

ADSORPTION STUDY – DYE REMOVAL USING CLAY

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ABSTRACT

The adsorption of textile dyes by clay was investigated using basic dye (Methylene Blue). Adsorption of dye effluent onto clay samples was carried by batch studies at room temperature, 25°C. The effects of adding clay with zeolite, pH and shaking time towards adsorption performance were investigated. The results from the mixture of 1.0 g clay and 0.01 g zeolite, the increases of pH, pH 9 and the optimum shaking time, 60 min have achieved the maximum dye removal. The adsorption data sucessfully were described by the Langmuir and Freundlich isotherms.

CHAPTER I

INTRODUCTION

Malaysia is a developing country that has many potential in industrial sector. One of the industries that grow finely is the textile industry. When talking about textile, the famous textile industry in Malaysia is batik industry.

Textile industry effluents exhibit large amounts of dye chemicals which create severe water pollution. Therefore, it is important to reduce the dye concentration in the wastewater before discharging it into the environment. Discharging large amounts of dyes into water resources, accompanied by organics, bleaches, and salts, can affect the physical and chemical properties of fresh water (Erdem et al., 2004).

Dyes in wastewater can obstruct light penetration and it is highly visible and unacceptable, which is not good to water life. Dyes are also stable to light irradiation and heat and toxic to microorganisms. The removal of dyes is stringent due to their complex structure and synthetic origins (Hu et al., 2004).

One of the powerful treatment processes for the removal of dyes from water at low cost is adsorption. Adsorption techniques have proven successful on lowering dye concentration from industrial effluents by using adsorbents such as activated carbon, peat, chitin, clay, and others (Tahir, 2005). Adsorption is a process by which atoms, molecules or ions are retained on the surfaces of solids by chemical or physical bonding.

Activated carbon has been the most widely used adsorbent because of its high capacity for the adsorption of organic species and dye. However, due to the difficulty and expense involved in regeneration, clays are considered as alternative low cost absorbent. Since some clay derivatives can be easily prepared and regenerated they are proposed as an inexpensive removal technique (Orthman et al., 2006).

Clay is a soil particle smaller than 0.002 mm or 2 μm , with high specific area which mainly influenced the soil colloidal properties as well as stability of soil structure. Besides, it has high stability in both wet and dry conditions and in soil texture class. While colloid is a particle, which may be a molecular aggregate, with a diameter of 0.1 to 0.001 μm , clay and soil organic matter are often called as soil colloids because they have particle sizes that are within, or approach colloidal dimensions.

Clay minerals which are clay-sized hydrous aluminium silicates have a large interlayer space that can hold significant amounts of water and other substances. They encompassed of large surface area that allow swelling and shrinking. The common examples of clay are montmorillonite or smectite and kaolinite.

In order to minimize the processing costs for textile industry effluents, one of the best ways is to manufactures the local sources. In many years, Malaysian industrial which produces dye effluents, especially in batik industry spend thousands of Ringgit Malaysia for adsorbents to make sure that the concentration of dye in effluents, are following the Department of Environment (DOE) standard index.

Most of the adsorbents that have in the market now, came from the other place all around the world such as diatomite (Middle East), and sepiolite (Turkey). This research is an approach of utilizing the low-cost adsorbent for treatment process of dye effluents.

1.2 PROBLEM STATEMENT

Looking for a local adsorbent that easy and has low expense of regeneration. Also give better performance in removal of dyes in batik industry.

1.3 OBJECTIVES

The research was conducted to investigate the removal of dye effluent through adsorption process using local clays. The objective of the study are :

1. To study the effect of adding zeolite with clay, on adsorption process.
2. To study the influence of pH toward dye removal performance.
3. To determine the optimum shaking time of the adsorption study.

CHAPTER II

LITERATURE REVIEW

2.1 Adsorption

One of the powerful treatment processes for the removal of dyes from water is adsorption. Adsorption techniques have been proven successful in removing coloured organics (Erdem et al., 2004).

Adsorption is the separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. It is the process that takes place when a liquid or most commonly a gas known as the adsorbate accumulates on the surface of a solid adsorbent and forming a molecular film.

