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A Study on Calcium Alginate Encapsulation of Kaolin on Methylene Blue Removal

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DECLARATION

I declare that this thesis entitled "title of the thesis" is the results of my own research except as cited in the references.

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A Study on Calcium Alginate Encapsulation of Clays on Methylene Blue Removal

ABSTRACT

The dye industry that operates causes a lot of environmental pollution, especially water pollution because of synthetic dyes that have significant environmental concerns. Methylene blue is an example of a dye that can harm human health and the environment because of its toxicity. Therefore, an efficient dye remove was prepared in this study through an adsorption method with clays such as kaolin (main), ball clay and bentonite clay as the adsorbents as they are abundantly and it is excellent cost- effective adsorbent in dye removal. The objectives of this research are to prepare sodium alginate encapsulation of clay beads (CB), to determine the ideal parameters for the clay beads (CB) to achieve maximum efficiency in removing methylene blue and to characterize calcium alginate clay beads (CACB) using UV-visible spectrophotometer and X-ray Diffraction (XRD). Therefore, this study will be able to find out the best adsorption results among the available parameters. In this experiment, calcium alginate beads were made using a cross-linking technique together with clays. The best conditions of the adsorption MB were at 45 µm size, 0.5g dosage, pH7, 100 rpm of agitation speed, 10mL CAKB,18G of needle size and 2wt% of calcium alginate. The percentage of the best conditions of adsorption was at 99.94%. All of these parameters greatly affects the MB removal uptake rate and further through this study the problem of water pollution caused by dye will be overcome.

Keywords: Kaolin, ball clay, bentonite, methylene blue, adsorption, wastewater treatment

Kajian tentang Pengkapsulan Kalsium Alginat Tanah Liat pada Penyingkiran Biru Metilena

ABSTRAK

Industri pewarna yang beroperasi menyebabkan pencemaran alam sekitar yang tinggi, terutamanya pencemaran air kerana pewarna sintetik yang mempunyai kebimbangan alam sekitar yang ketara. Metilena biru ialah contoh pewarna yang boleh membahayakan kesihatan manusia dan alam sekitar kerana ketoksikannya. Oleh itu, teknik penyingkiran pewarna yang cekap telah disediakan dalam kajian ini melalui kaedah penjerapan dengan tanah liat seperti kaolin (utama), tanah liat bentonit dan tanah liat bentonit sebagai penjerap kerana ianya banyak dan ia merupakan penjerap berkesan kos yang sangat baik dalam penyingkiran pewarna. Objektif kajian ini adalah untuk menyediakan enkapsulasi natrium alginat bagi manik tanah liat (CB), untuk menentukan parameter yang ideal untuk manik tanah liat (CB) untuk mencapai kecekapan maksimum dalam mengeluarkan metilena biru dan untuk mencirikan manik tanah liat kalsium alginat (CACB) menggunakan UV. -spektrofotometer kelihatan dan Belauan sinar-X (XRD). Oleh itu, kajian ini akan dapat mengetahui keputusan penjerapan yang terbaik antara parameter yang ada. Dalam eksperimen ini, manik kalsium alginat dibuat menggunakan teknik ikatan silang bersama dengan tanah liat. Keadaan terbaik bagi MB penjerapan adalah pada saiz 45 µm, dos 0.5g, pH7, 100 rpm kelajuan pengadukan, 10mL CAKB, saiz jarum 18G dan 2wt% kalsium alginat. Peratusan keadaan terbaik penjerapan adalah pada 99.94%. Kesemua parameter ini banyak mempengaruhi kadar serapan penyingkiran MB dan seterusnya melalui kajian ini masalah pencemaran air yang disebabkan oleh pewarna akan dapat diatasi.

Kata kunci: Kaolin, tanah liat bola, bentonit, metilena biru, penjerapan, rawatan air sisa

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LIST OF ABBREVIATIONS

BOD	Biochemical oxygen demand
CACB	Calcium alginate clay beads
CAKB	Calcium alginate kaolin beads
CABC	Calcium alginate ball clay
CABB	Calcium alginate bentonite beads
CB	Clay beads
DO	Dissolved oxygen
Fe2+	Ferrous iron
FPase	Filter paper activity
FTIR	Fourier-transform infrared
G	Gauge
g/mol	Gram per mole
H202	Hydrogen peroxide
LTMX	Leuco methylthionimium bis(hydromethanesulfonate)
MB	Methylene blue
MG	Malachite green
Na2SO4	Sodium sulphate

NaCl	Sodium chloride
NaOH	Sodium hydroxide
pH	Potential of hydrogen
RO	Reactive ozone
rpm	Rotation per minute
UV-visible	Ultraviolet visible
XRD	X-ray Diffraction
Xrf	X-ray Fluorescence

LIST OF SYMBOLS

α	Alpha
%	Percentage
^{O}C	Degree celcius
mL	Mililiter
nm	Nanometer
µm	Micrometer

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The importance of wastewater treatment has grown in recent years as the world grapples with the growing challenge of water contamination. Methylene blue is a common contaminant in wastewater . In the textile industry, methylene blue is applied primarily for dyeing various fabrics (X.-J. Liu et al., 2021). It is also used to colour papers and leather. Methylene blue has been identified as an indirect food ingredient in the food sector. Indirect food additives are called additives that enter food “through processing, packaging, or storage”. Indirectly, foods may absorb trace amounts of packaging materials during storage. Methylene blue dye is also used in aquaculture to cure a variety of fish diseases, as well as in medicine, microbiology, and diagnostics as a sensitizer in organic molecule photo-oxidation (M. Muniyandi., 2021). However, because of its high toxicity and resistance, methylene blue is harmful to human health at certain concentrations, making it a potential threat to the ecosystem and human health. This rise is harmful to the environment and human health (Ahmad et al., 2015). Several studies have found that methylene blue dyes are mutagenic and may cause cancer.

Several sub-separation processes for the removal of methylene blue from effluent and sewage have been identified, including chemical/electrocoagulation, oxidation, photocatalyzed degradation, biodegradation, biocatalytic degradation, and adsorption. To remove dye from the environment, many treatment approaches such as biological methods (using enzymes and microorganisms), chemical methods (using sophisticated oxidation processes), and physicochemical methods (mainly adsorption) have been widely used. Adsorption is one of the physicochemical treatment methods, but are not limited to the use of rice husk, cow dung, and biochar, activated carbons derived from oil palm wastes, active banana peel waste, Palmyra (Palm), shell, zeolite, activated carbon, and carbon nanotubes derived from eucalyptus (A. Yadav et al., 2021) which have been explored and employed for dye removal from the environment.

There is a lot of interest in developing low-cost, high-efficiency adsorbents from abundant, naturally occurring resources. Underexplored materials like those made from silica-containing chemicals and aluminosilicate minerals (clay) (Grini, 2006). The parameters that influence the selection of adsorbents in wastewater treatment are cost, toxicity, availability, and reusability. Natural clay is abundantly present in nature in large quantities as a low-cost, accessible, non-toxic material with a high potential for ion exchange for charged pollutants, making it suitable for use in wastewater treatment. Clays are composed primarily of alumina-silicates with a layered structure and are one of the most natural materials used for almost all types of pollutant adsorption from wastewater (Usmani et al., 2016).

1.2 Problem Statement

Water pollution caused by the release of synthetic dyes, such as methylene blue, poses a significant environmental concern. Conventional wastewater treatment methods are often inefficient and expensive in removing these pollutants. Therefore, there is a need to develop a long-lasting and cost-effective adsorbent material capable of successfully removing MB from contaminated water. Dyes and other organic and inorganic contaminants are found in industrial wastewater from the textile industry. The discharge of effluents from various companies as a result of the increasing rate of industrialisation has generated major concerns. The presence of these colours in water bodies can put aquatic life in grave danger. One of the negative consequences of this presence is a reduction in dissolved oxygen (DO) levels in water caused by blocking sunlight from the water system and opposing photochemical reactions. Therefore, a good dye removal process can remove a large amount of dye from waste water in a short amount of time while causing no secondary pollution.

These organic or inorganic dye environmental rehabilitation approaches are very efficient, cost-effective, and environmentally safe. Various natural clay structures, such as montmorillonite clay mineral, pyrophyllite, bentonite, and mixed clay (kaolinite/pyrophyllite), have been used in water treatment (Monash & Pugazhenthi, 2009). Nanoclay minerals have a large specific surface area and a high adsorption capacity, which provide them with chemical stability and high structural features for contaminant removal (Awasthi et al., 2019).

1.3 Objectives

The objectives of this research are :

i. To prepare sodium alginate encapsulation of clays beads (CB) mainly kaolin
ii. Using parameters namely clays size, agitation speed, dosage, pH of methylene blue adsorption and needle size to achieve maximum efficiency in removing methylene blue
iii. To characterize calcium alginate clay beads (CACB) using UV-visible spectrophotometer and X-ray Diffraction (XRD)

1.4 Scope of Study

The study on the preparation of sodium alginate encapsulation of clay beads (CB) (mainly kaolin) as an adsorbent to remove methylene blue dye in an aqueous solution has gained significant attention due to its high adsorption properties. This can be attributed to the increased surface area and pore volume of the encapsulated clays. The encapsulated clay beads (CB) can be a potential adsorbent for the removal of dyes from wastewater. Next, the beads can be further characterized using a UV-visible spectrophotometer and XRD to help with data collecting about the morphology, pore size, and functional groups of the beads.

1.5 Significances of Study

The study's end outcome was linked to the desire to improve the restriction clay beads as an adsorbent. The research on encapsulated clay beads for methylene blue adsorption combines agricultural waste, environmental remediation, and sustainable approaches to present a potential solution for dye pollutants in water. It delves into the creation of efficient adsorbents and their practical uses in water treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Encapsulation

A technique or method that is used to enclose or encapsulate something within a containment or protective structure is referred to as encapsulation. Coated materials, core materials, payloads, internal phases, etc., are refered to the encapsulated sensitive agents the coating materials themselves may be referred to as shells, wall materials, capsules, carriers, membranes, films, the exterior shell, or packing materials (Madene et al., 2005). Discovering and optimizing the adsorption behaviour of beads on methylene blue dye removal, which can be manufactured using a simple gelation procedure, has a great deal of economic promise in the treatment of coloured wastewater (Park et al., 2007).

The covering gel protects the clays present within the beads from physical stress, allowing it to keep its high viability and consequently its high colour adsorption capacity. Encapsulation is widely used in the food industry, drug delivery system, medicine, fertilizer and others. As an example, drug encapsulation is a crucial technique used for compounds that have low solubility, are delicate, or are aggressive. This method can enhance the therapeutic effect of the drugs while reducing any negative side effects (Kita & Dittrich, 2011). Additionally, beads preparation is for environmental conservation and facilitates the recycling raw materials such as sugarcane bagasse, luffa aegyptiaca and other clays like kaolin, ball clay and bentonite clay. Clays have a high potential as a supporting material for encapsulation since it is stable, have a reasonably large pore aperture, and have high mechanical strength and thermostability (Edama, N., 2013). Encapsulating can make it easier to handle and apply. The technique of confining the particles within a protective covering or matrix material is referred to as encapsulation. This improves the physical qualities, making it easier to handle, transport, and use in a variety of agricultural or environmental applications.

2.2 Encapsulant materials

Clay's distinctive mineralogy, morphology, electrical non-conductivity, mechanical stability, high specific gravity, heat and chemical resistivity, chemical purity, softness, abundance, and environmentally friendly nature make it a versatile raw material suitable for a wide range of industrial applications, including paper, plastics, paint, ceramics, medicine, pharmaceuticals, cosmetics, refectories, and low-cost adsorbents (Awad et al., 2017). Because of its crystalline structure, which provides for a huge surface area that absorbs several times its weight in water and metal binding ability, kaolinite crystals are used as adsorbents for removing heavy metal ions, dyes such as methylene blue dye, and other organics from wastewater (Shaw, 2017). Clay can also be employed as a filer to improve adsorbent mechanical strength (Chai et al., 2020).

