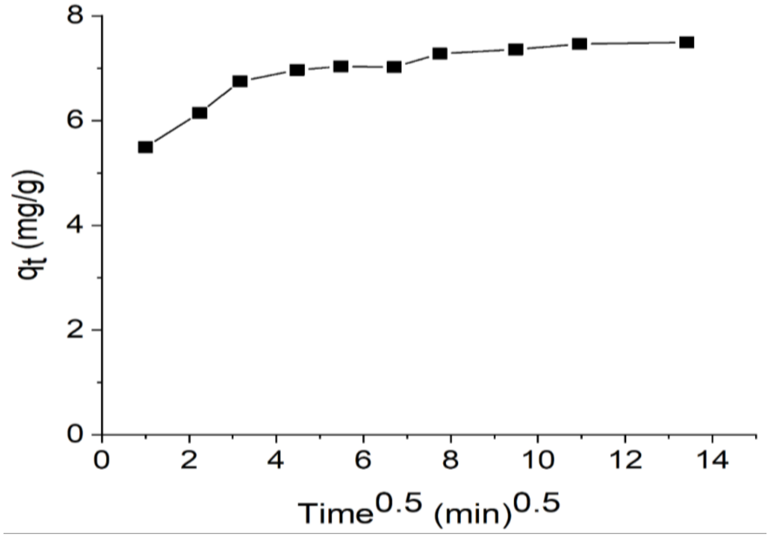


Fig.15 Plot of intra-particle diffusion adsorption of MB onto ASA

4.4.6. Adsorption isotherm study

Adsorption isotherm analysis is significantly important in describing how adsorbed molecules network with the adsorbent surface and emphasize the distribution of adsorbate molecules between the liquid and solid phases [83]. It is based on the set of assumptions which are mainly relate to the homogeneity or heterogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate variety [56,97]. In this study, the mathematical models, the Langmuir and Freundlich isothermal models were used to model the equilibrium data of MB dye adsorption onto RASA of fitting curves is given in Fig.16. The fitting curves showed that the higher R^2 & the smaller χ^2 values for the Langmuir isotherm model and for Freundlich isotherm model (Fig.16 and Table 2). This shows that the obtained experimental data better explained by using Langmuir model than the Freundlich model[53].