Adsorption, similar to surface tension, is a consequence of surface energy. In the bulk material, all the bonding requirements either ionic, covalent or metallic of the constituent atoms of the material are filled. However, atoms on the surface experience a bond deficiency, because they are not wholly surrounded by other atoms. It is then energetically favourable for these dangling bonds to react with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, which the process is generally classed as experimentally physisorption or chemisorption.

2.1.2 Physisorption and Chemisorption

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through weak intermolecular interactions. Physisorption is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent (Wang and etc, 2005). It is characterized by:

- a) Low temperature, always under the critical temperature of the adsorbate
- b) Type of interaction: Intermolecular forces (van der Waals forces)
- c) Low enthalpy: $\Delta H < 20 \text{ KJ/mol}$
- d) Adsorption takes place in multilayer
- e) Low activation energy

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to physisorption. It is characterized by:

- a) High temperatures.
- b) Type of interaction: strong; covalent bond between adsorbate and surface.
- c) High enthalpy: $\Delta H \sim 400 \text{ KJ/mol}$
- d) Adsorption takes place only in a monolayer.
- e) High activation energy

Table 2.1: Comparison between physical and chemical adsorption.

PHYSISORPTION	CHEMISORPTION
Molecular condensation in the capillaries.	Monomolecular layer of the adsorbate on the surface.
Without chemical bonding.	With chemical bonding.
Reversible can be desorption.	Non – reversible.
Nonselective surface attachment.	Selective surface attachment.

2.1.3 Adsorbent

The adsorbent is the separating agent used to express the difference between molecules in a mixture: adsorption equilibrium or kinetics. An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substances onto its surface by intermolecular forces. Several adsorbents are eligible for such a purpose.

Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as activated carbon, peat, chitin, and others (Tahir and Rauf, 2005). Activated carbon is the most popular adsorbent and has been used with great success (Erdem et al., 2004) and its have high capacity for the adsorption of organic species.

However, activated carbon suffers from high cost production and regeneration. Therefore, other adsorbents such as pillared-clays with higher surface areas are alternatives (Wang et al., 2006). Recent investigations have focused on the use of clays to remove dyes. For examples, Alkan et al. have studied the sorption of acid red 57 from aqueous solution onto sepiolite. The use of diatomite earth to remove textile dyes studied by Erdem et al. Orthman, Zhu and Lu have investigated the use of anion clay hydrotalcite to remove coloured organics from aqueous solutions. Removal of a cationic

dye from aqueous solutions by adsorption onto bentonite clay has been reported by Tahir and Rauf.

2.1.4 Factors affecting adsorption

There have several important factors affecting adsorption such as:

i) Surface area of adsorbent.

Large size simply greater adsorption capacity (Hafiz, 2005).

ii) Contact time / residence time

The longer time the more complete adsorption will be. However, the equipment will be larger (Hafiz, 2005). The adsorption of SB dye onto composite adsorber has been investigated as a function of time in the range of 1-30 min. A higher removal percentage of textile dyes is obtained at the beginning of the adsorption. Percent adsorption decreases sharply with increasing shaking time.

It is interesting to note that percentage adsorption later on decrease with longer periods of shaking (E. Erdem et al, 2005). The uptake of dye on BNa^+ reaches equilibrium in 45 min with 37% of dye removal, while on BP, it reaches equilibrium in 30 min with 60% of dye removal. In the case of BPS, the uptake was very rapid and it attained equilibrium at 15 min with 99% removal. BNa^+ , BP, BPS are the sample of clays (adsorbent) (Z. Bouberka et al, 2005).

iii) Particle size of adsorbent.

Small particle sizes reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly adsorption capability can be attained) (Hafiz, 2005).

The decreasing of particle size of diatomite (adsorbent) from 300 to 60 μm has increased the adsorption rate of SB (adsorbate aka dye). This is because increasing the external surface area of the diatomite particle exposes more active sites to SB molecules. There is a slight effect of particle size of diatomite on adsorption of textile dyes (Erdem et al., 2004).

iv) Solubility of solute (adsorbate) in liquid (wastewater).