Clay minerals can also be found in abundance as colloidal fractions in soils, sediments, rocks, and water. Because of their vast surface area, high ion exchange capacity, layered structure, chemical and mechanical stability, and low cost, clay minerals are considered an excellent cost effective adsorbent in the removal of cationic and anionic dyes

(H.G. Dill, 2016). Clays have several advantages over many other commercially available adsorbents, including low cost, abundant availability, high specific surface area, excellent adsorption properties, non-toxicity, and a large potential for ion exchange. Clays also contain exchangeable cations and anions that are held to the surface, and for these reasons, scientists all over the world are interested in using natural or modified clay materials as adsorbents for water treatment. Because of their high cation exchange capacity, surface area, and pore volume, most clay minerals are negatively charged and widely used to adsorb metal cations from solutions.

2.2.1 Natural polymers

2.2.1.1 Cellulose

Cellulose is the most abundant natural polymer compound on earth, consisting of β (1-4)-glycosidic-linked glucose units. Cellulose organizes in a rather intricate supramolecular structure formed by the intermolecular cohesion of cellulose molecules, which is an extended intra/intermolecular network of hydrogen bonds. Chitosan is a natural polycationic polymer with hydrophilic properties, consisting of the repeating residues of D-glucosamine and N-acetyl-D-glucosamine. It is obtained by the partial deacetylation of chitin, one of the most abundant polymers after cellulose, extracted from the fungal cell walls and the exoskeleton of crustaceans/insect (Ahn et al., 2021).

2.2.1.2 Collagen

Collagen, as one of the most abundant renewable natural polymers along with cellulose and chitosan, has significant applications in the biomedical (Zhang et al., 2018). It plays an important role in structural proteins for most tissues, i.e., skin, bones, muscles, blood vessels, and cartilages, and contains plenty of functional groups, i.e., hydroxyl, amino, carboxyl, guanidyl, and imidazoles, endowing collagen with many physical and chemical properties. Alginate is the best material to use in this study to make beads because of the low cost of these products, the fact that they do not have any adverse effects on the environment, and the biofunctionality of the products that are derived from them. Alginates are a family of The seaweed extraction process yields alginates, which are polysaccharides with a molecular weight ranging from 10 to 1000 kDa, made up of α-D-mannuronic acid and β-L-guluronic acid. The non-toxicity and biocompatibility of alginates are their primary characteristics. In addition to having mucoadhesive qualities, they are non-immunogenic and do not induce inflammatory reactions. The remarkable ability of alginate to soak up water anywhere from 200 to 300 times its own weight is what sets it apart. Hydragels derived from alginate also have a favourable degradation rate and high mechanical strength. Particles, fibres, scaffolds, sponges, and membranes are just a few of the interesting forms that biomaterials derived from alginate can take (Catoira et al., 2019).

2.2.2 Calcium alginate

Calcium alginate is a chemical produced from alginate, a polymer found in brown algal cell walls. They are made from alginate, a derivative of seaweed. (Dean A. Hendrickson, 2012) When calcium alginate comes into contact with divalent cations, primarily calcium ions, it forms a gel. Calcium ions crosslink alginate chains to produce this gel, resulting in a three-dimensional gel structure. Not only that, calcium alginate possesses excellent water-absorbing properties in terms of absorbent properties. Calcium alginate can serve as a matrix or binder for particles. When the particles are combined with a calcium alginate solution, the alginate creates a gel-like matrix that surrounds and adheres to the particles' surface. This encapsulation technique aids in the bonding of particles, providing structural stability and preventing dispersion or deterioration.

The calcium alginate matrix not only acts as a binder, but it also has additional advantages. It can improve the characteristics and give functionality like as higher water holding capacity, regulated release of nutrients or chemicals, and increased surface area for interactions with the surrounding environment. Because of its advantageous properties, sodium alginate is one of the most interesting, researched, and applied biopolymers. The most important is easy, simple, mild, rapid, non-toxic gelation by divalent cations (Mokarram et al., 2009). Furthermore, it is abundant, low-cost, eco-friendly, bio-compatible, bio-adhesive, biodegradable, and stable. Encapsulation with calcium alginate can be beneficial in a variety of applications, including environmental cleanup, agriculture, and controlled release systems. Encapsulated for example, can be used in environmental remediation to trap and immobilise pollutants, preventing them from seeping into the surrounding soil or water. Encapsulated can be used as a slow-release fertiliser in agriculture, giving plants with a consistent supply of nutrients. The calcium alginate matrix helps to regulate nutrient release and avoid quick leaching.

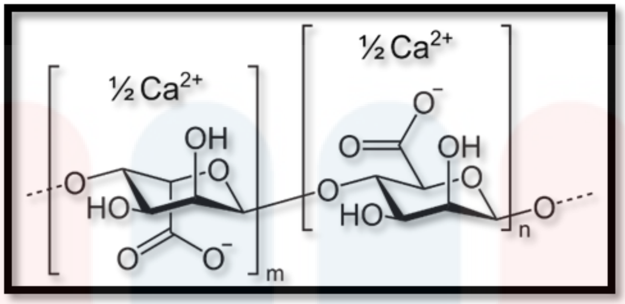


Figure 2.1: Chemical structure of calcium alginate

2.3 Adsorption materials

2.3.1 Natural clays

Natural clays have porous structures, tunable specific surface areas, remarkable thermal and mechanical stabilities, abundant reserves, and cost-effectiveness. Natural clay minerals possess almost similar elemental compositions and crystalline structures. The silica and alumina contents occupy a major component of the clay. The oxides of magnesium, iron, calcium, sodium and potassium occupy minor a proportion of different types of clays. **(** Uddin M. K., Chem. Eng. J. 2017)

2.3.1.1 Kaolin

Kaolin, also known as "kaolinite clay" or "China clay," is a popular industrial clay that is soft, lightweight, earthy, and white (Yaya et al., 2017; Heah et al., 2011). To that end, the global mined production of Kaolin in 2016 was anticipated to be 37.0 million tonnes (Detellier, 2018). Kaolin is primarily generated from the mineral kaolinite, which is hydrated aluminium silicate and contains other kaolin group minerals (Shaw, 2017). The stoichiometric formula Al2Si2O5(OH)4 describes kaolin (Hosseini and Ahmadi, 2015), which is also expressed by the formula Al2O3 2SiO2.2H2O. Kaolinite is classified as a 1:1 clay mineral based on the arrangement of its layer structure (Awad et al., 2017).

This indicates that a layer is made up of two distinct sheets (Detellier, 2018). Rectorite, halloysite, and chrysotile are also clay minerals (Heah et al. 2011). The formation of primary kaolin deposits resulted from the transformation of in-situ minerals such as feldspar and other aluminium silicates to kaolinite. Secondary deposits form as sediments, usually in fresh water, far from their original location. Depending on their qualities or function, different forms of secondary kaolins are known as ball clays, fireclays, or flint clays (New South Wales DMR, 1998).

Figure 2.2: Kaolin

2.3.1.2 Ball clay

Ball clays, also known as plastic clays, are fine-grained sedimentary clays that fire to a light or near-white colour. They are primarily used in the production of ceramic whiteware and are prized for their key properties of plasticity, unfired strength, and light fired colour. Ball clay is primarily composed of the mineral kaolinite but with a smaller crystal size than other clays. Increased workability of the body in the plastic state (Singer

& Singer, 1979). Ball clays have highly variable compositions and are made up of a mixture of kaolinite, mica, and quartz, each of which contributes different properties to the clay.

Ball clays are kaolinitic sedimentary clays with 20-80% kaolinite, 10-25% mica, and 6-65% quartz. The composition of localised seams within the same deposit varies, including the amount of major minerals, accessory minerals, and carbonaceous materials such as lignite. They have fine-grained and plastic characteristics. The crystallinity of kaolinite, the key component, has a significant impact on ceramic performance. It's been used to remove heavy metals and dyes from aqueous solutions. Ball clay, like other clays, is a negatively charged adsorbent that is frequently effective for cationic dye binding.

Figure 2.3: Ball clay

2.3.1.3 Bentonite clay

Bentonite is a widely distributed clay material formed through the devitrification and chemical alteration of glassy volcanic ash or tuff. Bentonite is a volcanic glass-derived rock made mostly of niontniorillonite, but can also contain beidellite. Its minerals are completely crystalline, have a niicaceous habit, high birefringence, and easy cleavage. It contains no gel colloids, and few of its crystal particles are small enough to be considered "colloidal size." It has high adsorptive properties, which are influenced by its physical form rather than chemical composition. The micaceous structure allows for easy cleavage, resulting in a large surface area and a felt-like texture (Ross & Shannon, 1926).

The most commonly used clay for water purification is bentonite, which is impure and made up of montmorillonite. Some clays may also contain rare minerals such as beidellite, saponite, hectorite, and nontronite. (Stockmeyer, 1991) investigated the adsorption of organic compounds in aqueous solutions using organophilic bentonites. Organoclays exhibit varying degrees of total cation exchange capacity (CEC) with organic counter ions (Stockmeyer, 1991). Bentonite clay is a cost-effective solution for dye removal.

Figure 2.4: Bentonite clay

2.3.2 Agrowaste

Agrowaste is the waste generated by various agricultural products which can also be one of the adsorption materials. Agriculture wastes include bagasse from sugarcane, wheat husk and straw from wheat, groundnut shell from groundnut, rice husk from paddy, and coconut shell from coconut, among others. Most developing countries generate around 400 million tonnes of agricultural waste each year. Some wastes, such as rice husk, bagasse, shelled ground nuts, and so on, are now partially used as a treatment for wastewater. This use produces ash, which creates a disposal issue. Furthermore, using these waste can solves the problem of environmental pollution and there is a strong need to use these wastes in this manner in order to keep the environment clean especially in wastewater treatment (Singh et al., 2016).

2.3.2.1 Luffa aegyptiaca

Luffa is the family of pumpkin, squash, and gourds (Cucurbitaceae) includes the genus Luffa, which includes tropical and subtropical plants. The term "luffa," which is frequently spelt "loofah," is typically used to describe the fruits of the Luffa aegyptiaca and Luffa acutangula species. It is grown and consumed like a vegetable, but to be edible, it must be harvested when it is still in the early stages of development. Besides, the fruit is quite fibrous when it has reached its peak ripeness. Luffa is a versatile plant as it has many functions. The luffa washing sponge used in bathrooms and kitchens is made from fully formed fruit. The luffa sponge is made of living, cell-based organisms. A luffa sponge can absorb almost the same amount of energy per unit mass as aluminium foam when crushed longitudinally. The complex network of fiber bundles that make up luffa sponges is coupled to create a three-dimensional, highly porous network.

2.3.2.2 Sugarcane bagasse

Sugarcane bagasse (SB) is one of the common agricultural wastes generated in India in a massive amounts every year, and it is typically either burned or discarded due to its low value. Biochar, derived from sugar bagasse through pyrolysis, is a more eco-friendly and stable adsorbent material. Sugarcane bagasse is an effective adsorbent for the elimination of a wide range of organic and inorganic pollutants, according to several studies. However, I found that sugarcane takes a long time to grow and is hard to find. In addition, sugarcane skin is very hard and difficult to grind compared to luffa. In addition, luffa is a material that is always used because it is a multi-purpose material. This is because luffa is a source of food in addition to being a natural sponge used when bathing. Not only that, luffa is easy to find because it is sold in the market.

2.4 Colour wastewater

Water contamination caused by textile factories' inability to properly dispose of wastewater is currently one of the world's major challenges. Textile industries have a substantial impact on the global economy and pollution in various countries, notably China and the estuaries of South Africa (Olisah et al., 2021). Textile wastewater has been shown to contain a wide range of toxic dyes, heavy metals such as mercury, chromium, cadmium, lead, and arsenic, as well as aromatic compounds used in the production of textile dye colour pigments. Heavy metals such as mercury, chromium, cadmium, lead, and arsenic are used in the creation of textile dye colour pigments. (Singha et al., 2021). These toxic compounds travel long distances alongside wastewater.

