REMOVAL OF REACTIVE ORANGE 16 (RO16) USING CHEMICALLY MODIFIED PINEAPPLE PEELS

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A project report submitted in partial fulfilment of the
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Bachelor of Engineering (Hons.) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **REMOVAL OF REACTIVE ORANGE 16 (RO16) USING CHEMICALLY MODIFIED PINEAPPLE PEELS** was prepared by TAY KIM MING has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

This research was conducted to study the feasibility of using pineapple (*Ananas comosus L. Merryl*) peels as biosorbent for the removal of Reactive Orange 16 (RO16) dye. Pineapple is mainly produced as canned fruits and consumed worldwide. During canned fruit and juice processing, pineapple peel is usually discharged and produce waste about 35% of the full fruit. From the points of the view of multipurpose utilization and environmental protection, utilization of pineapple peels is of important significance. Therefore, this study could help in converting these wastes into useful product by investigating its feasibility as biosorbent for dye removal. Pineapple peels was first pretreated with different chemicals to compare its adsorption capability. Following that, batch adsorption by using the most suitable pretreated biosorbent was conducted to investigate the effects of initial dye concentration, adsorbent dosage, and pH of solutions on adsorption performance. The results proved that chemical modification of pineapple peels with sodium hydroxide (NaOH) exhibited the most promising result in removing the RO16 from solution. The batch biosorption test revealed that % of RO16 removal is inversely proportional to initial dye concentration while directly proportional to adsorbent dosage. Not only that, results from this study also indicated that an increase in acidity from pH 7 to pH 1 will also improve the adsorption of RO16 on NaOH-treated pineapple peels. Adsorption isotherms analysis indicates that the adsorption of RO16 onto pretreated pineapple peels exhibit both Langmuir and Freundlich isotherm model characteristic reflecting the presence of more than one kind of adsorbent–adsorbate surface interaction. Three simplified kinetic models namely pseudo-first-order, pseudo-second-order, and Weber Morris intraparticle diffusion model were used to study kinetic of the adsorption process. Kinetic parameters, rate constants, equilibrium sorption capacities, and related correlation coefficients for kinetic models were determined. It was found that the present system of RO16 adsorption on NaOH-treated pineapple peels could be described more favorably by the pseudo-second-order kinetic model, indicating that chemisorptions or an effective electrostatic interaction plays a major role in the adsorption process. Analysis of kinetic data using Weber and Morris intraparticle diffusion model reveals that boundary layer of certain thickness exists in the NaOH-treated pineapple peels and the intraparticle diffusion was not the only rate controlling step. In conclusion, pineapple peels makes a good biosorbent for RO16 dye if pretreated with NaOH and used in adequate dosage. However, the possibility of industrial application requires further research using real wastewater from textile industry and pilot plant study.

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b	Langmuir constant, L/mg
C_e	Equilibrium dye concentration in sample, mg/L
C_i	Initial dye concentration in sample, mg/L
C_o	Highest initial dye concentration in sample, mg/L
h	Initial sorption rate, mg/g hr
k_1	Rate constant of pseudo-first-order biosorption, hr^{-1}
k_2	Equilibrium rate constant pseudo-second-order, g/mg hr
k_f	Freundlich constant, mg/g $(1/mol)^{1/n}$
λ_{max}	maximum wavelength, nm
M	Mass of the adsorbent used, g
q_e	Equilibrium dye concentration on adsorbent at any time, mg/g
$q_{e,cal}$	Calculated sorption capacity, mg/g
q_{max}	Maximum of Langmuir monolayer adsorption capacity, mg/g
q_t	Amount of dye uptake (mg/g) at time *t*, hr
R_L	Constant separation factor (Dimensionless)
R^2	Correlation coefficient (Dimensionless)
t	Time, hr
V	Volume of the dye solution, L

$CaCl_2$	Calcium chloride
FTIR	Fourier transforms infrared spectroscopy
HCl	Hydrochloric acid
NaOH	Sodium hydroxide
NTA	Nitrilotriacetic acid
RO16	Reactive orange 16
XPS	X-ray photoelectron spectroscopy

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CHAPTER 1

INTRODUCTION

Following the great leap in technological advancement, environmental pollution becomes one of the most critical issues today. The rises in environmental awareness worldwide dictates that controlling pollution should be the main concern above all other priorities. Among all industrial effluents, wastewater generated by the textile industry is rated as one of the most polluting agents considering both the volumes discharged and the effluents composition. Overall at present there are more than 100,000 commercial dyes with a rough estimated production of 7×10^5 to 1×10^6 tons per year (Christie, 2007). Of such a huge production, the exact data on the quantity of dyes discharged in environment is not available. However, it is reported that 10 to 15% of the used dyes enter the environment through wastes (Hai, Yamamoto, & Fukushi, 2007).

Based on applications, textile industry dyes can be categorized into acid, basic, direct, disperse, mordant, reactive, sulfur, azoic, and vat dyes. In the present study, Reactive Orange 16 (RO16) is used. RO16 is a type of reactive dye. Reactive dyes are mainly azo compounds with different reactive groups such as vinyl sulfone, chlorotriazine and also a metal nucleus. It is different from other types of dyes since it is covalently bind to textile fibres and cannot be easily removed by conventional treatment processes (Horton, 2009). The hazardous effects of reactive dyes come from its discharge into receiving waters. Once released, toxic amines are produced by the reductive cleavage of azo linkages resulting in severe effects on human beings through damaging the vital organs such as the brain, liver, kidneys, central nervous system, and reproductive systems. Even a very small amount of reactive dye in water affects the aesthetic value, water transparency, and gas solubility in water bodies. Moreover, it may also affect photochemical activities in aquatic systems by reducing light penetration. It has also been reported that several reactive dyes are carcinogenic and mutagenic for aquatic organisms (Mittal & Gupta, 1996).

The conventional decolourization methods of dye bearing wastewaters involve the combination of physical and chemical processes such as reverse osmosis, flocculation, oxidation, precipitation, sedimentation, ultrafiltration, flotation, colour irradiation, ozonation, and coagulation (Iqbal, 2008). However these methods are ineffective, especially for the removal of brightly coloured, water-soluble reactive and acid dyes. This is because dyes exhibit stability when exposed to many types of chemicals, oxidizing agents, sunlight, and biological degradation (Pearce, Lloyd, & Guthrie, 2003). Adsorption is an effective alternative process for the treatment of dye contaminated wastewater. Currently, activated carbon is the most popular and extensively used commercial biosorbent material due to its high adsorption capacity, surface area and degree of surface reactivity as well as microporous structures. But it shows some disadvantages such as high operating costs and regeneration problems (Iqbal, 2008).