Substances slightly soluble in water will be more easily removed from water (i.e., adsorbed) than substances with high solubility. Also non-polar substances will be more easily removed than polar substances since the latter have greater affinity for water (Hafiz, 2005).

v) Degree of ionization of the adsorbate molecule.

More highly ionized molecules are adsorbed to smaller degree than neutral molecules (Hafiz, 2005).

vi) pH

The degree of ionization of a species is affected by pH (e.g., a weak acid or a weak basis). This in turn affects adsorption (Hafiz, 2005). The adsorption of the dye increases from 29% to 91% with an increase in pH of the solution from 2.0 to 9.0 and then remains almost constant with dye concentration, shaking time, and amount of bentonite were fixed at 56.8 mg/cm^3 , 10 min, and 0.05g respectively (Tahir and Rauf, 2005).

The acid red 57 removal by sepiolite decreased with increasing pH and can be explained on the basis of a decrease in H^+ on the surfaces sites and by a decrease in positive surface charge, which result in less repulsion of adsorbing dye (Alkan et al., 2004).

vii) Numbers of carbon atoms.

For substances in the same homologous series a larger of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed (e.g., the degree of adsorption increases in the sequence formic-aceticpropionic-butyric acid) (Hafiz, 2005).

viii) Size of molecule with respect to size of the pores.

Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes (Hafiz, 2005).

Temperature also can affect adsorption process. A study of the temperature dependence of adsorption reactions gives valuable information about the enthalpy and entropy changes during adsorption. Greater adsorption is often found at lower temperatures (M. Alkan et al, 2004). In general, the use of adsorbents for adsorption process depends on cases (M. Hafiz, 2005).

2.1.5 Adsorption Mechanism

Adsorption occurs in three steps. First step, the adsorbate diffuses from the major body of the stream to the external surface of the adsorbent particle. Second step, the adsorbate migrates from the relatively small area of the external surface to the pores within each adsorbent particle. The bulk of adsorption usually occurs in these pores because there is the majority of available surface area. Final step, the contaminant molecule adheres to the surface in the pore. This overall diffusion and adsorption process is illustrated in Figure 2.1