Water contamination caused by the textile industry's failure to properly dispose of its waste water is one of the most severe concerns affecting the world today. China's and South Africa's estuaries are just two examples of countries with significant textile industry that contribute significantly to global economic and environmental pollution (Olisah et al., 2021). Textile production generates large amounts of highly colored effluent containing a range of persistent contaminants; this wastewater is a severe polluter of the environment and also has an impact on human health. Ali et al., 2022; Almroth et al., 2021). Over 7107 tonnes of synthetic dyes are generated worldwide each year, with the textile industry using over 10,000 tonnes (Chandanshive et al., 2020).

Toxic compounds found in industrial wastewaters such as electroplating or acid mine wastewaters include cyanides, alkaline cleaning agents, degreasing solvents, oil, fat, and metals. Most metals, including copper, nickel, chromium, silver, and zinc, are hazardous when discharged without treatment (Heidmann, I., & Calmano, W., 2008). Heavy metal treatment approaches include included precipitation, adsorption, biosorption, ion exchange, electrodialysis, and membrane separation. Precipitation is the most practical of these approaches and is thought to be the most cost-effective (Ahmed Basha et al., 2008).

Industrial wastewater is a major source of pollution in water habitats, containing high levels of heavy metals and other persistent harmful chemicals. The rapid advancement of science and technology has propelled the sector to new heights of development. However, everything has a cost; a massive amount of industrial effluent released into rivers and lakes kills the environment, human life, and all other living beings. Some of the most harmful minerals found in industrial effluent include copper, nickel, zinc, and lead, which are soluble and can be absorbed by living beings. significant health problems1. Once these hazardous elements enter our food chain, a high concentration of heavy metal ions accumulates in the human body, causing major health problems (Babel, S., & Kurniawan, T. A., 2003;).

It uses chemical coagulation to remove colloidal matter as hydroxides by adding lime to raise the pH and aluminum or iron salt to remove colloidal matter as hydroxides. Although it has been demonstrated to be highly effective in treating industrial effluents, chemical coagulation may generate secondary contamination due to additional chemical compounds.

This disadvantage, combined with the necessity for low-cost effective treatment, prompted numerous investigations on the use of electrocoagulation for the treatment of various industrial effluents (ADHOUM et al., 2004).

Wastewater with added colour is notoriously difficult to handle because of the wide variety of chemical and colouring compounds it contains. The effluent from textile and dyeing mills is typically quite vividly coloured since these facilities utilise a wide variety of synthetic composite dyes. The environmental protection legislation for the receiving waters requires that these wastes be treated before release. Effluents from the textile industry are often treated using biological techniques. Waste colour cannot be effectively removed using these methods (Aziz et al., 2007; Basava Rao and Maohan Rao, 2006), despite their effectiveness in eliminating biochemical oxygen demand (BOD) and suspended solids (TSS). This means that even after treatment, some waste effluents may still be noticeably discoloured. These days, treatments consist of a variety of physicochemical processes such as adsorption, oxidation, chemical precipitation, etc. There are advantages and disadvantages to using each. Methylene blue has a significant affinity for water in normal conditions, and it is famously difficult to biodegrade and remove from wastewater using basic conventional treatment procedures (J. Magn. Magn Mater.,2020). To avoid the hazardous consequences on human health and the environment methylene blue must bee be removed from effluent wastes (S. Afr. J. Chem. Eng.,(2020). Controlling the amount of methylene blue used in medicine is an important aspect of its use. Therefore, industrial wastes and effluents are the primary targets of removal strategies.

2.5 Dye

Dye, one of the most common water pollutants, is a chemical compound with complex organic molecular structures (Yagub et al., 2014). Moreover, dyes are chemical compounds that possess chromophores, which are responsible for the color of the dye.

Chromophores are groups of atoms within a molecule that absorb certain wavelengths of visible light, resulting in the perception of color. Different types of chromophores can absorb different colors of light, which can lead to a wide range of colors in dyes. In addition to chromophores, dyes may also contain other functional groups that can affect their properties, such as solubility, stability, and reactivity. The choice of dye and its chemical composition will depend on the desired color, application, and other factors. Dyes are commonly used in tethe xtile, leather, and paper industries, as well as in food, cosmetics, and other consumer products. They can be derived from natural sources, such as plants and animals, or synthesized through chemical reactions in a laboratory. A dye is a chemical ingredient that is applied the o fabric to change its colour and then bonds strongly tofibersibres of the fabric. There needs to be a high level of durability in dyes against the effects of sun, heat, and moisture. Soluble dyes are dyes that can be dissolved in water and then attached to the fibres at the molecular level. Dyes are a type of coloured substance, but not all coloured compounds are dyes.

Different types of dyes can be distinguished by their origin, chemical make-up, and typical uses (Holkar et al., 2016; Akpomie and Conradie, 2020). Synthetic dyes used in the textile industry include azo, direct, reactive, mordant, acid, basic, dispersion, and sulphide hues. Wool, cotton, silk, polyester, polyamide, and acrylic are examples of natural and synthetic fibres used in the textile business. (Deopura and Padaki, 2015; Silva et al., 2021). Sizing, softening, desizing, whitening, and finishing treatments are just some of the many examples of highly harmful chemicals used by the textile industry (Kishor et al., 2021). Textile dyes pose significant ecotoxicological issues since they do not stick tightly to fabric and are discarded as effluent alongside wastewater into aquatic habitats such as lakes, rivers, streams, and ponds (Parmar et al., 2022). A high level of affinity between the dye and the substrate is crucial for a successful dyeing process. Therefore, azo dye is considerably easier to construct than other types of dyes when trying to build a dye that has stronger affinity towards the substrate than the medium. Methylene blue, a very simple dye, is an example of an azo dye.

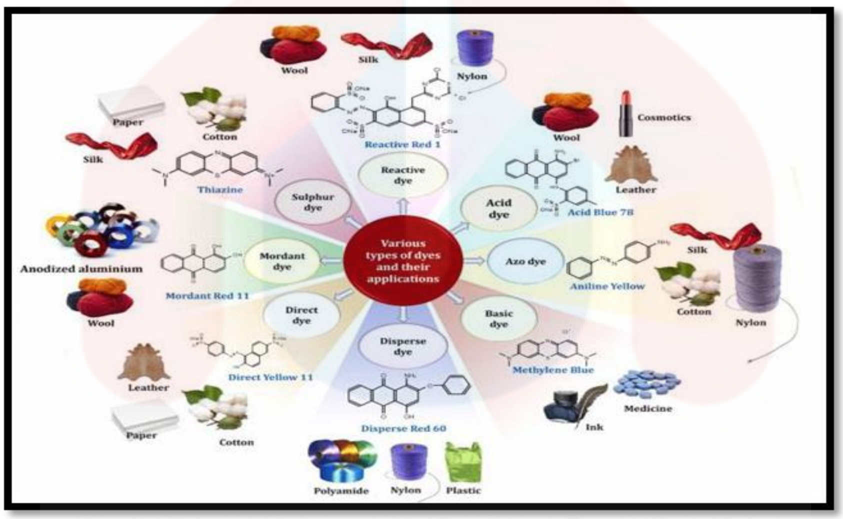


Figure 2.5: Various dye classifications and their potential industrial applications. (Source: Al-Tohamy et al., 2022)

2.5.1 Direct dye

In addition to azo dyes such as methylene blue, there are also several dyes that are used in the textile industry, direct dye is a type of dye that is applied to the substrate directly in a neutral or alkaline solution (Kiron, Mazharul Islam, 2012). An aqueous dyebath containing a sodium chloride (NaCl) or sodium sulphate (Na2SO4) electrolyte is typically used. Direct dyeing is a simple technique. Although the majority of direct dyeing is done in a neutral or slightly alkaline dyebath at or near boiling point, the majority of direct dyeing requires a separate post treatment to promote wet fastness, such as cationic dye fixing. They are complicated sulfonic acid salts chemically. Over 75% of all direct dyes are unmetallised azo compounds, with disazo or polyazo forms accounting for the vast majority. They have an anionic ionic nature and are water soluble. Cotton, viscose, silk, jute, linen, and other fibres are among their favourites.

2.5.1.1 Methylene blue

Methylene blue (methylthioninium chloride) (MB) is a cationic dye from the phenothiazines family that is soluble in both aqueous and organic mediums. It has a long history of medical application, including in the treatment of malaria and methemoglobinemia. Methylene blue was the first synthetic drug used as a medical antiseptic; it is excreted in the urine as a combination of methylene blue, leucomethylene blue, and demethylated metabolites. Huntingtin in Huntington's disease, prion protein in Alzheimer's disease, and tau protein in tauopathies are just a few examples of how methylene blue can modulate proteins implicated in these degenerative brain conditions.

Consequently, in the formation of a disulfide bond, tau monomers become incapable of aggregating into hazardous structures. Recent mouse studies have shown that methylene blue has a greater impact on cognitive function in the early stages of Alzheimer's disease than in later stages. Methylene blue protects synapses and enhances protein clearance via autophagy, both of which it does by increasing proteasome activity. Phase II and III clinical trials have already begun with methylene blue and TRx0237 (LMTX). The fact that methylene blue decreases fibre formation while preserving large amounts of tau oligomers, an important species for neuronal death, may explain why it has done poorly in clinical trials for Alzheimer's disease.

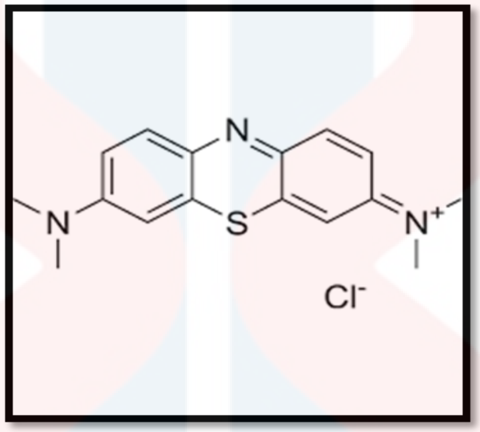


Figure 2.6: Chemical structure of methylene blue

2.5.1.2 Melachite green

Next, Malachite green (MG) is a synthetic dye used to dye silk, cotton, leather, wool, and paper similar to methylene blue. It is also applied as a fungicide and disinfectant in the fish farming sector, providing control of fish parasites and diseases (Vergis et al., 2017). MG is a cationic triphenylmethane molecule that is extremely soluble in water (Kabeer et al., 2019). Malachite green, a triarylmethane dye (C23 H26 N2O, CI 42,000), is a dark green crystalline solid created by combining benzaldehyde and diemethylaniline in the presence of strong sulfuric acid or zinc chloride. Malachite green can be found in a variety of forms, including oxalate or hydrochloride salts in a 50% solution of acetate and hydrochloride. Malachite green hydrochloride is an industrial quality product that is precipitated with zinc chloride, resulting in a double zinc salt. This dye, like other triphenylemethanes, has two ionic forms: dye salt and carbinol/pseudobase.

2.5.1.3 Rhodamine B

Not only that, Rhodamine B (RhB) dye, commonly used in textile industries, has been linked to carcinogenic and neurological effects, potentially leading to many human disorders. The molecular formula of Rhodamine B (RB) is C28H31ClN2O3. Rhodamine B (RhB) is a water soluble organic dye used in the textile industry for various applications, including fabric coloring, water tracing, fluorescent markers for microscopic structural testing, photosensitizers, and laser dyes. However, due to its carcinogenic properties, it has been banned from use in food processing for decades (Yahia et al., 2013).

2.5.2 Acid dye

Acid dyes are commonly utilised in the textile industry as well. The technique of dyeing in an acidic aqueous solution (pH 2.6) is referred described as "acid dye" (Kiron, Mazharul Islam, 2012). Two causes contribute to the name "acid dyestuff." The dyestuffs were immersed in mineral or organic acids such as sulphuric, acetic, or formic acid, and the bulk of them are sodium salts of organic acids. In 1862, Nicholson made acid dye by treating an insoluble dye. They are commonly used to colour protein fibres (such as wool and silk) as well as nylon fibres. Acid dyes are anionic in nature, and their negatively charged anions are drawn by positively charged amino groups in wool in acidic circumstances. One thing these dyes have in common is their interaction mechanism with fibre polymers, which results in strong dye binding to the substrate. At least in part, the dye binding can be explained by an ion-exchange process. The charged groups of the fibre polymer and the charged dyestuff molecule establish ionic connections. At low pH, it is necessary to colour protein fibres (wool, silk) and polyamides with ammonium groups. The chemistry of acid dyes is complex and diverse. Based on their chemical structure, acid dyes are classed as azo, anthraquinone, triphenylmethane, pyrazolone, azine, nitro, and quinoline. Azo dyes are the most common and important group, followed by antraquinone and traylmethane dyes.