Biosorption is defined as a property of certain molecules (or types of biomass) to bind and concentrate selected ions or molecules from aqueous solutions. It is a passive binding process utilizing dead biomass (or some molecules or their active groups) as biosorbent (Volesky, 2007). Biosorption process has received great attention in recent years as a more economical alternative method in place of current adsorption processes since it utilize not only plant materials but also a wide variety of microorganisms in dead, pretreated and immobilized forms as adsorbing agents. These materials are cheap to produce and carry wide range of binding sites for dye molecules. Therefore they are subjected to many researches to be investigated for the removal of various dyes from aqueous solutions.

Over the years, considerable amount of researches have been done on the development of effective, low cost, and easily available alternative biosorbents.

Different agricultural biomasses such as coconut shell, coffee beans, corn grain, bamboo, sesame, cotton, cherry stones, apricot stones, nutshell, oil-palm fibre, vine shoots, rice husk, coir pitch, tree fern, peanut hull, sugarcane dust, apple pomace and wheat straw, bark, palm kernel fibre, orange peel, linseed cake, and sawdust have been previously tried for the removal of different types of dyes, but high effective and more economical biosorbent materials are still in need of search (Waranusantigul, Pokethitiyook, Kruatrachue, & Upatham, 2003).

The objectives of this study are:

a) To study the feasibility of using pineapple (*Ananas comosus L. Merryl*) peels as biosorbent for the removal of Reactive Orange 16 (RO16) dye.
b) To investigate the effect of acid and alkaline pretreatment on the sorption capacity of pineapple (*Ananas comosus L. Merryl*) peels towards RO16 dyes.
c) To investigate the effect of different initital pH and initial dye concentration on the sorption of Reactive Orange 16 by pineapple (*Ananas comosus L. Merryl*) peels.
d) To study the sorption isotherm and kinetic modelling of Reactive Orange 16 removal process.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes and Colour

Dye is a coloured organic compound that absorbs light strongly in the visible region and can firmly attach to the fibre due to some affinity to the fibre to which it is being applied (Arnold, 2009). It is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fibre. Dyes are very important groups of chemicals and have very wide applications since it can impart colour. An early theory of dyes first formulated by Otto Witt in 1876 provided a basis for understanding the reaction between colour and structure of the molecule (Arnold, 2009).

According to Witt colour theory, a dye is made up of two essential kinds of parts, auxochromes and chromophores (Arnold, 2009). Auxochromes refer to the functional groups in a dye molecule which are saturated and the presence of these groups in a compound greatly increases the colour-yielding power of the compound by altering the overall energy of the electron system and provides solubility and adherence of the dye to the fibre (Hunger, 2003). A few examples of the most effectives auxochromes are $-NH_2$, $-NR_2$, -NHR, -COOH, -OH, $-SO_3H$, and $–OCH_3$ groups (Rocca, 2002). On the other hand, chromophores are the functional groups which are unsaturated and its presence determines the colour of the dyes (Hunger, 2003). Examples of chromophores are -N=N-, -C=C-, -C=N, $-NO_2$, -NO,-and -C=O. Figure 2.1 shows the structure of some of the most important chromophores.

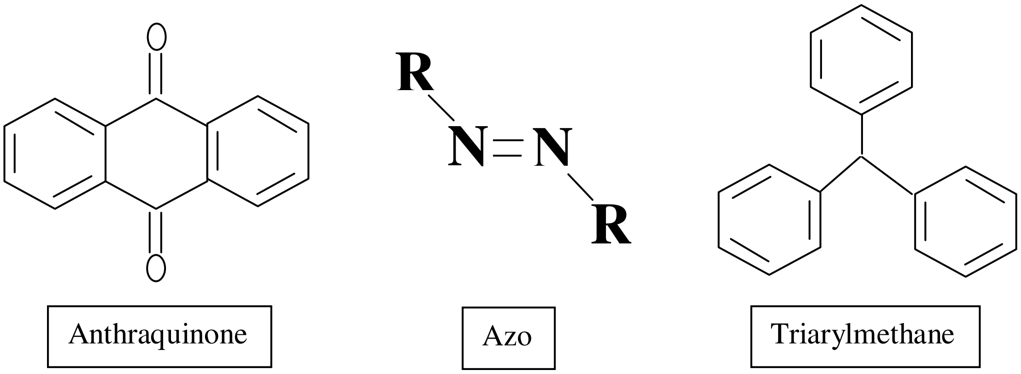

Figure 2.1: Some of the Most Important Chromophores (Source: Iqbal, 2008).

As time pass by, the Witt theory like so many others has also been replaced by modern electronic theory such as valence bond approach. According to valence bond approach theory, it is the resonance stabilization of excited states that is responsible for the absorption in the visible region (Hunger, 2003). When ultraviolet or visible light is absorbed by a molecule, an electron is excited, that is, it is promoted to an orbital of higher energy. The wavelength of light absorbed depends on the energy difference between the excited and ground states of the molecule. The smaller difference between the two states, the longer is the wavelength of the light absorbed. The energy required to promote an electron depends upon the environment of the electron. Sigma (σ) bond electrons are firmly held and very high energy (or short wavelength) is necessary to promote electrons and may at times break the molecule and form free radical. Pi (π) electrons are less firmly held and require less energy (or longer wavelength) to excite. Electrons belonging to conjugated systems required even less energy (still longer length). Conjugation and resonance stabilize the excited state by sharing and delocalizing higher energy of the excited electron. As conjugation and resonance increases, the wavelength of light absorbed also increases and when the wavelength is long enough to be in the visible region, colour is observed (Christie, 2001).

The process of dyeing is defined as the transition of the colour from the dye bath to the substrate (Aspland, 1997). There are three ways in which a dye can be retained by a substrate. These three ways are physical sorption, mechanical retention, and reaction with the fibre. Physical sorption of a dye to a substrate relies on the same intermolecular forces that promoted exhaustion from the dye bath (Horton, 2009). One example of dye classes that exhibit physical sorption as a retention mechanism is direct dyes for cellulose. Mechanical retention involves the formation of an insoluble pigmentary material out of previously soluble chemicals that diffused into the fibre (Horton, 2009). Vat, sulfur, and azoic combinations are some examples of dye classes that use mechanical retention. The third retention method occurs through reaction with the fibre where the dyes form a chemical bond with the fibre (Horton, 2009). Reactive dyes are the only dye class that forms a covalent bond with fibres, whether they are cellulosic or protein while acid and basic dyes use ionic bond formation as the retention method (Hunger, 2003). A reaction between the reactive dye molecule and the fibre results in a coloured derivative of the fibre. The solubility of the reactive dye molecule is decreased exponentially after bond formation while polymer and fibre solubility is not affected (Aspland, 1997).