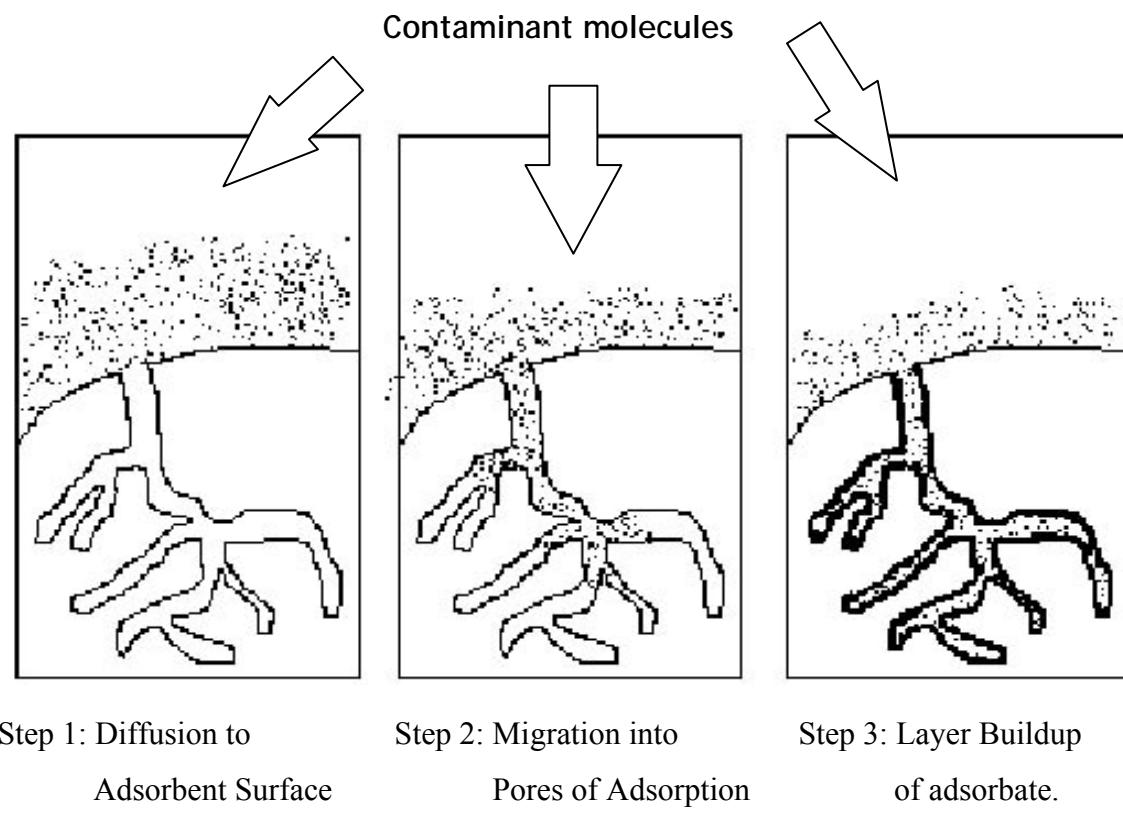


Figure 2.1 Mechanism of Adsorption

2.2 Dye

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is usually used as an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. In contrast, a pigment generally has no affinity for the substrate, and is insoluble.

Organic dyes. Thousands of dyes have since been prepared and, due to the vastly improved properties imparted upon the dyed materials, organic dyes have replaced the traditional natural dyes. Dyes are now classified according to how they are used in the dyeing process.

Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dyebaths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cations groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Figure 2.2 is the sample of acid dyes structure.

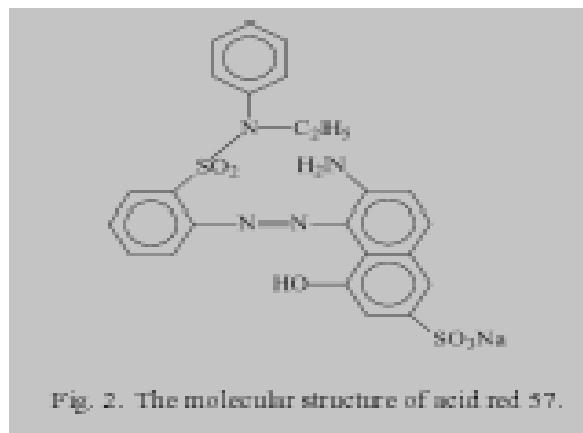


Figure 2.2 Chemical structure of acid dye

Basic dyes are water – soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dyebath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