2.6 Colour wastewater treatment

To prevent dye used in textile from entering the environment, numerous technologies have been suggested and developed for its extraction from waste and effluent. There are three types of effective removal technologies: physical, chemical, and biological. This suggests that the three listed approaches are standard and have been extensively examined by scientists and/or ecologists.

2.6.1 Biological treatment

Toxins can be broken down by the enzymes produced by filamentous fungus, which can be found both inside and outside the cell. They can be extracted from any organic substance, including soil and compost. Filamentous fungus use both the biosorption process and extracellular enzymes they manufacture to decolorize and break down azo dyes (Dhir B., 2022). There have also been studies conducted on both living and dead biomass systems, looking into the potential of filamentous fungi as a biosorbent for dye-containing effluents.

Multiple rresearchershave compared two methods of applying fungal biomass for colour treatments. Both living and dead cells were shown to be equally effective at removing dye pigment. In a large-scale screening of various species of bacteria, dead forms had higher decolorization rates for Reactive Black 5 and Reactive Blue 19. Przytas et al. examined the efficacy of immobilised fungus in living and autoclaved forms. (specifically, Pleurotus ostreatus BWPH, Gleophyllym odoratum DCa, and Polyporus picipes) (Przysta W et al., 2018).

The two methods for making use of fungal biomass each have their benefits and drawbacks. Dye decolorization and degradation methods in living cells are diverse, as was discussed earlier. However, the capability of fungi to release enzymes is sensitive to a wide range of operational variables, including pH, moisture, temperature, nutrient availability, and culture upkeep. However, decomposing organic matter shows promise as a biosorbent, but with the same disposal concerns as any (physical) adsorbent. Particularly relevant is the then dye-enriched adsorbent in this regard. Dye absorbed by fungi may remain at the disposal site and weather, but the mushrooms themselves are likely to degrade fast.

2.6.2 Physicochemical treatment

A wide range of chemical and physical techniques have been investigated. Methods that rely on the physical properties of matter include adsorption and filtration (Popli S., Patel U., 2015). Adsorption uses materials such as activated carbon to remove pollutants from wastewater by accumulating them on the surface of the carbon. Activated carbon has been the go-to for this kind of therapy, but its expensive cost has kept it from seeing widespread application. Peat, banana peels, mud, corn cob, maize ,and wheat straw are just some of the alternatives that have been tried. However, there are limitations because of the difficulty in properly discarding the trash produced by these less expensive options. Filtration is another common physical technique. To purify water and get rid of impurities, membrane filtration is commonly used. While efficient, it does come with a few drawbacks, including as high initial investment and material prices, membrane degradation or membrane fouling, the generation of potentially toxic sludge, and the recurrence of waste management issues.

A variety of chemicals and processes, including coagulation-flocculation, Fenton's reagent, ozone, and electrochemical approaches, are used in chemical therapy. Sedimentation and subsequent coagulation-flocculation are utilised in typical wastewater treatment plants (Sonal S., Mishra B.K. 2021). Coagulants are used to reduce the reactivity of suspended particles, which are typically charged in the opposite direction of the coagulant. When the charge is removed, the solids in suspension can collide and organise into microflocs. These microflocs can coalesce into macroflocs and sediment during flocculation, at which point they are more easily separated from the water and removed by gravity. Toxic wastewater contaminants can be neutralised by generating hydroxyl radicals with Fenton reagent (H2O2 and Fe2+ ions). The process as a whole may be inexpensive, but it may generate a lot of sludge as a byproduct. Dye chromophores are oxidised and disassembled preferentially using reactive ozone (O3) in ozonation, however, ozone's instability renders it unsuitable for wastewater treatment.

Among the several ways (physical, chemical, and biological methods) thoroughly explained or explored in this synthesised text, adsorption technology has been shown to have low constraints and to be an effective means of removing methylene blue from (waste)water. Given the financial and other constraints of biological and chemical methylene blue eradication approaches, (P.O. Oladoye, 2022), it is challenging to efficiently decolorize methylene blue loaded wastewater utilising simple "traditional techniques." Many benefits have been identified for adsorption technology, including its user-friendliness, insensitivity to toxic contaminants, straightforward design, high efficiency, low cost, an abundance of readily available natural adsorbent, and absence of dangerous by-products. Since optimising the operating conditions and parameters that affect methylene blue uptake on different adsorbents is critical to designing an effective wastewater treatment facility, this section will focus on those issues.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter explained the materials and methods that were used to complete this study. The process included preparation using clays and preparation of calcium clay beads for adsorption studies to find the optimum conditions for methylene blue solution removal. After that, the beads were characterized using UV-Vis and XRD.

3.2 Materials

Sodium alginate powder with molecular weight of 147.01 g/mol were purchased from R&M Chemicals. While methylene blue powder of 319.865 g/mol was purchased from HmBG Chemicals. Other chemicals that use is calcium chloride. Besides, material that use is clays that is kaolin, ball clay received from DR Teo and bentonite clay. There will be three stages in the research flow chart. As illustrated in Figure 3.2, stage 1 is for material preparation, and stage 3 is for analysis, assessment, and comparison of the obtained experimental data.

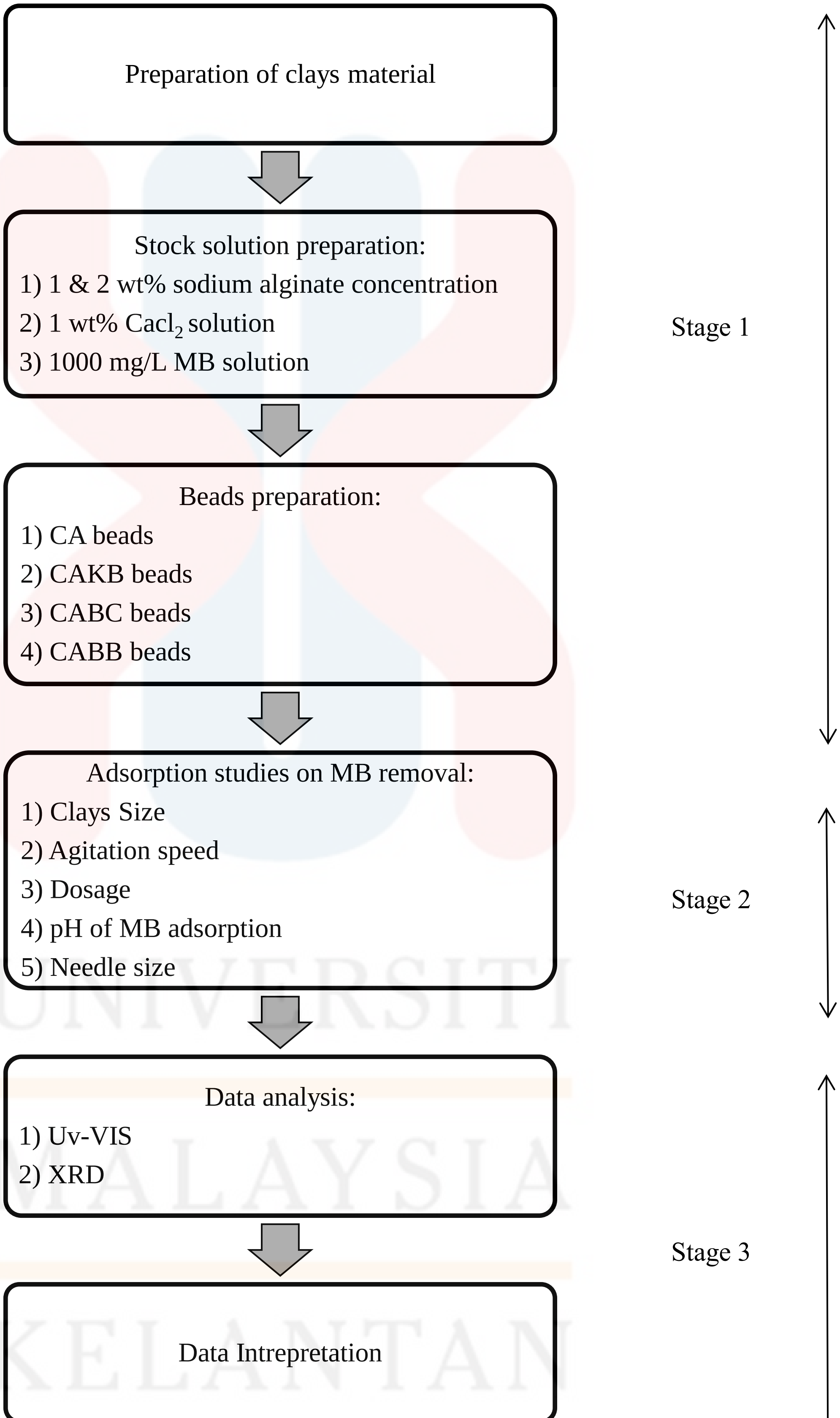


Figure 3.1: Research flow for calcium alginate clays beads (CB).

3.3 Method

3.3.1 Preparation of clays

Clays is use to prepare clays beads. Clays powder were sieved using 4 different siever, namely 45 µm, 63 µm, 125 µm and 250µm. After sieved the clays powder according to a certain size, put the clays powder in a plastic container to be used as a stock.

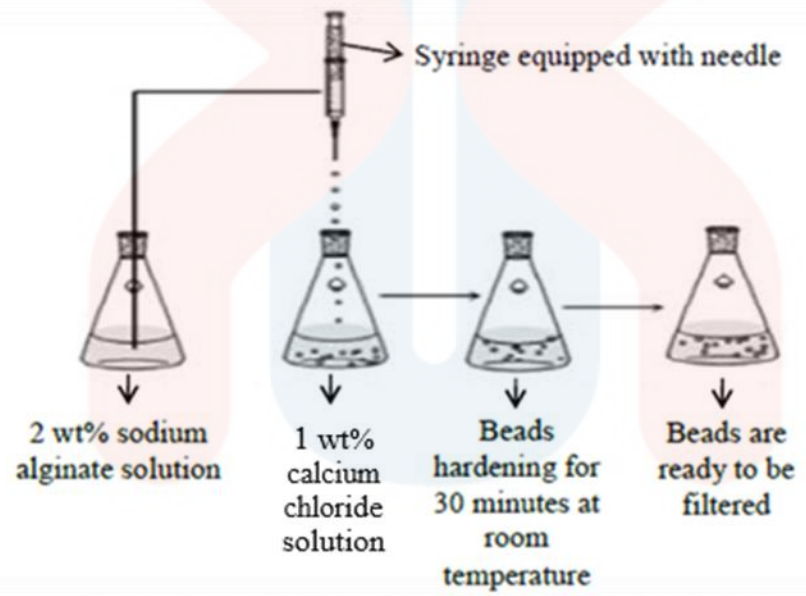


Figure 3.2: The process of making calcium alginate beads, depicted in a schematic.

3.3.2 Beads praparation (Preparation of calcium alginate beads)

As the calcium chloride was being stirred at 0, 50 and 100 rpm, 10 mL of a 1 and 2 wt% aqueous solution of sodium alginate was added dropwise from a glass syringe with a size of 18 and 26G needle while stirring the formed beads with calcium chloride solution..

After the beads have been formed, the calcium alginate beads were filtered, rinsed with distilled water, and air dried for a full day.

3.4 Characterization of calcium alginate clays beads

This data analysis made use of the best raw material and conditions for calcium alginate clays beads to remove methylene blue solution from prior trials.