2.1.1 Classification of Dyes

Dyes can be classified according to origin, chemical structure, physical properties, or applications. Among these, the classification by chemical structure is the most appropriate system with many advantages. First of all, it readily identifies dyes as belonging to a group that has characteristic properties, for example, azo dyes (strong, good all-round properties, cost-effective) and anthraquinone dyes (weak, expensive) (Pearce, Lloyd, & Guthrie, 2003). Second, there are a manageable number of chemical groups (about a dozen) (Pearce, Lloyd, & Guthrie, 2003). Most importantly, it is the classification used most widely by both the synthetic dye chemist and the dye technologist (Hunger, 2003). However, the classification based on application is advantageous before considering chemical structures in detail because of the complexities of the dye nomenclature from this type of system. It is also worth to point that classification by application is the principal system adopted by the Colour Index (C.I.). Classification of dyes based on their usage are summarised in Table 2.1.

Table 2.1: Classification of Dyes (Rocca, 2002).

Class of Dyes	Description
Acid dyes	Water-soluble anionic dyes that are applied to fibres such as silk, wool, nylon, and modified acrylic fibres using neutral to acid dyebaths. Attachment to the fibre is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fibre. Acid dyes are not substantive to cellulosic fibres. Most synthetic food colours fall in this category.
Basic dyes	Water-soluble cationic dyes that are mainly applied to acrylic fibres, but also have some use for wool and silk. Usually acetic acid is added to the dyebath to help the uptake of the dye onto the fibre. Basic dyes are also used in the coloration of paper.
Direct dyes	Dyeing of direct dyes normally carried out in a neutral or slightly alkaline dyebath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.
Mordant dyes	Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final colour significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool; these comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-treatment. It is important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them.

Table 2.1 (continued).

Class of Dyes	Description
Vat dyes	Vat dyes are essentially insoluble in water and incapable of dyeing fibres directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fibre.
Reactive dyes	Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. Cold reactive dyes, such as Procion MX, Cibacron F, and Drimarene K, are very easy to use because the dye can be applied at room temperature. Reactive dyes are by far the best choice for dyeing cotton and other cellulose fibres at home.
Azo dyes	Azo dyes is a technique in which an insoluble azoic dye is produced directly onto or within the fibre. This is achieved by treating a fibre with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. Azo dyes are basically characterized by the presence of one or more azo groups (-N = N-). They are usually complex aromatic compounds which are chemically stable and more difficult to biodegrade in nature.

2.2 Reactive Dyes

Reactive dyes have good wet-fastness, resulting from the conversion of soluble substances in the dye bath into relatively insoluble compounds within the fibres by the formation of covalent bonds between hydroxyl groups in cellulose and reactive groups on the dye molecules (Trotman, 1984). The dyes have bright colours and the dyeing process is simple. The molecular structure of a reactive dye can be divided into five major parts which are chromagen (C), solibilizing group (S), bridging group (B), reactive group (R), and leaving group (X), as illustrated in Figure 2.2. The combination of these groups in the molecular structure allows reactive dyes to react with cellulosic and protein fibres to produce covalently bound colour bodies. Each group contributes to the physical properties of the dye molecule including colour, size, substantivity, diffusion, fastness, and solubility (Aspland, 1997).

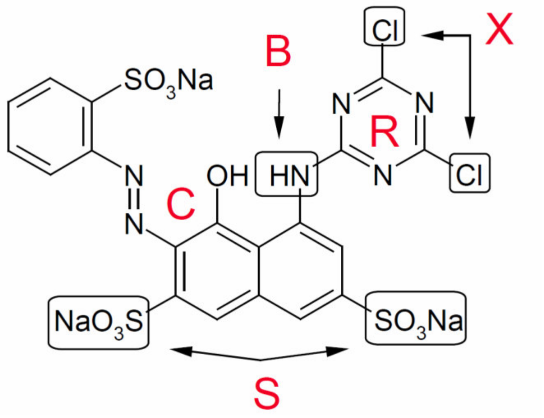

Figure 2.2: Molecular Structure of a Reactive Dye (Source: Horton, 2009).

The chromagen is the colour producing part of any dye molecule. It is the combination of extended conjugation and one or more chromophores. There are many types of chromagens in reactive dye design including azo, anthraquinone, phthalocyanine, triphenodioxazine and formazan systems as shown in Figure 2.3. The first three are the main groups used in reactive dye systems with triphenodioxazine and formazan based dyes replacing the tinctorially weaker anthraquinone dyes (Waring & Hallas, 1990). The chromagen contributes to the affinity of the dye to fibre because it impacts size and molecular shape as well as possible sites of attraction between the dye and substrate (Berger, 2005).

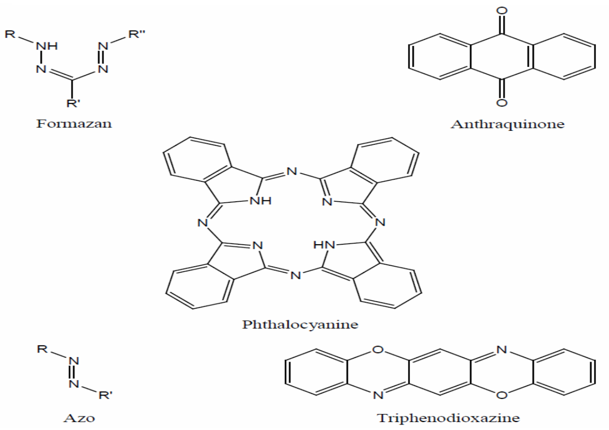

Figure 2.3: Chromophorics System in Reactive Dyes (Source: Horton, 2009).

The most notable solubilizing group present in reactive dyes is the sulfonic acid group. Solubilizing groups imparts solubility to the reactive dyes and in other words, allows the reactive dyes to be readily soluble in water (Aspland, 1997). Greater numbers of solubilizing groups are needed for dyes with heavier molecular weight to remain soluble since solubility is inversely proportional to molecular weight (Trotman, 1984). Therefore, water solubility of the reactive dyes increase with the number of sulfonic acid groups on the molecule. However, this could lead to decrement of substantivity of the dyes for the fibres. Hence, in order to obtain the best result, a balance must be achieved for optimum dyebath exhaustion. Another example of solubilizing group that imparts water solubility to a reactive dye is sulfonamide (-SO_2NH_2) group. Figure 2.4 shows the structure of the solubilizing group of reactive dyes.

Sulfonic Acid group

Sulfonamide group

Figure 2.4: Solubilising Group of Reactive Dyes (Source: Aspland, 1997).

The bridging group in the reactive dyes molecule act as connectors between the reactive group and chromagen and it must possess sufficient stability under basic and/or acidic conditions (Aspland, 1997). In most cases bridging groups consist of N, O, or S linkages. The main parameters that affect the strength of the bridge are the type of bridge, the dyeing conditions, and the substituents that are connected by the bridge (Aspland, 1997). The most typical bridging group for reactive dyes contain nitrogen in either the amine or imine structure before reaction (Trotman, 1984). The bridging group affects substantivity based on the composition of the two molecules it is used to bridge, chromagen, and reactive group (Horton, 2009).