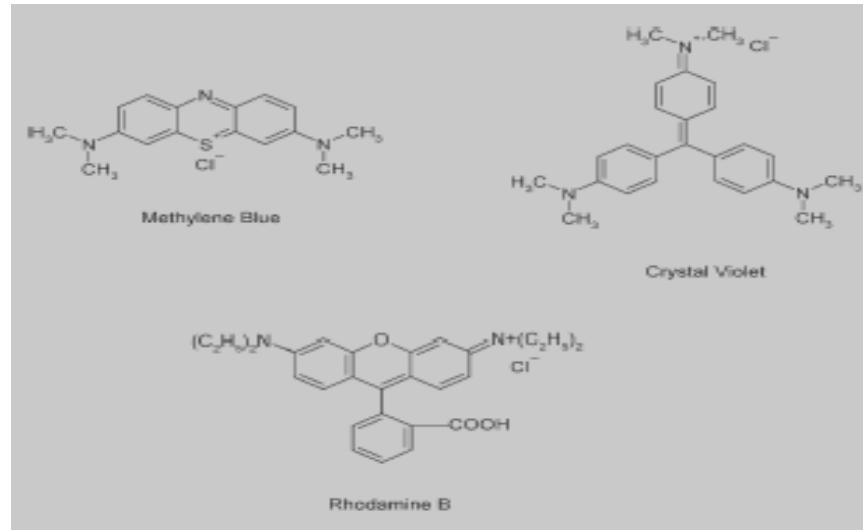


Figure 2.3.1 Chemical structure of basic dyes

Sulfur dyes are the biggest volume dyes manufactured for cotton. They are cheap, generally have good wash-fastness and are easy to apply. The dyes are absorbed by cotton from a bath containing sulfide and are insolubilised within the fibre by oxidation. During this process the dyes form complex larger molecules which are the basis of their good wash-fastness. These dyes produce robust dyeing that has all round fastness except to chlorine. Due to the high polluting nature of the let out dye-baths, slowly the use of sulfur dyes is getting stopped.

2.2.2 Why dye must be separated from wastewater?

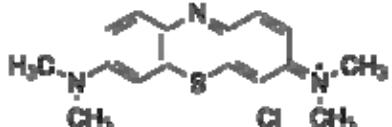
Industrial wastewater contains high concentration of coloured toxic compound. This can bring risk of harm to the health in the population. Dye in wastewater :

- a) Obstruct light penetration
- b) Highly visible and unacceptable
- c) Stable to light irradiation and heat
- d) Become as a toxic to microorganisms
- e) Hard to remove due to their complex structure and synthetic origins

It is important to reduce the dye concentration so it can't bring any harm to the important source of life, water.

2.2.3 Methylene Blue

Methylene blue is a heterocyclic aromatic chemical compound. It has many uses in a range of different fields, such as biology or chemistry and also in textile industries. At room temperature it appears as a solid, odorless, dark green powder, which yields a blue solution when dissolved in water.

Methylene blue	
	
<u>Chemical name</u>	3,7-bis(Dimethylamino)-phenazathionium chloride, Tetramethylthionine chloride

<u>Chemical formula</u>	C ₁₆ H ₁₈ N ₃ ClS
<u>Molecular mass</u>	319.85 g/mol
<u>CAS number</u>	[61-73-4]
<u>EC number</u>	200-515-2
<u>Density</u>	- g/cm ³
<u>Melting point</u>	100 °C
<u>Boiling point</u>	Decomposes
<u>SMILES</u>	CN(C)c3ccc2nc1ccc(N(C)C)cc1[s+]c2c3.[Cl-]

Figure 2.4 MSDS Methylene Blue

Methylene blue is highly stable in the human body, and if ingested, it resists the acidic environment of the stomach as well as the many hydrolytic enzymes present. It is not significantly metabolized by the liver, and is instead quickly filtered out by the kidneys. Therefore, it is necessary to make sure the effluent contained methylene blue was treated first before released it to environment.

2.3 Clay

Clay is a generic term for an aggregate of hydrous silicate particles less than 2 μm (micrometres) in diameter. Clay consists of a variety of phyllosilicate minerals rich in silicon and aluminium oxides and hydroxides which include variable amounts of structural water. There are three main groups of clays: kaolinite-serpentine, illite, and smectite. For this research natural clay was chosen. Commercial monmorillonite clay was used as a comparison.



Figure 2.5 Types of clay

2.3.2 Clay Minerals

Clay minerals are hydrous aluminium phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations. Clays have structures similar to the micas and therefore form flat hexagonal sheets. Clay minerals are common weathering products and low temperature hydrothermal alteration products. Clay minerals are very common in fine grained sedimentary rocks such as shale, mudstone and siltstone and in fine grained metamorphic slate and phyllite. Clay minerals include the following groups:

- Kaolinite group which includes the minerals kaolinite, dickite, halloysite and nacrite.

- Some sources include the serpentine group due to structural similarities (Bailey, 1980).
- Smectite group which includes pyrophyllite, talc, vermiculite, saucomite, saponite, nontronite and montmorillonite.
- Illite group which includes the clay-micas. Illite is the only common mineral.
- Chlorite group includes a wide variety of similar minerals with considerable chemical variation.