3.4.1 Analysis using Uv-visible (UV-vis) spechtrophometer

The absorbance was first measured at a wavelength of 665 nm using a UV-visible spectrophotometer after 5, 10, 20, and 40 minutes to determine the percentage of eliminated methylene blue that was Equation 3.1 was used to determine the percentage of methylene blue that was eliminated using equation

$$\frac{\text{Initial absorbance reading} - \text{Final absorbance reading}}{\text{Initial absorbance reading}} \times 100\ \% \qquad \textbf{Equation 3.1}$$

3.4.2 Analysis Using X-ray Diffraction (XRD)

Next, the composition and crystalline of structural and layer spacing changes that occurred in the clays that is ball clay, ball clay 45 µm, ball clay 250 µm, kaolin 45 µm and kaolin 250 µm were studied using the X-ray diffraction technique. The typical characteristic peak of was detected at a 2θ. Equation 3.2 was used to determine the crystallinity of each xrd sample

$$\frac{\text{Area of crystalline peaks}}{\text{Area of all peaks (crystalline+Amourphous)}} \times 100 \qquad \textbf{Equation 3.2}$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Adsorption studies

Various operational variables of the CACB beads have been studied in this research on methylene blue removal. The effectiveness of each parameter on MB dye removal for each parameter and the control is as shown in Table 4.1.

Table 4.1: The efficiency of every parameter on MB dye removal

Sample Abbv.	Parameter	Absorption
Kaolin		
Control/pH7/100rpm/10mLCA	Control	35.21%
45µm/0.5g/100rpm/10mLCAKB/18G/2wt%	Kaolin clay size	99.94%
63µm/0.5g/100rpm/10mLCAKB/18G/2wt%		98.90%
125µm/0.5g/100rpm/10mLCAKB/18G/2wt%		98.80%
250µm/0.5g/100rpm/10mLCAKB/18G/2wt%		98.04%
125µm/0.5g/100rpm/10mLCAKB/18G/2wt%	Kaolin clay	98.80%
125µm/1g/100rpm/10mLCAKB/18G/2wt%	dose	99.42%
125µm/0.5g/0rpm/10mLCABCB/18G/2wt%	Agitation speed	88.84%
125µm/0.5g/50rpm/10mLCAKB/18G/2wt%		98.73%
125µm/0.5g/100rpm/10mLCAKB/18G/2wt%		98.80%
125µm/0.5g/pH4/100rpm/10mLCAKB/18G/2wt%	pH	96.83%
125µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%		98.80%
125µm/0.5g/pH9/100rpm/10mLCAKB/18G/2wt%		98.04%
125µm/0.5g/100rpm/10mLCAKB/18G/2wt%	Needle size	98.80%
125µm/0.5g/100rpm/10mLCAKB/26G/2wt%		98.68%
Ball Clay		
45µm/0.5g/100rpm/10mLCABCB/18G/2wt%	Ball clay size	98.27%
63µm/0.5g/100rpm/10mLCABCB/18G/2wt%		98.10%
125µm/0.5g/100rpm/10mLCABCB/18G/2wt%		98.39%
250µm/0.5g/100rpm/10mLCABCB/18G/2wt%		98.96%
125µm/0.5g/100rpm/10mLCABCB/18G/2wt%	Needle size	98.39%
250µm/0.5g/100rpm/10mLCABCB/18G/2wt%		98.96%

125µm/0.5g/100rpm/10mLCABCB/26G/2wt%		97.87%
250µm/0.5g/100rpm/10mLCABCB/26G/2wt%		98.91%
Bentonite		
125µm/0.5g/100 rpm/10mLCABB/18G/2wt%	Bentonite clay	99.94%
250µm/0.5g/100rpm/10mLCABB/18G/2wt%	size	99.48%

4.1.1 Calibration curve of methylene blue

A series of methylene blue concentration was prepared in range of 2-10 mg/L by diluting the methylene blue stock dilution with distilled water. Next, the absorbance reading of the methylene blue concentrations were measured using UV-vis spectrophotometer at 665 nm wavelength and can be seen in Figure 4.1.

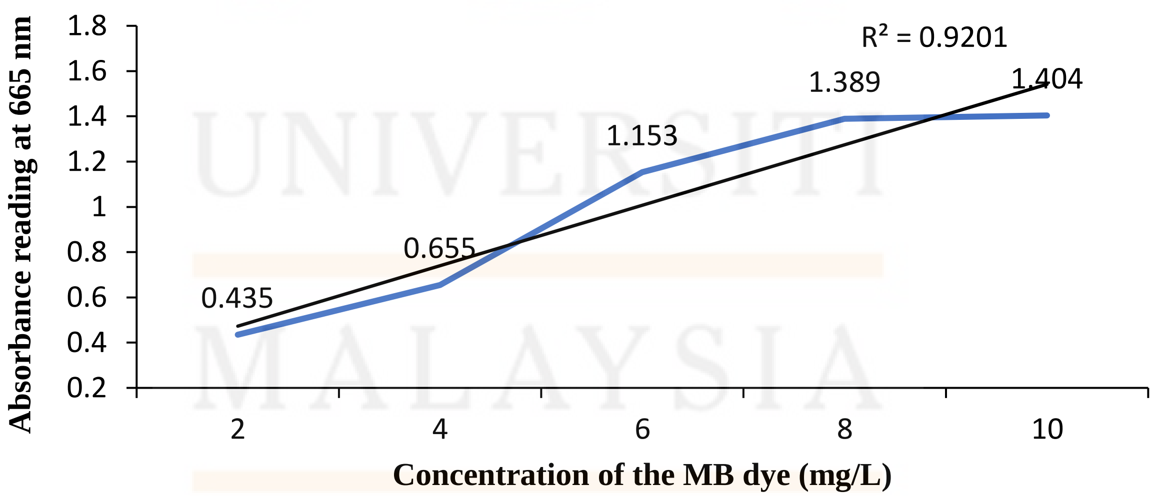


Figure 4.1: The methylene blue dye calibration curve was measured at 665 nm

The graph in Figure 4.1 showed a value of 0.9201 which is the coefficient of determination , R-squared (R^2). The coefficient indicates the best value because the value is close to the number 1. The observation of colour changes in methylene blue solution at different concentration showed in Figure 4.2. Cuvette arrangements from left to right are methylene blue at concentration of 10,8, 6, 4 and 2 mg/L.

Figure 4.2: Cuvette arrangements from left to right are methylene blue at concentration of 10,8, 6, 4 and 2 mg/L.

4.2 Effect of clay size and type

This parameter is used to assess the impact of the size in MB removal. Figure 4.3 illustrates the percentage of MB removal achieved by employing CAKB and CABCB beads of different sizes, specifically 45, 63, 125, and 250 µm.

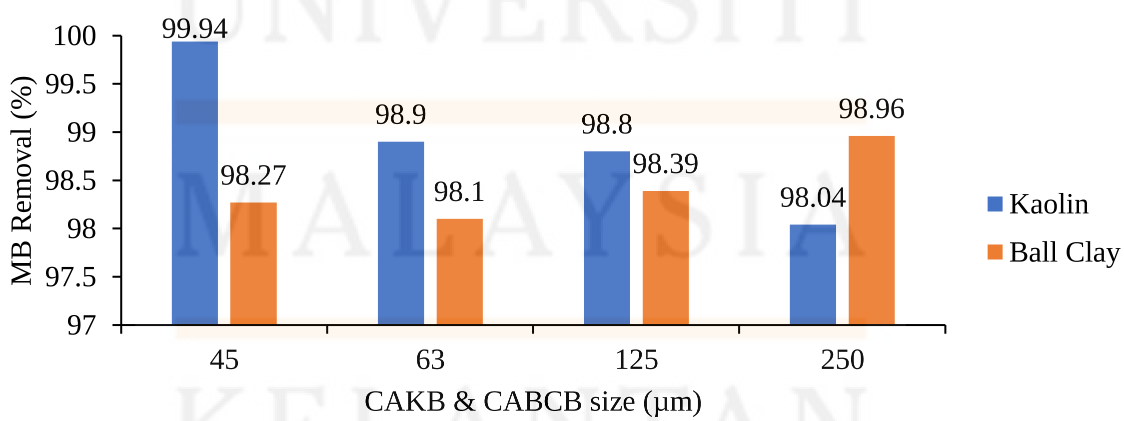


Figure 4.3: The effect of CAKB & CABC of MB removal according to the size of the clays

According to the graph in Figure 4.3, size parameters of materials such as kaolin according to the desired trend respectively from sizes 45, 63, 125 and 250 µm. In this trend, size 250 µm recorded the lowest MB removal percentage of 98.04% followed by MB removal percentage for size 125 µm of 98.8%, and size 63 µm had a percentage of 98.9% while size 45 µm was the highest at 99.94%. This is because the smaller size has the highest absorption than the smaller size. When compared to a low adsorbent dosage, a high adsorbent dosage had a larger surface area and might provide more chances to adsorb dye molecules, hence improving dye removal from solution. (Rida K, Bouraoui S, Hadnine S.,2013).

However, ball clay do not follow the opposite trend where larger sizes show more absorption than smaller sizes starting from sizes 250, 125, 63 and 45 µm. This is because the mineral content found in ball clay is different from the mineral content found in kaolin clay. This can be proven through the XRD test that has been carried out and discussed on the Figure 4.14. The figure showed a significant methylene blue color change from blue to clear over size of kaolin clay. This can be seen when CAKB beads of size 45 µm show a more effective color change from minutes 0, 5, 10, 20 and 40 minutes followed by sizes 63, 125 and 250 µm.

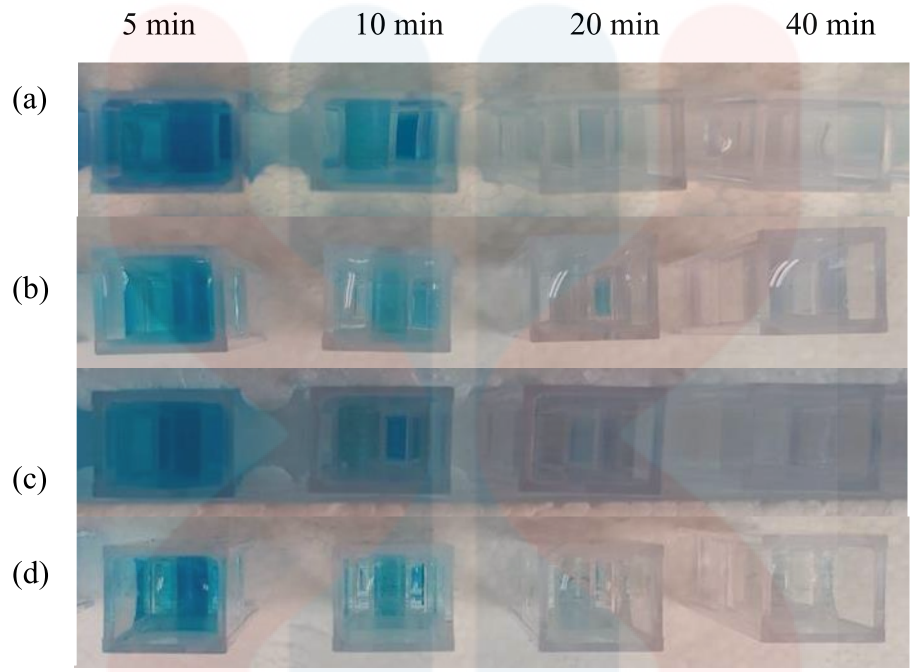


Figure 4.4: The observation of colour intensity changes in methylene blue solution over increasing of size: (a) 45µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%, (b) 63µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%, (c) 125µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%, (d) 250µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%

4.3 Effect agitation speed

This parameter is used to assess the impact of the agitation speed in MB removal. Figure 4.5 illustrates the percentage of MB removal achieved by employing CAKB beads of 3 different agitation speeds starting with 0rpm, 50rpm and 100rpm.