Reactive group undergoes chemical reaction with a functional group present on the substrate to create a coloured derivative (Waring & Hallas, 1990). It can do so due to the presence of electron deficient carbon atoms in the structure that is capable of nucleophilic attack by either substitution or addition (Aspland, 1997). A nucleophile is an atom that has an abundance of electrons, lone pairs, which bond with the electron deficient atom (Rosenthal, 1976). The major problems that dye chemists face when choosing a reactive group are systems that are suitable for efficient reaction with the substrate and also produce high fastness properties (Rosenthal, 1976). In order to produce high fastness properties, the reactive group must be able to align itself with the surface of the substrate to favour the reaction. Once the dye-fibre bonding is completed, the stability of the bond becomes of importance due to subsequent treatment of the coloured substrate (Taylor, 2000). Commonly, the stability of the subsequent bond decreases with the increasing reactivity of the group (Aspland, 1997). The effect of reactive groups on substantivity is dependent on the group.

The leaving group is associated with the reactive group upon reaction of the nucleophile with the electron deficient carbon located on the reactive group. A suitable leaving group is an atom or molecule electronegative in character and relatively stable once in solution (Taylor, 2000). Typical leaving groups for reactive groups that undergo nucleophilic substitution or addition include halogens and molecules that from stable ions in solution, chlorine or fluorine and quaternary ammonium or sulfato respectively. The reactivity of a reactive group can be changed by variation of the electronegativity of the leaving group associated with the system (Aspland, 1992).

2.2.1 Reactive Orange 16

In the present study, Reactive Orange 16 (RO16) is used as a model reactive dye and it is of analytical grade that was purchased from Sigma–Aldrich (M) Sdn. Bhd. As shown in Figure 2.5, RO16 has two sulfonate groups, which have negative charges in aqueous solution. The general characteristics of RO16 are summarized in Table 2.2.

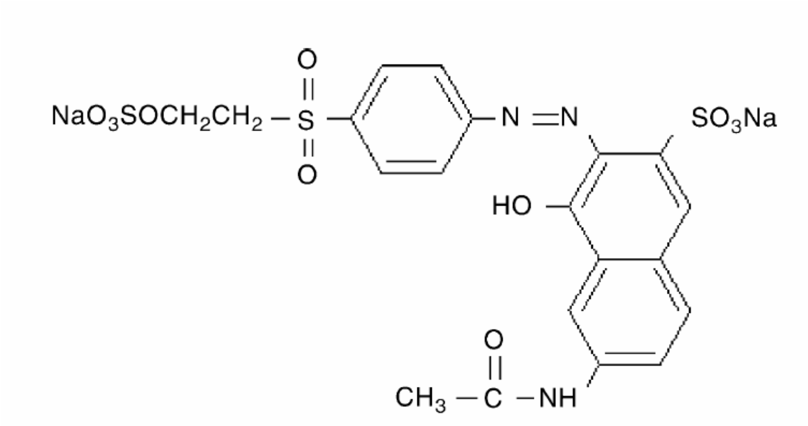

Figure 2.5: Chemical Structure of Reactive Orange 16 (Source: Sung, Sun, & Yeoung, 2006).

Table 2.2: General characteristics of Reactive Orange 16 (Source: Sung, Sun, & Yeoung, 2006).

Characteristics	Description
IUPAC Name	disodium (3Z)-6-acetamido-4-oxo-3-[[4-(2-sulfonatooxyethylsulfonyl) phenyl]hydrazinylidene]naphthalene-2-sulfonate
Chemical formula	$C_{20}H_{17}N_3Na_2O_{11}S_3$
Molar mass	617.54
Maximum wavelength, λ_{max} (nm)	494
H-Bond Donor	2
H-Bond Acceptor	13

2.3 Conventional Dye Removal Methods

Traditional wastewater treatment technologies have proven to be markedly ineffective for handling the effluents containing synthetic dyes because of the chemical stability of these pollutants. So far, there is no single and economically attractive method for decolourisation of textile wastewaters, although notable achievements were made in the use of biotechnological approaches to this problem in recent years, as reviewed by dos Santos et al. (2007). Besides biological treatment, many physical and chemical methods have been used for the decolourisation of dye bearing wastewater.

In physical treatment methods, the applications of physical forces predominate (Waring & Hallas, 1990). Physical methods include different precipitation methods (coagulation, flocculation, and sedimentation), adsorption (on a wide variety of inorganic and organic supports), filtration, reverse osmosis, ultrafiltration and nanofiltration (Waring & Hallas, 1990). Biological treatments differ according to the presence or absence of oxygen to aerobic and anaerobic treatment. Since biological treatments simulate degradation processes that occur in the environment, it is also called biodegradation (Aspland, 1992). Chemical treatment methods are those, in which the removal or conversion of dyes and other contaminants is brought about by the addition of chemicals or by chemical reactions (reduction, oxidation, compleximetric methods, ion exchange and neutralization) (Arnold, 2009).

2.3.1 Physical Methods

One of the physical methods employed for textile wastewater treatment is the filtration method. In the textile industry the filtration methods such as ultrafiltration, nanofiltration and reverse osmosis can be used for both filtering and recycling not only pigment-rich streams, but also mercerising and bleaching wastewaters (Arnold, 2009). The specific temperature and chemical composition of the wastewater determine the type and porosity of the filter to be applied (Arnold, 2009). The main drawbacks of the membrane technology are high investment costs, the potential membrane fouling, and the production of a concentrated dyebath which needs to be treated (Arnold, 2009).

Another physical method is coagulation-flocculation methods where coagulant agents like aluminium sulphate, ferrous and ferric sulphate, ferric chloride, calcium chloride, copper sulphate, as well as several co-polymers like pentaethylene, hexamine and ethylediene dichloride are used to form flocs with the dye, which are then separated by filtration or sedimentation (Arnold, 2009). The flocs settleability can also be improved by adding polyelectrolyte during the flocculation phase. This technique has both its advantages and drawbacks. The main advantage of these processes is the decolouration of the waste steam are done by removing the dye molecules from the dyebath effluents, instead of through partial decomposition of dyes, which can lead to an even more potentially harmful and toxic aromatic compound while the major drawbacks of this processes is the production of sludge (Arnold, 2009).

Perhaps the most popular choice of dye decolouration by physical method is adsorption. Adsorption is the process of collecting soluble substances that are in solution on a suitable interface (Robinson, McMullan, Marchant, & Nigman, 2005). Adsorption methods for decolouration are based on the high affinity of many dyes for adsorbent materials. Dye removal by adsorption is influenced by some physical and chemical factors like dye-adsorbent interactions; adsorbent surface area, particle size, temperature, pH and contact time (Robinson et al., 2005). The main criteria for selection of an adsorbent should be based on characteristics such as high affinity and capacity for target compounds and the possibility of adsorbent regeneration (Robinson et al., 2005).