2.3.3 Structure

Like all phyllosilicates, clay minerals are characterised by two-dimensional *sheets* of corner sharing SiO_4 and AlO_4 tetrahedra. Each tetrahedron shares 3 of its vertex oxygen atoms with other tetrahedra. The fourth vertex is not shared with another tetrahedron and all of the tetrahedra "point" in the same direction (i.e. all of the unshared vertices are on the same side of the sheet). These tetrahedral sheets have the chemical composition $(\text{AlSi})_3\text{O}_4$.

In clays the tetrahedral sheets are always bonded to octahedral sheets formed from small cations, such as aluminium or magnesium, coordinated by six oxygen atoms. The unshared vertex from the tetrahedral sheet also form part of one side of the octahedral sheet but an additional oxygen atom is located above the gap in the tetrahedral sheet at the center of the six tetrahedra. This oxygen atom is bonded to a hydrogen atom forming an OH group in the clay structure. Clays can be categorised depending on the way that tetrahedral and octahedral sheets are packaged into layers. If there is only one tetrahedral and one octahedral group in each layer the clay is known as 1:1 clay. The alternative, known as a 2:1 clay, has two tetrahedral sheets with the unshared vertex of each sheet pointing towards each other and forming each side of the octahedral sheet.

Depending on the composition of the tetrahedral and octahedral sheets, the layer will have no charge, or will have a net negative charge. If the layers are charged this charge is balanced by interlayer cations such as Na^+ or K^+ . In each case the interlayer can also contain water. The crystal structure is formed from a stack of layers interspersed with the interlayers. The entire structures are shown in Figures 2.6, 2.7 and 2.8.