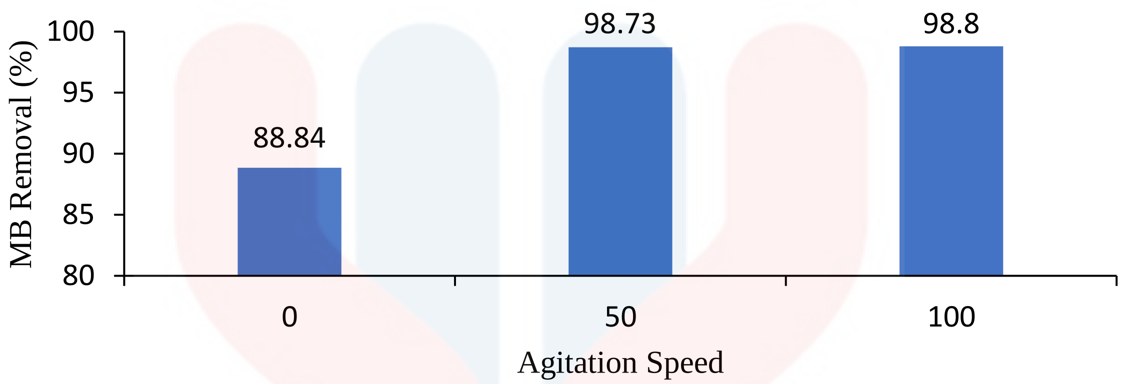


Figure 4.5: The effect of CAKB of MB removal according to the agitation speed of the clays

Figure 4.5 showed that the rate of adsorption increases with agitation speed. Increased turbulence leads to thinner boundary layers around adsorbent particles. The figure showed that the adsorbent's maximum adsorption capacity occurs at 100 rpm. According to the MB removal percentage graph for agitation speed 0 rpm recorded the lowest percentage of 88.84% followed by agitation speed 50 rpm of 98.73% and the highest removal percentage which is 100 rpm which is 98.8%. When increasing the agitation speed, the diffusion rate of dye molecules from the bulk liquid to the liquid boundary layer surrounding particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. (Hamdaoui, O., & Chiha, M. ,2007). The figure hows a significant methylene blue color change from blue to clear over size of kaolin. This can be seen when CAKB beads of size 125 µm change from 0rpm to 50rpm and 100rpm show a more effective color change from minutes 0, 5, 10, 20 and 40 minutes followed.

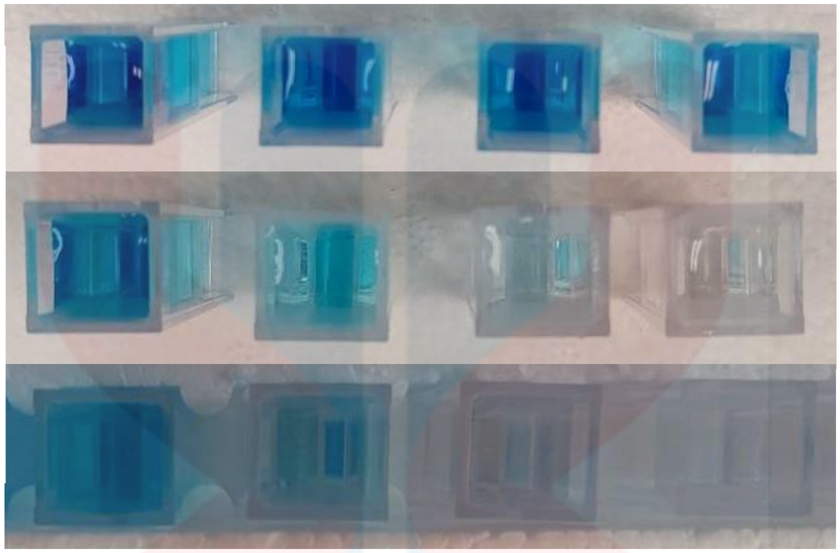


Figure 4.6: The observation of colour intensity changes in methylene blue solution over increasing of agitating speed: (a) 125µm/0.5g/pH7/0rpm/10mLCAKB/18G/2wt%, (b) 125µm/0.5g/pH7/50rpm/10mLCAKB/18G/2wt%, (c) 125µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%

4.4 Effect of clay dosage

This parameter is used to assess the impact of the clays dosage in MB removal. Figure 4.7 illustrates the percentage of MB removal achieved by employing CAKB beads of 2 different dosage.

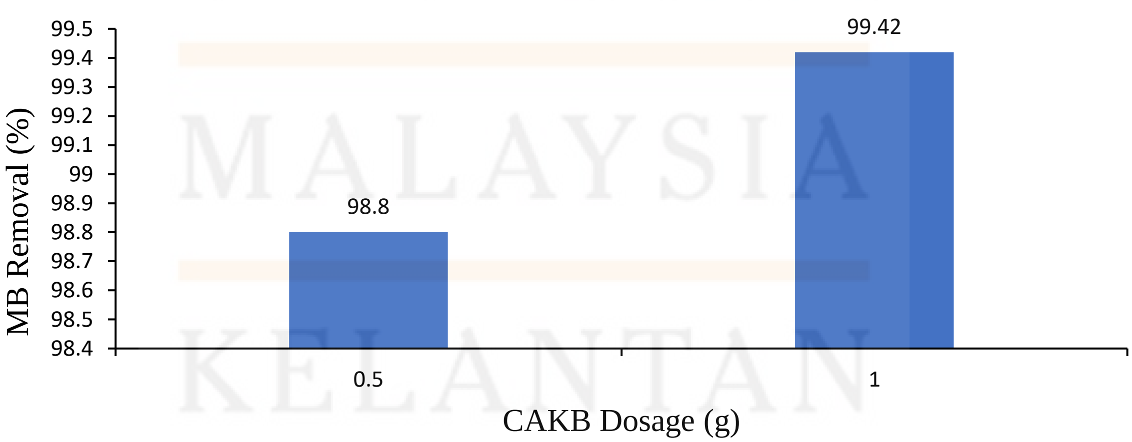


Figure 4.7: The effect of CAKB of MB removal according to the dosage of the clays

The Figure 4.7 showed the percentage of MB removal when using CAKB prepared with the dosage of 0.5g and 1g. According to the MB removal percentage graph for dosage 0.5g recorded a low removal percentage compared to the 1 g dose that is as much as 98.68% compared to the 1g dose which recorded a high percentage of removal which is as much as 99.42%. This is due to increase in adsorbent dosage attributed to increase in surface area and availability of more adsorption sites. On the other hand, the adsorption sites remained unsaturated. Similar observations were reported elsewhere (Malik et al., 2007; Yener et al., 2008). The Figure 4.8 showed a significant methylene blue color change from blue to clear over dose of kaolin. This can be seen that the 1g dose shows a significant color change compared to 0.5g dose show a more effective color change from minutes 0, 5, 10, 20 and 40 followed.

5 min 10 min 20 min 40 min

(a)

(b)

Figure 4.8: The observation of colour intensity changes in methylene blue solution over dosage: (a) 125µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%, (b) 125µm/1g/pH7/100rpm/10mLCAKB/18G/2wt%

4.5 Effect of pH of methylene blue adsorption

This parameter is used to assess the impact of the clays dosage in MB removal. Figure 4.9 illustrates the percentage of MB removal achieved by employing CAKB beads of 3 different pH of methylene blue solution.

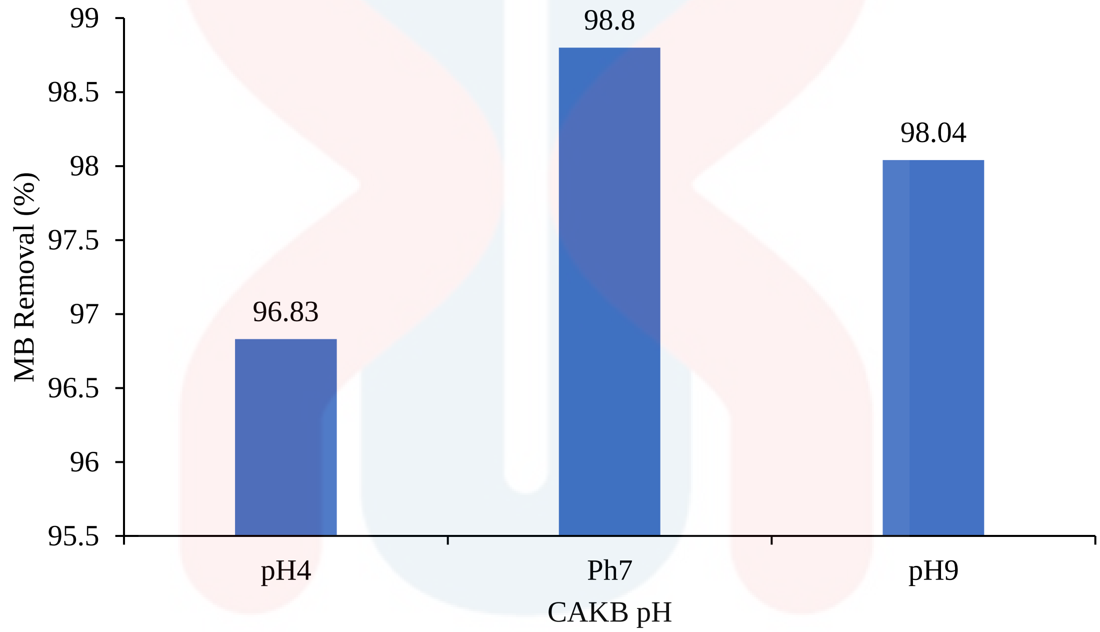


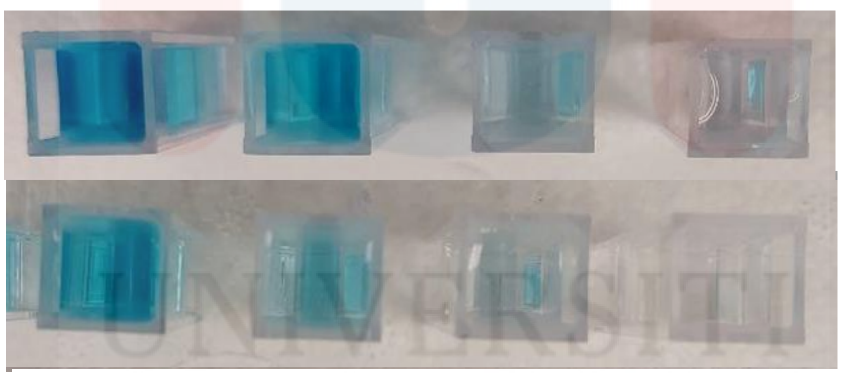
Figure 4.9: The effect of CAKB of MB removal according to the pH of methylene blue solution

The effect of solution pH on adsorption was investigated by varying pH values under a specific initial MB concentration of 10 mg/L. Basically, adsorbent surface charges vary with the solution pH, which affects the rate of adsorption (Sen et al., 2010). As can be seen, the adsorption increased rapidly with increasing pH 7 to 9. The figures showed that the percentage of methylene blue removal was increased gradually from 96.83% to 98.8% using kaolin and drop afterward. According to the journal namely removal of methylene blue dye using kaolin, it showed that pH 3 to 7 were 90% of MB removal and drop afterward at 85%

at pH 9. The highest percentage of MB removal of pH MB solution was at pH 7 that is 98.8% compared to the value of pH 9 which is 98.04%. It is because the functional groups of the calcium alginate beads and the cationic dye molecule are still attracted to each other by electrostatic forces. The basic dye gives positively charged ions when dissolved in water. Thus, in acidic medium the positively charged surface of sorbent tends to oppose the adsorption of the cationic adsorbate. When pH of dye solution is increased the surface acquires a negative charge, there by resulting in an increased adsorption of MB due to an increase in the electrostatic attraction between positively charged dye and negatively charged adsorbent (Abd et al., 2009; Malik, 2003).

5 min 10 min 20 min 40 min

(a)



(b)

Figure 4.10: The observation of colour intensity changes in methylene blue solution pH: (a) 125µm/0.5g/pH4/100rpm/10mLCAKB/18G/2wt%, (b) 125µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%, (c) 125µm/0.5g/pH9/100rpm/10mLCAKB/18G/2wt%

4.6 Effect of needle size

This parameter is used to assess the impact of the clays needle size in MB removal. Figure 4.11 illustrates the percentage of MB removal achieved by employing CAKB beads of 2 different needle size.