Currently, the most commonly used adsorption agent in industry is activated carbon that was successfully tested for the removal of various kinds of synthetic dyes. Performance of removal depends on the type of carbon used and characteristic of the wastewater. It is, like many other dye-removal treatments, well suited for one particular waste system and ineffective for another. Activated carbon has relatively high operating costs and problems with the regeneration of the spent activated carbon hamper its large-scale applications (Arnold, 2009). Therefore, a number of non-conventional sorbents have been tried for the treatment of wastewaters. The major drawbacks of adsorption processes are that the adsorbent needs to be regenerated, which adds to the cost of the process, and is sometimes a very time-consuming procedure (Arnold, 2009).

2.3.2 Chemical Methods

Oxidation is the most widely used chemical decolouration process due to its simplicity of application. Conventional oxidation treatments are ineffective in removing modern dyes which are resistant to mild oxidation conditions such as those found in biological treatment systems (Arnold, 2009). The limitations of conventional chemical oxidation techniques can be overcomed by the development of so-called advanced oxidation processes (Arnold, 2009). Advanced oxidation processes generate free hydroxyl radicals (OH•), which may represent a rate increase of one to several orders of magnitude compared with normal oxidants in the absence of catalysts (Arnold, 2009). Table 2.3 shows the oxidation potential of common species. The dyes and toxic organic compounds that cannot be oxidized by conventional oxidants are oxidized by the hydroxyl radicals. In advanced oxidation processes, oxidizing agents such as ozone and hydrogen peroxide are used with catalysts (Fe, Mn, TiO2) either in the presence or absence of an irradiation source (Arnold, 2009).

Table 2.3: Oxidation Potential of Common Oxidizing Agents (Source: Arnold, 2009).

Oxidizing agents	Oxidation potential/V
Fluorine (F_2)	3.06
Hydroxyl radical (OH•)	2.80
Atomic oxygen	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.78

Table 2.4 (continued)

Oxidizing agents	Oxidation potential/V
Potassium permanganate ($KMnO_4$)	1.67
Hypochlorous acid (HClO)	1.49
Chlorine (Cl_2)	1.36
Bromine (Br_2)	1.09
Molecular oxygen (O_2)	1.23

Ozone is a very powerful and rapid oxidising agent that can react with most species containing multiple bonds and with simple oxidisable ions such as S^{2-}, to form oxyanions such as SO_3^{2-} and SO_4^{2-} (Gogate & Pandit, 2004). Once dissolved in water, ozone reacts with a great number of organic compounds in two different ways, namely direct molecular and indirect free radical-type reactions (Gogate & Pandit, 2004). The direct reactions are often highly solute selective, slow, and are dominant in acidic solutions. The indirect hydroxyl radical reactions are non-selective, fast, proceed more rapidly with increasing pH and constitute a significant portion of ozonation at basic pH (Gogate & Pandit, 2004). The advantages of ozonation are one step decolouration and degradation, minimal danger to human, no sludge generation, all residual ozone can be decomposed easily into oxygen and water, small space requirement, and easy to perform (Gogate & Pandit, 2004). On the other hand, ozone process also has its own limitations such as very short half-life in water and also relatively high cost of ozone generation process (Arnold, 2009).

2.3.3 Biological Methods

Biological methods of dye removal involved biodegradation or breakdown of dye by living organisms (Arnold, 2009). Biodegradation processes may be anaerobic, aerobic, or involve a combination of both. The efficiency of biological treatment systems is greatly influenced by the operational parameters (Arnold, 2009). Examples of these parameters are level of aeration, temperature, pH, and redox potential of the system, which must be optimised to achieve the maximum rate of dye reduction (Arnold, 2009). The concentration of the electron donor and the redox mediator must be balanced with the amount of biomass in the system and the quantity of the dye present in the wastewater (Arnold, 2009). The compounds present (sulphur compounds, salts) in the wastewater may have an inhibitory effect on the dye reduction process (Arnold, 2009). For these reasons it is important to study the effect of these factors on decolouration before the biological system can be used to treat industrial wastewater (Pearce, Lloyd, & Guthrie, 2003).

Aerobic biodegradation of azo dyes are a dye removal process that occurs through the reduction of the azo linkage by some specific aerobic bacterial cultures via an enzymatic reaction under aerobic condition (Arnold, 2009). In some studies, aerobic colour removal of certain azo dyes was achieved, but all these stains required an additional energy and carbon source for growth (Arnold, 2009). Since the supply of this additional substrate could have easily led to the formation of anaerobic michroniches, the occurrence of anaerobic azo dye reduction certainly cannot be excluded (Arnold, 2009). The aerobic biodegradation of different aromatic amines (aniline, carboxylated aromatic amines, chlorinated aromatic amines, benzidines, sulfonated aromatic amines) has been extensively studied and many of these compounds were found to be degraded (Arnold, 2009).

Colour removal under anaerobic conditions is also referred as anaerobic biodegration. Many bacteria under anaerobic conditions reduce the highly electrophilic azo bond in the dye molecules and produce colourless aromatic amines (Razo, Luijten, Donlon, & Lettinga, Field, 1997). The exact mechanism of azo dye reduction is not clearly understood yet. The different mechanisms may be involved like enzymatic, non-enzymatic, mediated, intracellular, extracellular and various combinations of these mechanisms (Razo et al., 1997). Much effort has been devoted to the study of the influence of various modern technologies on the decomposition rate of the dyes and the effect of the presence of the other compounds in the media (Razo et al., 1997). The effect of nitrate and sulfate salts used in textile dyeing on the microbial decoloration of a reactive azo dye has been studied (Razo et al., 1997). The results indicated that nitrate delays the onset of decolouration while sulphate did not influence the biodegradation process (Carliell, Barclay, Shaw, Wheatley, & Buckley, 1998). Biological treatment method is advantageous over the physical-chemical techniques as it is inexpensive and more environmental friendly.

2.4 Biosorption

Biosorption is defined as a property of certain molecules (or types of biomass) to bind and concentrate selected ions or molecules from aqueous solutions (Volesky, 2007). It is an alternative technology to remove heavy metals from dilute aqueous solutions using inactive and dead biomasses (various kinds of microorganisms, agricultural and fermentation wastes) to bind and accumulate these pollutants by different mechanisms such as physical adsorption, complexation, ion exchange, and surface microprecipitation (Aksu, Kutsal, Haciosmanoglu, & Gholaminejad, 1991). Biosorption process has received great attention in recent years as a more economical alternative method in place of current adsorption processes since it utilize not only plant materials but also a wide variety of microorganisms in dead, pretreated and immobilized forms as adsorbing agents. These materials are cheap to produce and carry wide range of binding sites for dye molecules.