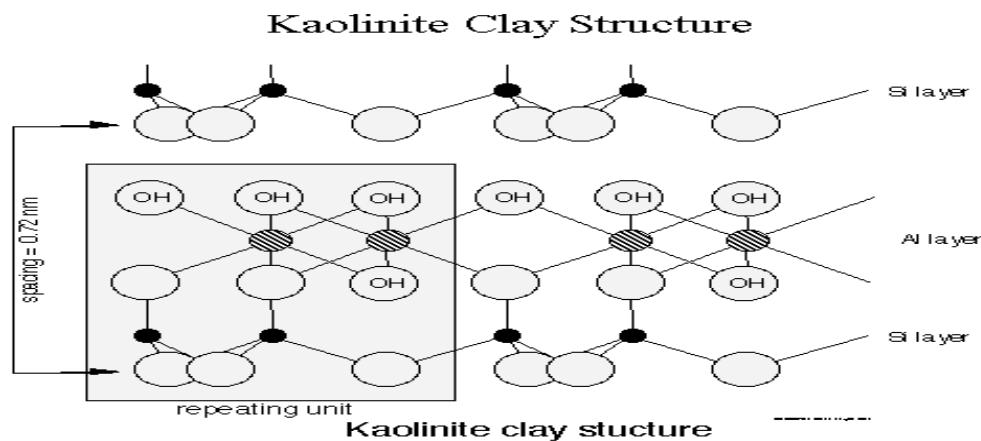


Figure 2.6

Basic building blocks of soil

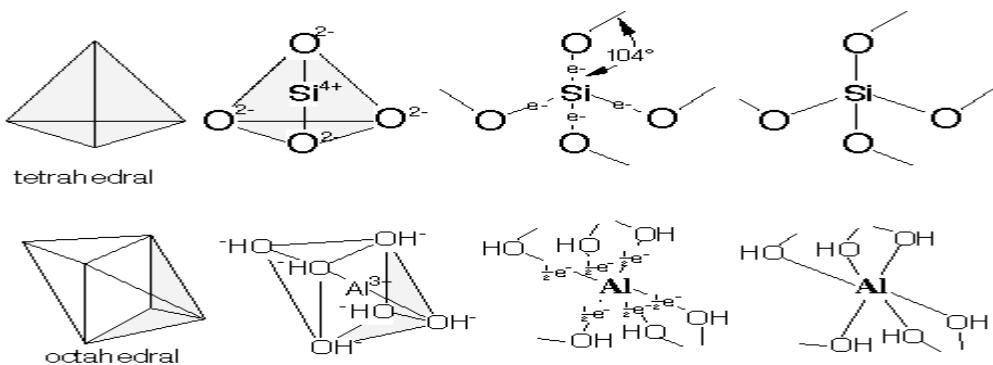


Figure 2.7

Soil Properties- Isomorphous Substitution

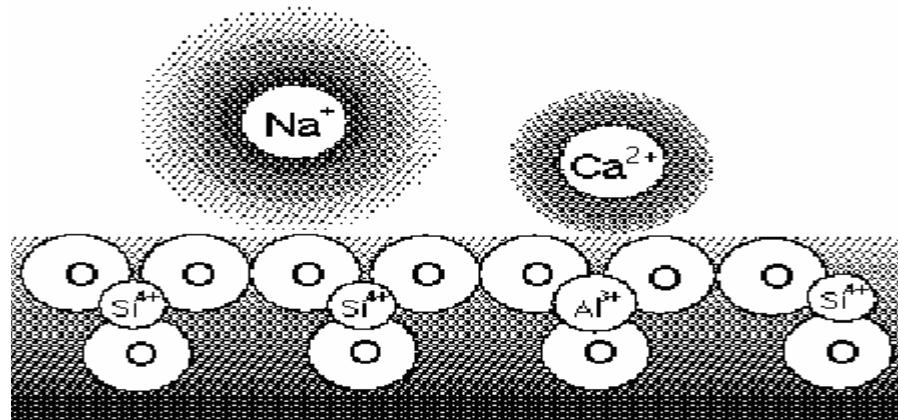


Figure 2.8

2.3.4 Soil Smectite

The term smectite is used to describe a family of expandable 2:1 phyllosilicate minerals having permanent layer charge between 0.2 and 0.6 charges per half unit cell. Specific minerals included in the smectite family are **montmorillonite**, beidellite, saponite, nontronite, and several less common species.

Smectites are constructed of a single octahedral sheet sandwiched between two tetrahedral sheets, with the octahedral sheet sharing the apical oxygens of the tetrahedral sheet. The octahedral sheet may be either dioctahedral or trioctahedral. Layer charge arises from substitutions in either the octahedral sheet (typically from the substitution of low charge species such as Mg^{2+} , Fe^{2+} , or Mn^{2+} for Al^{3+} in dioctahedral species) or the tetrahedral sheet (where Al^{3+} or occasionally Fe^{3+} substitutes for Si^{4+}), producing one negative charge for each such substitution.

The interlayer (the space between the sheets) is hydrated and expandable; that is, the separation between individual smectite sheets varies depending on the interlayer cations present, the ionic strength of the surrounding solution, and other factors. The thumbnail image below is a TEM of a smectite embedded in a plastic resin after

expansion of the interlayer with dodecalamine. Smectite layers are oriented both parallel to the C axis (the dark blob in the center of the image) and perpendicular to the image, as shown by the curving layers in the upper left part of the image.

2.3.5 Montmorillonite

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately 1 micrometre. The particle thickness is extremely small (~ 1 nm).

It is the main constituent of the volcanic ash weathering product, bentonite. Montmorillonite's water content is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(\text{Na,Ca})_x(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Potassium, iron, and other cations are common substitutes, the exact ratio of cations varies with source.

Similar to other clays, montmorillonite swells with the addition of water. However, some montmorillonites expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. The amount of expansion is due largely to the type of exchangeable cation contained in the sample. The presence of sodium as the predominant exchangeable cation can result in the clay swelling to several times its original volume. Hence, sodium montmorillonite has come to be used as the major constituent in non-explosive agents for splitting rock in natural stone quarries in order to limit the amount of waste, or for the demolition of concrete structures where the use of explosive charges is unacceptable.

2.4 Zeolite

Zeolites are microporous crystalline solids with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. About 40 natural zeolites have been identified during the past 200 years and more than 150 zeolites have been synthesized. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

The shape-selective properties of zeolites are the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. Compositionally, zeolites are similar to clay minerals. More specifically, both are alumino-silicates. They differ, however, in their crystalline structure.