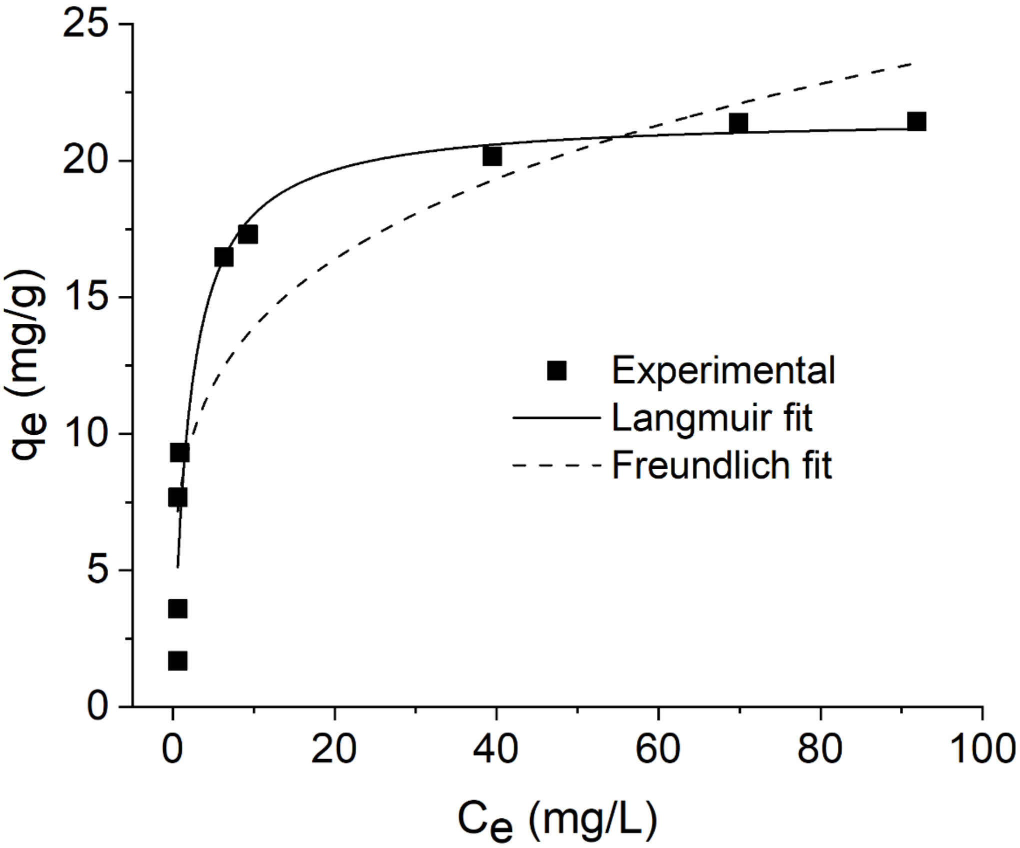


Fig.16 Langmuir and Freundlich isotherm model for the adsorption of MB onto ASA.

The applicability of the isotherm equation was judged by the determination of correlation coefficients, R^2 and the other parameters of isotherm shown in Table 2. In order to determine the best isotherm that could describe adsorption process of MB, data analysis was performed using nonlinear regression that fitness of the models is often evaluated based on the value of the correlation coefficients, R^2 and Chi-square, χ^2 analyses[50]. If the data from the model are similar to the experimental data, χ2 will be a small number, and if they are differing χ2 will be a large number. The Langmuir isotherm model (R^2 = 0.942 and χ^2 = 4.003) is better fit to the experimental data than Freundlich isotherm model (R^2 = 0.832 and χ^2 = 11.565) for MB adsorption onto ASA[9] as given in Table 2. In this study, R_L was found to be 0.0099 - 0.167 for MB adsorption onto ASA. The R_L values were in the ranges ($0 < R_L < 1$), which indicate favorable adsorption of MB onto ASA[9, 79]. In the Freundlich isotherm, the heterogeneity factor (1/n) is related to the intensity of the adsorption where n is a measure of the deviation from linearity of adsorption[9]. Its value of n = 4.198 is greater than one indicating that the adsorption process is favorable and physical process[79].

Table 2 Parameters on ASA Langmuir and Freundlich isotherms of MB dye.

	Isotherm	
Parameters	**Langmuir**	**Freundlich**
q_{max}(mg/g)	21.63	
K_L (L/mg)	0.501	
R_L	0.0099 - 0.167	
χ^2	4.003	11.565
K_F ((mg$^{1-1/n}$ L$^{1/n}$)/g)		8.030
n		4.198
R^2	0.942	0.832

4.5. Comparison of MB adsorption onto ASA with other adsorbents

The adsorptive capacity of the adsorbent used in this study was compared with that of others reported in the literatures as shown in Table 3. As shown in Table 3, ASA has higher adsorption capacity of MB dye compared to several other adsorbents such as hyacinth root powder, fly ash, corn husk, canola biomass, and natural zeolite and wheat shells. However, Rice husk, Activated Ficus carica bast, Red mud activated graphite composite and Treated Orange peel have higher capacity than ASA. This could be primarily due to the initial carbon content of the raw material, variation of activation process and optimized parameters Hence, ASA can be considered to be good adsorbent for the removal of MB dye from aqueous solutions in which providing a solution for safe management of water treatment sludge while providing a resource for water/waste water treatment.

Table 3 Comparison of adsorption capacity of MB dye onto ASA with other adsorbents reported in various studies

S/No	Adsorbents	pH	q_{max} (mg/g)	Dose (g/L)	Time (min)	Reference
1	Hyacinth root powder	8	8.04	1	90	[54]
2	Fly ash	7.5	3.074	40	60	[30]
3	Corn husk	6.2	8.51	0.5	15	[55]
4	Wheat shells	5	20.83	0.5	75	[87]
5	Natural Zeolite	7.5	16.75	0.5	180	[96]
6	Canola biomass	>7	16.7	3.5	60	[91]
7	**Alum Sludge (AS)**	**7**	**21.63**	**5**	**60**	**This Study**
8	Rice husk	8	40.58	0.12	40	[76]
9	Activated Ficus carica bast	7.8	47.62	5	120	[37]
10	Red mud activated graphite	6	89.28	0.01	120	[20]
11	Treated Orange peel	4.5	192.31	5	120	[59]