In the past few years, extensive research has been undertaken to develop alternative and economic adsorbents (Akar, S.T., Ozcan, A.S., Akar, T., Ozcan, A., & Kaynak, 2009). An economic adsorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires little processing (Akar, et al., 2009). One type of adsorbent that fulfil these requirements are agricultural waste. Agricultural waste biosorbents generally used in biosorption studies are inexhaustible, low-cost and non-hazardous materials, which are specifically selective for heavy metals and easily disposed by incineration (Akar et al., 2009). Agricultural by-products as a whole exceed 320,000,000,000 kg/year (Aksu & Isoglu, 2005). Most of these by-products are considered to be low value products. The agricultural by-products such as peat, wood, pine park, rice bran, wheat bran, peanut shells, wool, rice milling by-products (hulls and bran), grape stalks wastes, sugar beet pulp, olive mill solid residue, sawdust, and leaves have been demonstrated to remove heavy metal ions from wastewater (Aksu & Isoglu, 2005).

Adsorption of the dye molecules on the surface of absorbents are typically highly heterogeneous by its nature and are rather complicated process, in which various mechanisms may be effective (Muraleedharan, Iyenger, & Venkobachar, 1991). Due to the ionic nature of the dye species in aqueous solutions, electrostatic forces-attraction or repulsion between the dye species and ionized active groups on the absorbent surface plays an important role (Aksu & Isoglu, 2005). Chemisorption as well as ion-exchange and other physical phenomena will participate in the dyes absorption process, but their proportions and significance may differ for different dyes and different kinds of absorbents (Volesky, 2007). Carboxylic and hydroxylic functional groups are commonly present in the structure of most natural absorbents (Aksu & Isoglu, 2005). These groups undergo dissociation at suitable pH values, forming negatively charged sites on the absorbent surface, which facilitates the retention of cationic dyes (Aksu & Isoglu, 2005).

Synthetic dyes, as relatively large organic molecules containing usually several aromatic rings, may also exhibit a certain affinity towards less polar (organophilic) moieties that may be present in the structure of the non-conventional sorbents (Arnold, 2009). Therefore, this kind of non-specific interactions should be also considered. The dye sorption is usually a quite rapid process, in which most of the dye is retained in a time scale of a few hours or even minutes, rather than days (Azizian, 2004). To express the sorption kinetics in a mathematic form, two models are applied most often, namely pseudo-first order model and a pseudo-second order model (Azizian, 2004). These models are commonly used to describe the sorption of dyes as well as other pollutants (heavy metals) on solid sorbents, although, as pointed out by Ho and McKay (1998), an application of a single kinetic model to the sorption on solid absorbents may be questionable because of a heterogeneity of the absorbent surfaces and diversity of sorption phenomena (transport, surface reactions). Recently, Azizian (2004) showed that the pseudo-first order kinetic model is more suitable for lower concentrations of solute, whereas the pseudo-second order model is more appropriate at high solute concentrations.

Biosorption involves integration both of active and passive transport mechanisms starting with the diffusion of the adsorbed component to the surface of the cell (Arnold, 2009). Once the component has diffused to the cell surface, it will bind to sites on the cell surface, which exhibit some chemical affinity for the component (Dogar, Gurses, Acikyildiz, & Ozkan, 2010). The interactions between absorbents and dyes depend on the chemical properties of all the reaction partners. Each dye has certain affinity to various absorbents and on the other side one absorbent is able to bind to more than one type of dyes (Dogar et al., 2010). In order to prepare the absorbents for biosorption, all the biomasses both living and dead are heat killed, dried, acid and/or otherwise chemically treated first (Azizian, 2004). The main advantages of using biosorbents to remove dyes are:

i) It is abundantly available.
ii) Most of the types of biosorbents are ready to be used and do not require a complex pretreatment step or activation process before applications.
iii) Regeneration of these adsorbents may not be necessary (unlike activated carbon, where regeneration is essential).
iv) Minimum maintenance and supervision are required for the operation of the adsorption process.

2.5 Pineapple (*Ananas comosus L. Merryl*)

Pineapple (*Ananas comosus L. Merryl*) is the leading edible member of the family Bromeliaceae. It is a terrestrial herb 0.75 to 1.5 m high with a spread of 0.9 to 1.2 m, a very short, stout stem and a rosette of waxy, straplike leaves, long-pointed, 50 to 180 cm 1ong, usually needle tipped and generally bearing sharp, upcurved spines on the margins (Tran, 2006). The leaves may be all green or variously striped with red, yellow or ivory down the middle or near the margins (Tran, 2006). At blooming time, the stem elongates and enlarges near the apex and puts forth a head of small purple or red flowers, each accompanied by a single red, yellowish or green bract. The stem continues to grow and acquires at its apex a compact tuft of stiff, short leaves called the "crown" or "top" (Augstburger et al., 2001). Occasionally a plant may bear two or three heads, or as many as twelve fused together, instead of the normal one (Augstburger et al., 2001).

Figure 2.6: Pineapples (*Ananas comosus L. Merryl*) (Source: http://fruit4you.net)

As individual fruits develop from the flowers they join together forming a cone shaped, compound, juicy, fleshy fruit to 30 cm or more in height, with the stem serving as the fibrous but fairly succulent core (Tran, 2006). The tough, waxy rind, made up of hexagonal units, may be dark-green, yellow, orange-yellow or reddish when the fruit is ripe (Chen, Paull, Chen, & Saradhuldhat, 2003). The flesh ranges from nearly white to yellow. If the flowers are pollinated, small, hard seeds may be present, but generally one finds only traces of undeveloped seeds. Offshoots, called "slips", emerge from the stem around the base of the fruit and shoots grow in the axils of the leaves (Chen et al., 2003).

Pineapple is mainly produced as canned fruits and consumed worldwide. During canned fruit and juice processing, pineapple peel is usually discharged before or after bromelain is extracted (Tran, 2006). Both the discharges of pineapple peel in these two ways produce waste about 35% of the full fruit and this burdened the canned pineapple industry because the need for these peels are negligible, thus it becomes an issue and contributes to serious environmental problems (Tran, 2006). From the points of the view of multipurpose utilization and environmental protection, utilization of pineapple peels is of important significance. Therefore, this study could help in converting these wastes into useful product by investigating its feasibility as biosorbent for dye removal.

2.6 Previous Works on Biosorption

Over the years, considerable amount of researches have been done on the development of effective, low cost, and easily available alternative adsorbents. However, none of the material studied so far can fulfil all the requirements effectively. Even so, understandings of previous works by other authors are very important and valuable for future works. The following discussion are some of the absorbents studied previously for dye removal.