Figure 2.9 several types of zeolite

Many types of clay have a layered crystalline structure (similar to a deck of cards) and are subject to shrinking and swelling as water is absorbed and removed between the layers. In contrast, zeolites have a rigid, 3-dimensional crystalline structure (similar to a honeycomb) consisting of a network of interconnected tunnels and cages.

Water moves freely in and out of these pores but the zeolites framework remains rigid. Another special aspect of this structure is that the pore and channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve.

The porous zeolite is host to water molecules and ions of potassium and calcium, as well as a variety of other positively charged ions, but only those of appropriate molecular size to fit into the pores are admitted creating the "sieving" property. Because of their regular and reproducible structure, they behave in a predictable fashion.

The application of zeolites for dye removal from wastewater has rarely been previously reported. Balkose et al. reported a investigation using poly(vinyl chloride)-zeolite composites for methylene blue adsorption and found that the adsorption capacity of zeolite decreased when it was embedded in composites. Meshko et al. studied the adsorption of basic dyes from aqueous solutions onto granular activated carbon and natural zeolite. The equilibrium studies have shown that the granular activated carbon has a higer adsorption capacity than the natural zeolite. The results from tested a natural zeolite for dye removal from aqueous solution, shows the natural zeolite exhibits a higher adsorption capacity than fly ash but still lower than unburned carbon in fly ash (Wang et al., 2006).

2.4.2 EZA Type A

The type of zeolite that we used in this research is EZA type A. has many synonyms name such as Abscents 3000, Calsit, Bactekiller BM 101A and etc, type A remain the dominant zeolites and molecular sieves that are commercial use for adsorption and ion exchange.

The structural unit in Type A zeolite is the truncated octahedron. This unit is also called sodalite cage or beta cage, as sodalite is formed by directly fusing the four-member rings of the units. The four-member rings of the sodalite units can also be linked through four-member prisms, as shown in Figure 2.10 which is Type A zeolite.



Figure2.10 type A zeolite ‘unit cell’

The unit cell of type A zeolite, as shown in this figure, contains 24 tetrahedra, 12 AlO_4 and 12 SiO_4 . When fully hydrated, 27 molecules are contained in the central cage or cavity (also called supercage) of the unit cell, in the eight smaller sodalite cages. The free diameter in the central cavity is 11.4 Å, which is enter through six 8-member oxygen-ring apertures with an unobstructed diameter of 4.4 Å. There are 12 negative charges that are balanced by cations in each unit cell.

The most probable locations for the cations are indicated in figure 2.11. Type I is at the center of the six member ring (with free diameter of 2.8 Å, which is approximately the dimension of water) and thus sits at one of the eight corners of the cavity. Type II is at the eight-member aperture directly obstructing the entrance. Type III is near the four-member ring inside the cavity.

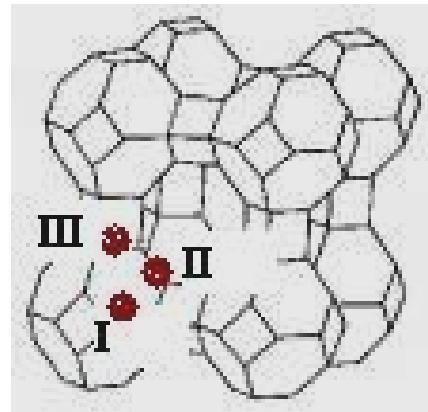


Figure 2.11

CHAPTER III

METHODOLOGY

3.1 Introduction

The natural clay used in this study was obtained from paddy field in Parit, Perak without any treatment. Usually SiO_2 and Al_2O_3 are the major element in the clay.

Methylene blue was taken as the sample representing the effluent of dyes from batik industry. In order to measure the dye concentration, solutions were analyzed by U-8000 UV-Vis spectrometer at wavelength of 665 nm corresponding to the maximum adsorbance. The Methylene blue is prepared in the range of 5 to 100 mg/l.

The additional adsorbent, EZA zeolite A used in this research will be provided by KUKTEM (Sigma-Aldrich).