4.6. Adsorption cycle experiment

Adsorption cycle of adsorbent was the use of adsorbent without desorption more than one time. In this study, experiments were performed at pre-optimized setting and done by using distilled water up to five cycles. As revealed in the Fig.17, the adsorption efficiency of adsorbent become declined gradually & continuously starting the first cycle to last cycle. Here the adsorption of the adsorbent declined gradually and remove until the saturation of active site. This was due to the high adsorption capacity of the adsorbent & usage of the same initial concentration of MB (10mg/L) which tend to done for the cycles until the saturation. This was happened due to the loading of active binding sites with MB molecules and the ratio of competing active site decreases after each cycle [17]. However, there is some reduction in adsorption efficiency and this may be due to MB dye not being released completely from adsorption sites between cycles.

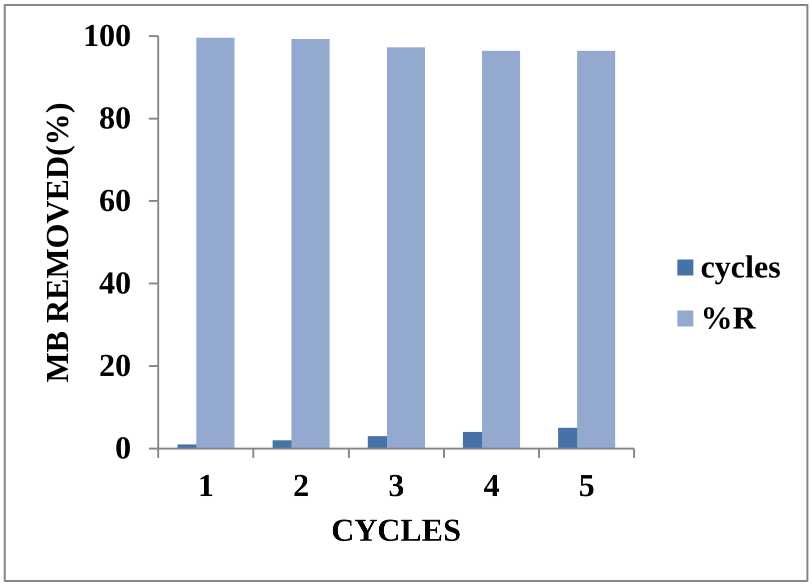


Fig.17 Test of adsorption cycle of MB on ASA, initial concentration (10 mg/L), adsorbent dose (5 g/L), speed of shaker (200rpm)

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The results obtained in this study show that water treatment alum sludge or Alum sludge Adsorbent (ASA) is effective adsorbents for removal of Methylene blue (MB) dye from aqueous solution using batch adsorption process. The adsorption of MB on the surface of ASA is found to depend mainly on the pH of the solution. The optimum pH of the solution was achieved at 7; while the removal efficiency decrease as the pH increases above pH 7. The equilibrium adsorption was achieved within 60 min. The optimum dose for equilibrium MB was 5 g/L. As the MB initial concentration increases, the adsorption capacity increases, but the removal efficiency decreases. The adsorption of MB and its kinetics could be the overall effect of the external diffusion transport of MB, The intraparticle diffusion of the ions and the adsorption of MB by the active sites on the functional groups of adsorbent. Therefore, kinetic data of the adsorption of MB on to ASA better fit to pseudo-second-order; R^2 (0.859) and χ^2 (0.074). The adsorption of MB on to ASA better fit to the Langmuir isotherm model; R^2 (0.942) and χ^2 (4.003), with maximum adsorption of 21.63 mg/g. Comparing the adsorption capacity of various materials showed that ASA can be used as a low cost and efficient adsorbent for MB dye removal. The finding could provide a solution for the safe management of water treatment waste while providing a resource for water treatment.

5.2. Recommendations

Based on the finding of the study, the following recommendations are forwarded:

It is better to study the common ion effect on the removal efficiency and the application of water treatment sludge (WTS) on the real sample.

Better to investigate the adsorption capacity and removal efficiency of water treatment sludge (WTS) to heavy metals and other water contaminants.

Since the finding is based on batch adsorption study, column study is needed for pilot and large scale application.

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