2.6.1 Orange Peels

Orange peel waste was used by Namasivayam, Muniasamy, Gayatri, Rani, & Ranganathan (1996) for the adsorption of congo red, procion orange, and rhodamine B dyes. The process was studied at different concentrations of dyes, adsorbent dosage, agitation time, and pH and was found to obey both the Langmuir and the Freundlich isotherms. Also, the authors suggested that acidic pH is favourable for the adsorption for all three dyes. Orange peel has also been investigated as an adsorbent by Sivaraj, Namasivayam, & Kadirvelu (2001), for the removal of acid dye: acid violet 17. The material is a waste product with practically no cost but its adsorption capacity of 19.88 mg/g makes it an adsorbent of a little importance for dyes removal from wastewater. Orange peel as adsorbent has also been studied by Arami, Limaee, Mahmoodi, & Tabrizi (2005) for the removal of direct dyes: direct red 23 and direct red 80. The authors investigated the effects of initial dye concentration (50, 75, 100, 125 mg/L), pH, mixing rate, contact time, and quantity of orange peel at 25 ºC. The adsorption capacity was found to be 10.72 and 21.05 mg/g at initial pH 2, for direct red 23 and direct red 80, respectively. A numerical finite element model to simulate the removal of dissolved textile synthetic dyes from wastewater by orange peel taking into consideration both the linear and the Langmuir isotherms to describe adsorption process has been proposed (Ardejani et al., 2007). The modelling results were compared to those results obtained from experimental tests for the removal of direct red 23 and direct red 80 dyes from textile wastewater using orange peel adsorbent. The model predictions somewhat agree with the experimental measurements.

2.6.2 Rice Husks

Rice husk as obtained from a local rice mill grounded, sieved, washed and then dried at 80 ºC was used for removal of two basic dyes safranine and methylene blue and adsorption capacity of 838 and 312 mg/g was found (McKay, Porter, & Prasad, 1999). Since disposal or regeneration of spent adsorbent is one of the important economic factors in assessing the feasibility of an adsorption system, authors suggested that as the purchase costs of material is negligible and it is primarily carbonaceous and cellulosic, the preferred disposal method is by dewatering, drying and burning. Also it was suggested that the heat of combustion can be recovered as waste heat and used for adsorbent drying and steam generation.

2.6.3 Cotton

Cotton is one of the most important and widely used fibers by humans. Cotton found naturally and consisting cellulose exhibits excellent physical and chemical properties in terms of stability, water absorbency and dye removal ability. A study dealing with the adsorption of dyes in a continuous system on treated cotton was performed by Bouzaida and Rammah (2002). The authors found the adsorption capacities of cotton for acid blue 25, acid yellow 99 and reactive yellow 23 to be 589, 448 and 302 mg/g, respectively. Adsorption behaviour of direct dye on cotton in Aerosol-OT (AOT) reverse micellar system was studied by Sawada and Ueda (2003), exhaustion of dye was suggested to be perfect and superior to that in aqueous system. In a study to evaluate the performance of cotton waste for dye removal, McKay, Porter, & Prasad (1999) found that the cotton waste had the potential to adsorb 875 and 277 mg/g of basic red 2 and basic blue 9, respectively.

2.6.4 Wood

Wood as an adsorbent was investigated by Poots, McKay, & Healy (1976b, 1978), who studied the removal of acidic (telon blue, i.e., acid blue 25) as well as basic (astrazone blue, i.e., basic blue 69) dyes thereby making an attempt to overcome the economic disadvantages of activated carbon. The adsorbent was studied without any pretreatment and was sieved into different size ranges prior to use. The kinetics of the process was found to be dependent on the particle size, being minimum (longer than 3 hours) for small particle size (150 to 250 mm) and maximum (longer than 6 hours) for large particle sizes (710 to 1000 mm) in case of acidic dye, however compared to the acid dye the removal of basic dye (astrazone blue) was found to be in less contact time (2 hours). The monolayer coverage of telon dye on wood varied from 6.95 to 11.56 mg/g for particle sizes ranging from 710 to 1000 and 150 to 250 mm, respectively. However, a higher adsorption capacity of 100.1 mg/g for particles of size 150 to 250 mm was observed for basic dye astrazone blue.

Poots, McKay, & Healy (1976b, 1978) suggested that because of its low cost, the wood adsorbent does not need to be regenerated after use and may be disposed of by burning and the heat so evolved can be used for generating steam. The drawbacks were longer contact time (8 h) and also low adsorption capacity of the wood for acidic dye telon blue. Morais, Freitas, Goncalves, Vasconcelos, & Gonzalez Beca (1999) used eucalyptus bark without any pretreatment for removing reactive dyes. The adsorption on bark was suggested because of its high tannin content, the polyhydroxy polyphenol groups of tannin are thought to be the active species in the adsorption process. The process was found to be exothermic and dye adsorption varying from 4 to 90 mg/g, depending on experimental conditions. The higher value of 90 mg/g was observed at pH 2.5 and with 50 g/L sodium chloride concentration.

CHAPTER 3

METHODOLOGY

3.1 Preparation of Adsorbent

The adsorbent under investigation in this study is pineapple (*Ananas comosus L. Merryl*) peels. The pineapple peels were obtained from various fruit stalls in Wangsa Maju and Genting Klang. In order to use it for the biosorption experiment, these pineapple peels are required to undergo some processing. First of all, the pineapple peels were cleaned under the running tapped water for several times to remove dirt and sand particles. Next, it was rinsed with distilled water and dried in the oven at 50°C for 24 hours. The dried samples were then grinded and sieved to different particle size range before stored into sealed plastic bag according to their size range with silica gel to minimize dampness. The samples in the size range with the most amounts were chosen to be used in the experiment and in the case of this study, the particles with 300 µm to 600 µm are selected.

3.2 Preparation of Dye Solutions

The dye used in this study is Reactive Orange 16 (RO16) purchased from Sigma-Aldrich (M) Sdn. Bhd. Stock solution with concentration of 500 mg/L was prepared by dissolving 0.5 g of dye powders in 1000 mL of distilled water. Dye solutions of different concentrations were then prepared by adequate dilution on the stock solution with distilled water when necessary.

3.2.1 Calibration Curve

Five samples of different concentration of RO16 (20 mg/L, 40 mg/ L, 60 mg/L, 80 mg/L, and 100 mg/L) were prepared from the dilution of the stock solution. Next, maximum wavelength of Reactive Orange 16 and the absorbance value for each sample were taken using Cary 100 Conc. UV-Visible Spectrophotometer and the calibration curve was constructed (Appendix A). For future reference, the concentration of a sample can be found directly from the calibration curve using its absorbance value.