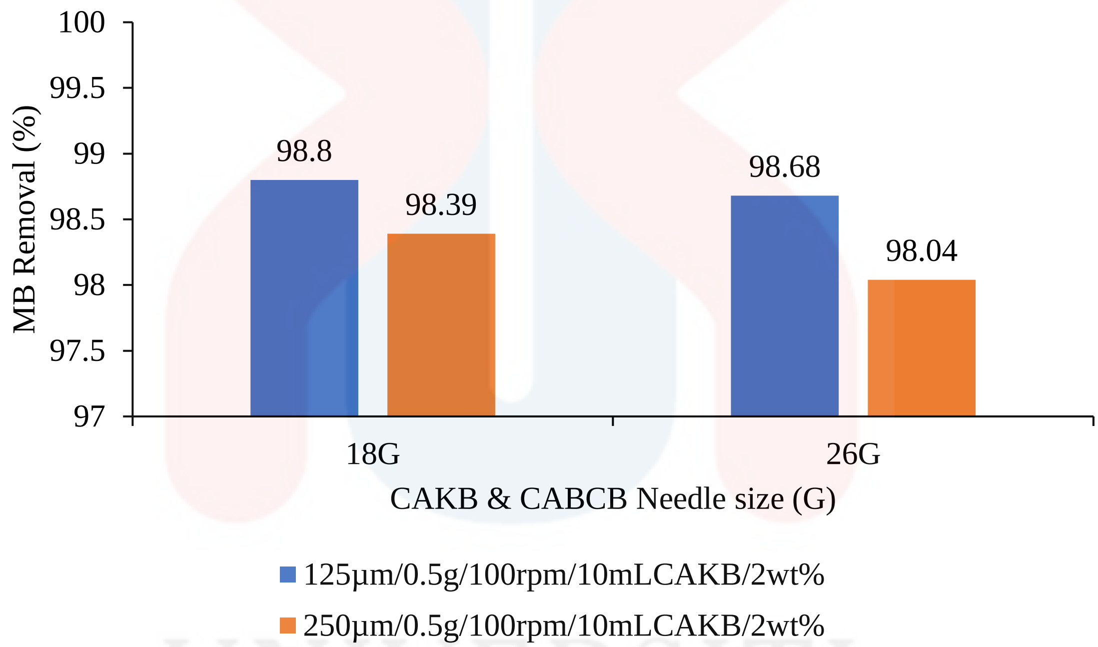
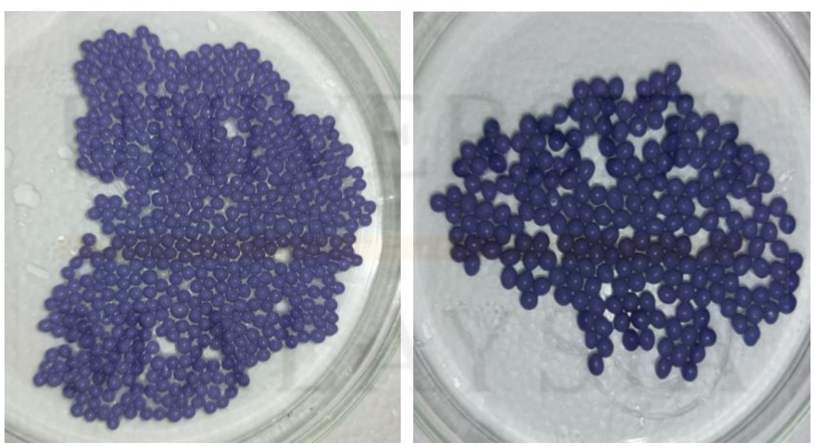


Figure 4.11: The effect of CAKB and CABCB of MB removal according to the needle size of the clays

The effect of methylene blue removal onto CAKB was studied at two different needle size that is 18 G and 26G. Needle size is one of the most crucial parameters that influencing the adsorption performance. The result in figure showed that the adsorbed methylene blue dye particles onto the CAKB increased with the increase of needle size. As can be seen, the adsorption increased respectively 98.68% of needle size 26G to 98.8% of needle size 18G.

This is because needle size 18G can form larger beads compared to the 26G size and subsequently cause more MB absorption compared to the smaller size beads.

Figure 4.12: The observation of colour intensity changes in methylene blue solution 0f needle size: (a) 125µm/0.5g/pH7/100rpm/10mLCAKB/18G/2wt%, (b) 125µm/0.5g/pH7/10rpm/10mLCAKB/26G/2wt%,



(a) (b)

Figure 4.13: (a) The successfully prepared CAKB beads using 26G, (b) The successfully prepared CAKB beads using 18G.

4.7 Characterization with X-Ray Diffraction (XRD)

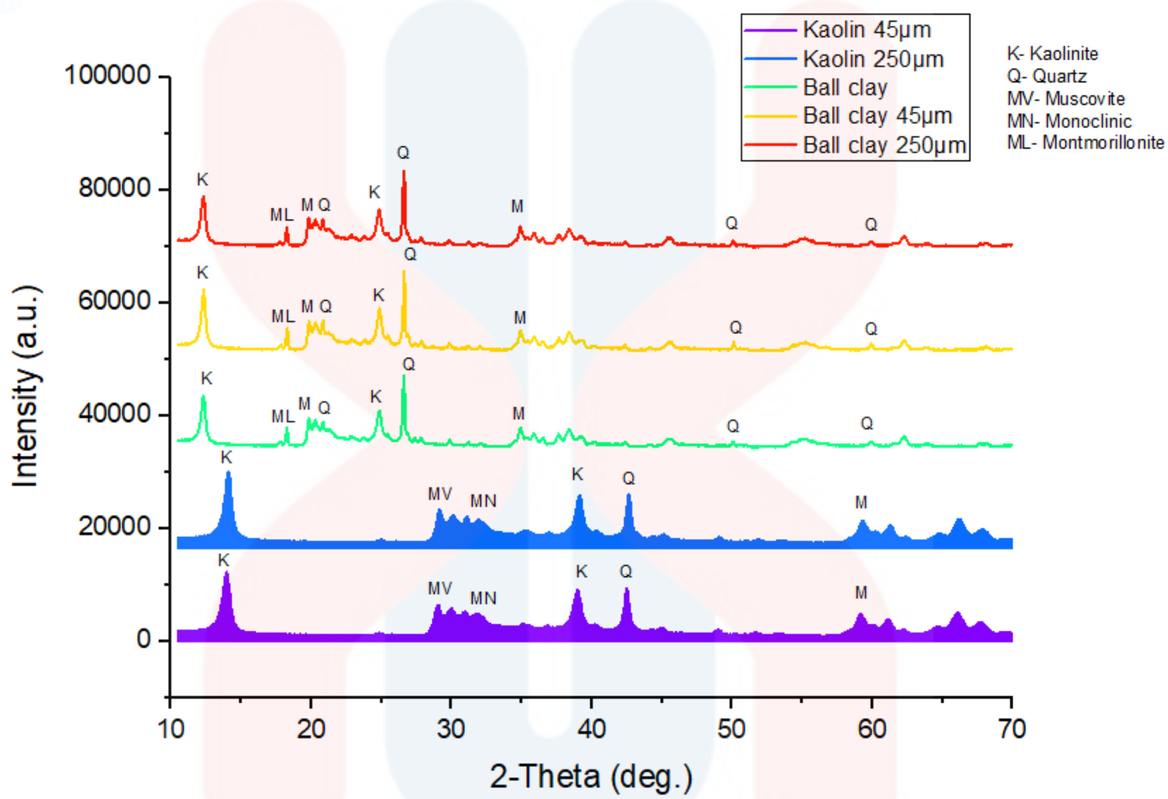


Figure 4.14: XRD pattern on 5 clays

XRD analysis results shows the results of kaolin clay and ball clay according to different size were given in Figure 4.3. The typical characteristic peak of was detected at a 2θ. From the XRD pattern, each clays samples mostly contain kaolinite, quartz, and muscovite which confirmed the presence of the smectite phase (Gates 2006; Holmboe et al. 2012). The sample tested consisted of kaolin clay consisting of sizes 45 µm and 250 µm while ball clay consisted of samples that had not been sieved (as a control), sizes 45 µm and 250 µm. Figure 4.3 shows, the highest crystalinity is kaolin 45 µm which is 80.9%. The peaks of kaolinite was the highest at 63%, compared to quartz which is 45% and followed by others minerals for kaolin 45 µm. Next, kaolin 250 µm noted crystalinity at 80.6%. Kaolin 250 µm also contains 87% of kaolinite which is the highest peak followed by 65% of quartz.

This is proven through the xrd results that have been carried out. Also, from to Figure 4.3, it shows, ball clay 250 µm contain 99% of quartz followed by kaolinite 64%, and the crystallinity is 79.8%. For, ball clay 45µm noted crystallinity at 80.6%, while the composition contain 99% of quartz and 68% of kaolinite. Ball clay that is not sieved noted the crystallinity at 80.1 % and the highest peak was quartz at 94% and kaolinite at 66%. Through the xrd results that have already been carried out, it is proven that ball clay that has a lot of quartz content affects mb adsorption with " According to a report by S.S. Owoeye, et al, (2018), ball clay contained higher quartz percentage compared to kaolin, which may help to increased the MB adsorption despite of the size or surface area". This explain earlier results in subsection 4.2 where larger ball clay sizes to have higher MB adsorption compared to smaller sizes.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research looks at how to make clay beads and sees if they can be used to treat wastewater in this experiment. This study shows that clays work especially well for treating wastewater in this way. You can also find a lot of clay minerals in soils, sediments, rocks, and water as colloidal fractions. In this study, calcium alginate is very important because it helps to absorb methylene blue. This is because clays have a lot of tiny holes in them. Calcium alginate turns into a gel when it comes in contact with divalent cations, mostly calcium ions. This gel is made when calcium ions link together alginate chains, creating a three-dimensional gel structure. Also, calcium alginate is very good at absorbing water, which is another thing it does well. In this study, the best conditions for removing methylene blue from wastewater were 45 µm size, 0.5g/dose, pH7, 100rpm agitation speed, 10mLCAKB, 18G needle size, and 2wt% alginate concentrations. The dye removal rate was 99.94%.

5.2 Recommendations

The suggestions in order to improve this research can be done with adding one more parameter which is the alginate concentration. In this study, all the beads were prepared with 2wt% alginate concentration except for bentonite clay. Next, the agitation time can be added a little more rather than only two hours of the turbulence time to find out if 100% efficiency in dye removal could be achieved. In addition, each parameter can be increased in terms of numbers, for example increasing the number of dosages to 3 that is 0.5g, 1g and 1.5g. This will be able to help to get the best MB adsorption rate comparison. Besides, for futher study xrf can be used to know in more detail about the size of 25 µm of ball clay recording a higher percentage of adsorption than the smaller size. Not only that, using SEM it can observe the surface morphologies of the sample.

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APPENDIX A

TRANSMITTANCE GRAF

A.1 Transmittance graf from UV-Vis

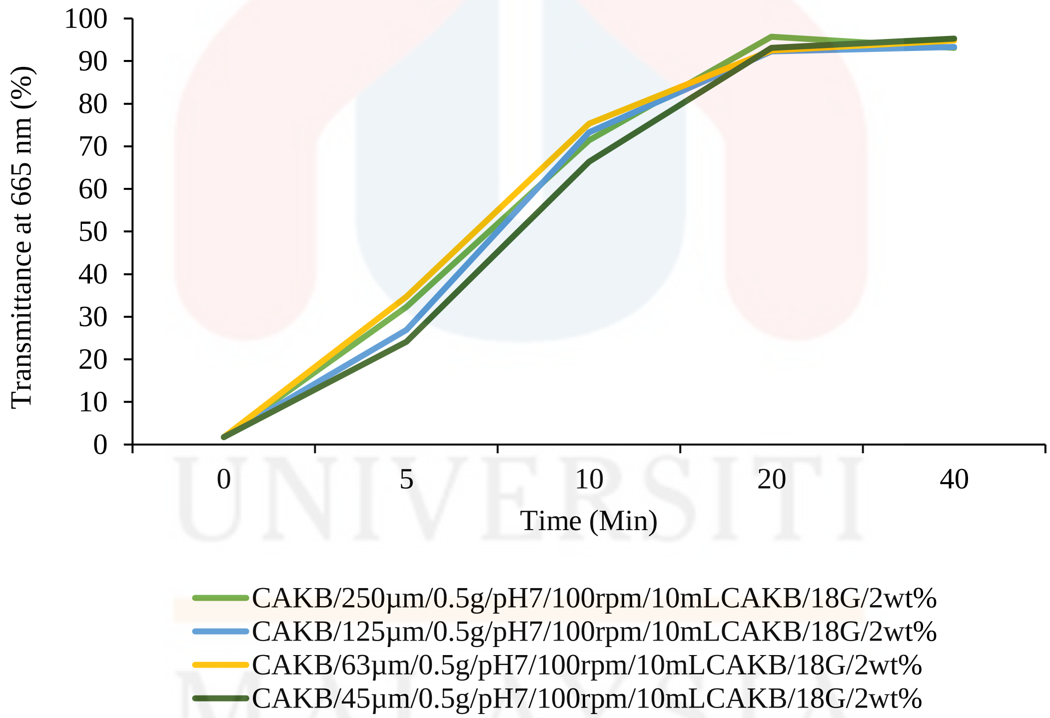

Figure A.11: The effect of CAKB of transmittance according to the size of the clay

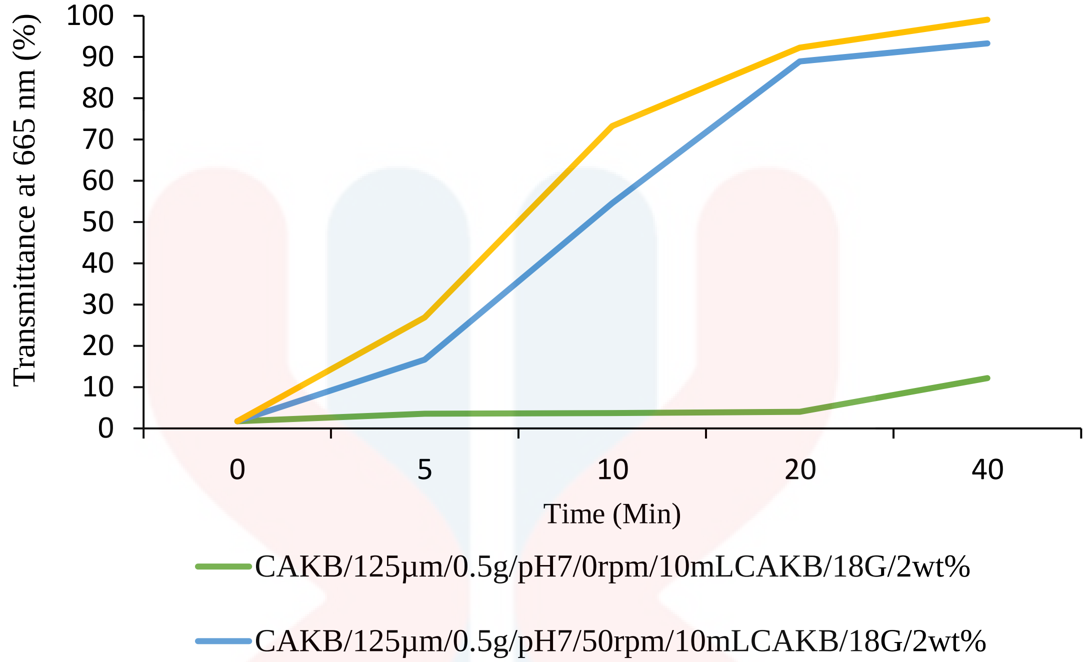

Figure A.12: The effect of CAKB of transmittance according to the agitation speed of the clay

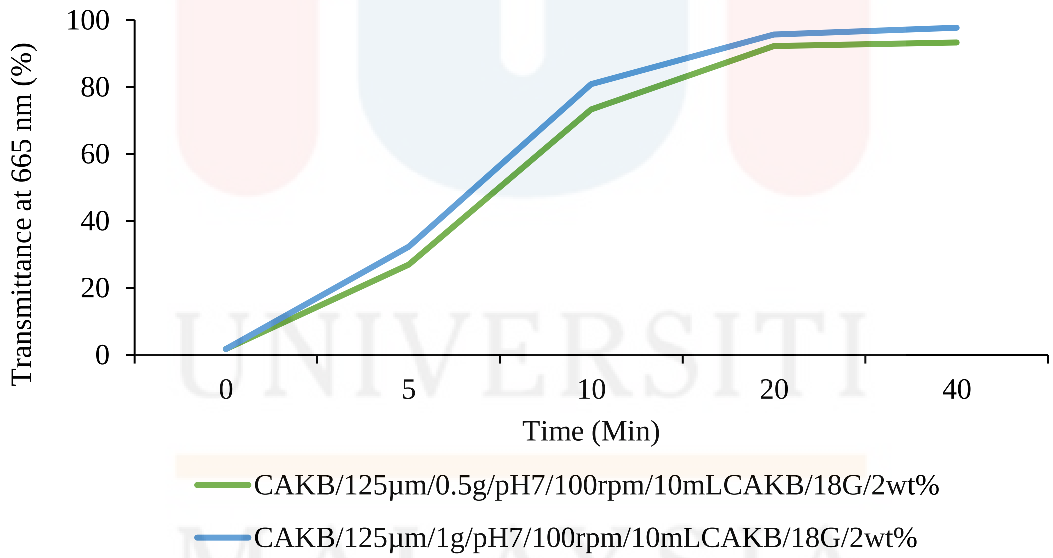

Figure A.13: The effect of CAKB of transmittance according to the dosage of the clay

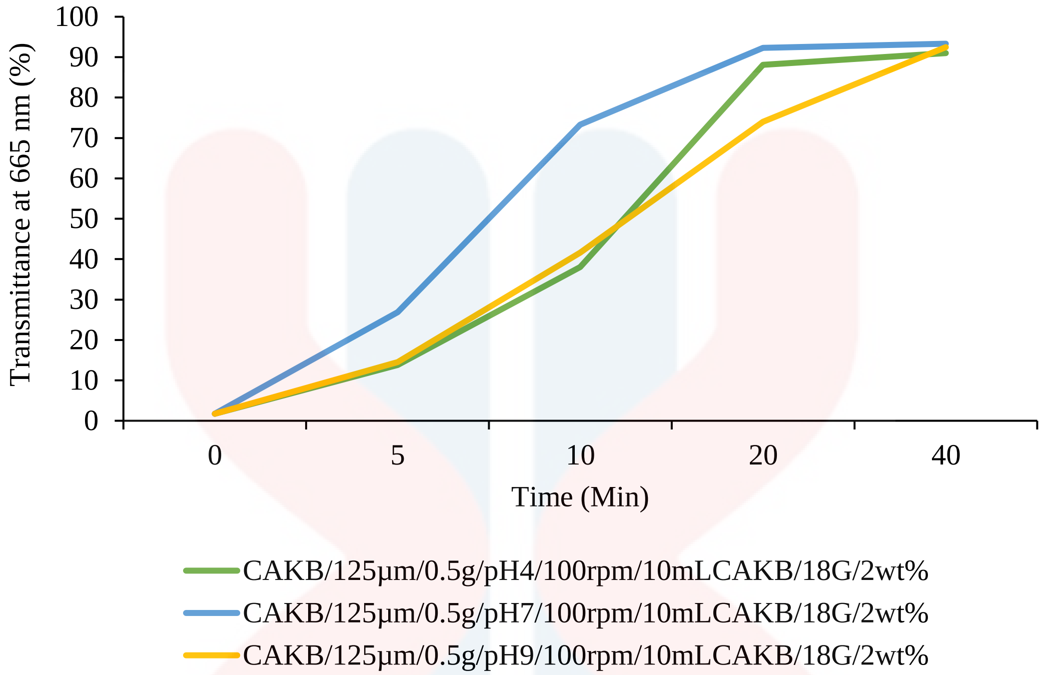

Figure A.4: The effect of CAKB of transmittance according to the pH of methylene blue solution

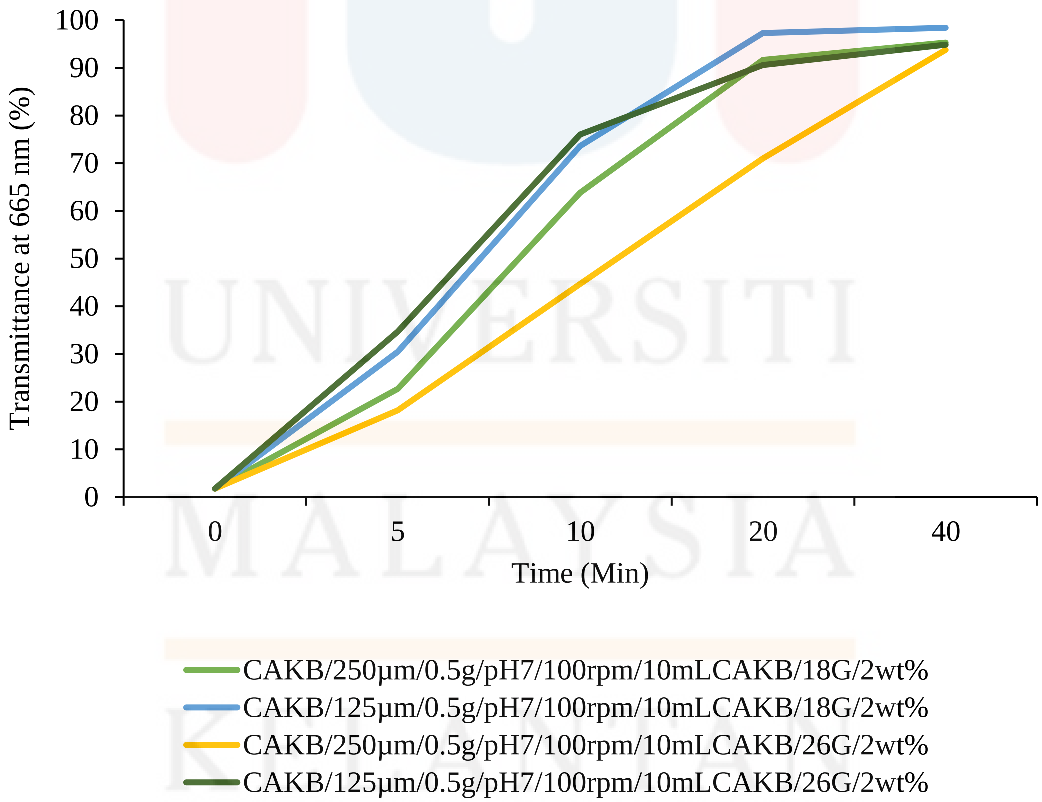

Figure A.15: The effect of CAKB of transmittance according to the needle size of the clay

APPENDIX B

BEADS PREPARATION

B.1 Beads preparation

Figure B.11: The prepared calcium alginate beads: (a) Blank calcium alginate beads, (b) calcium alginate beads after treated with methylene blue solution, (c) The successfully prepared CAKB, CABC and CABB beads.

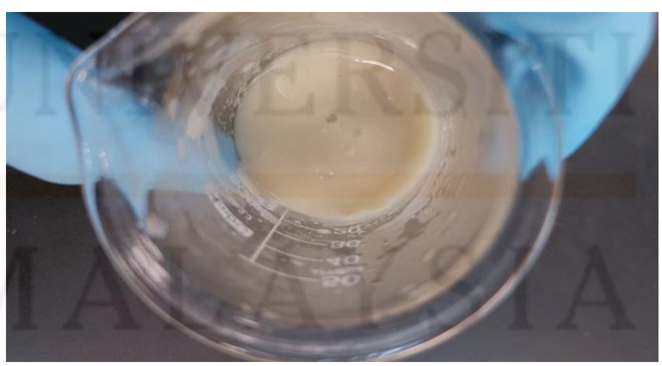

Figure B.12: Calcium alginate mix with kaolin clay