3.3 Batch Biosorption Experiments

In this study, the biosorption experiments were carried out in an orbital shaker at a constant speed of 150 rpm at room temperature using 250 mL conical flask. Three flasks, each contain 1.0 g of adsorbent sample in 100 mL dye solution of 100 mg/L concentration were placed in the shaker, unless otherwise stated. In the sorption experiment, samples were withdrawn from the flasks at pre-determined time intervals (24 hours interval) to measure the intensity of dye. The samples were first centrifuged at 9000 rpm for 5 minutes in Sartorius Sigma 3-18K centrifuge before being measured for its absorbance value at maximum wavelength of the dye using Cary 100 Conc. UV-Visible Spectrophotometer. Absorbance values found were then used to estimate the corresponding concentration by using the calibration curve.

All the experiments were carried out in triplicates and the average value of the result is presented in the form of percentage uptake and sorption capacity. Percentage removal was calculated using Equation 3.1 and amount of dye adsorbed on the adsorbent was calculated using Equation 3.2.

$$Percentage\ Removal\ (\%) = \frac{C_i - C_e}{C_i} \times 100\% \qquad (3.1)$$

where,

C_i= initial dye concentration in sample (mg/L)

C_e= equilibrium dye concentration in sample (mg/L)

$$q_e = \frac{V(C_i - C_e)}{M} \tag{3.2}$$

where,

q_e= equilibrium dye concentration on adsorbent at any time (mg/g)

M = mass of the adsorbent used (g)

V = volume of the dye solution (L)

3.3.1 Preparation of Chemically-Pretreated Adsorbent

The first parameter investigated in this study is the effect of chemical modification on adsorbent in removal of RO16, as compared to untreated peels. Adsorbent were modified using five different types of chemicals in order to enhance the sorption capacities of adsorbent towards RO16. Five chemically-pretreated absorbents and its natural state were studied and compared for its performance in dye removal and the type of modified adsorbents which exhibit highest percentage of uptake were chosen for subsequent study. The five chemical used to pretreat the adsorbent are sodium hydroxide, formaldehyde, calcium chloride, nitrilotriacetic acid, and hydrochloric acid.

Formaldehyde treated adsorbent was prepared by mixng six grams of natural pineapple peels with 68 mL of 36% formaldehyde and 132 mL 0.1 M HCL solutions. The mixture was left at room temperature for 1 hour under gentle mixing. The treated seaweed was then filtered and rinsed with distilled water. The resulting product was subsequently washed with 0.2 M Na_2CO_3 and rinsed again with distilled water washed. After drying at 60°C overnight in the oven, it was finally heated at 110°C for 2 hour. The dried formaldehyde-treated adsorbent were then stored in a sealed plastic bag with silica gel for further use.

Nitrilotriacetic acid-treated adsorbent was prepared by treating natural pineapple peels with 1.2 M nitrilotriacetic acids solution and placed in the oven overnight at 50°C. The mixture was subsequently heated at 140°C for 2 hour and the washed with distilled water until neutral. It was dried again in the oven overnight at 50°C. The resulting product was stored in a sealed plastic bag with silica gel and labelled as nitrilotriacetic acid-treated pineapple peels.

Calcium chloride modifications were carried out by treating 6 g of natural pineapple peels with 200 mL of 0.2 M $CaCl_2$ solution. The mixture was then shaken for 24 hour at 130 rpm, at room temperature. It was then filtered and washed with distilled water to remove excess of calcium. The treated pineapple peels was dried in the oven at 60°C for 24 hour and labelled as calcium chloride-treated pineapple peels.

Hydrochloric acid modifications were carried out by treating the natural adsorbent with 300 mL of 0.1 M HCl solution. The mixture was agitated at 200 rpm in a shaker for 2 hours at room temperature. Next, the HCL-treated adsorbent were then filtered and rinsed with distilled water until neutral pH before dried in oven at 50℃ for 24 hours. The dried HCL-treated adsorbent were then stored in a sealed plastic bag with silica gel for further use. The same procedure was carried out to prepare NaOH-treated adsorbent by using 0.1 M NaOH solution while natural adsorbent are the original adsorbent sample without any pretreatment process.

3.3.2 Effect of Initial Dye Concentration

Dye solutions with different concentrations (40 mg/L, 80 mg/L, 100 mg/L, 120 mg/L, and 170 mg/L) were prepared by diluting the stock solution accordingly. Using the most effective chemically modified adsorbent, batch biosorption experiment was then carried out for each of the dye concentration prepared.

3.3.3 Effect of Adsorbent Dosage

The amount of adsorbent used to removed RO16 were varied (1 g, 1.5 g, 2 g, 2.5 g, and 3 g) for five samples with same initial dye concentration of 100 mg/L. The batch biosorption experiment was then carried out for each of the samples to investigate the effect of adsorbent dosage on RO16 percentage removal and sorption capacity of adsorbent dosage.

3.3.4 Effect of pH

Four samples of 100 mL dye solution with 100 mg/L concentration were prepared at different pH (pH 1, pH 3, pH 5, and pH 7). The pH value of the samples was adjusted using 5 M HCl solution and 5 M NaOH solution. The batch biosorption was then carried out using the dye solution with different pH and the most effective chemically modified adsorbent found in first parameter.

3.4 Adsorption Isotherm Analysis

In this study, both Langmuir's and Freundlich's adsorption isotherm equilibrium models were used for the analysis of the algal-dye sorption system. The linearised form of Langmuir isotherm (as shown in Equation 3.3) was used to characterise the adsorption process of RO16 onto pineapple peels.

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{bq_{max}}\right)\left(\frac{1}{C_e}\right) \tag{3.3}$$

where,

q_e = Equilibrium dye concentration on adsorbent at any time (mg/g)

q_{max} = maximum of Langmuir monolayer adsorption capacity (mg/g)

b = Langmuir constant (L/mg)

C_e = Equilibrium dye concentration in sample (mg/L)

The linearised form of Freundlich is shown in Equation 3.4.

$$logq_e = logk_f + \left(\frac{1}{n}\right) logC_e \tag{3.4}$$

where,

q_e = Equilibrium dye concentration on adsorbent at any time (mg/g)

k_f = Freundlich constant (mg/g (1/mol)$^{1/n}$)

1/n = exponential constant

C_e = Equilibrium dye concentration in sample (mg/L)

3.5 Adsorption Kinetic Studies

Kinetic adsorption data of dye by adsorbent at various initial dye concentrations is fitted with pseudo-first-order (Equation 3.5) and pseudo-second-order kinetic models (Equation 3.6).

A linear form of pseudo-first-order model is:

$$\log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \tag{3.5}$$

where,

q_e= Equilibrium dye concentration on adsorbent at any time (mg/g)

q_t = amount of dye uptake (mg/g) at time, *t* (hr)

k_1= rate constant of pseudo-first-order biosorption, (hr^{-1})

A linear form of pseudo-second-order model is:

$$\left(\frac{1}{q_t}\right) = \frac{1}{k_2 {q_2}^2} + \frac{1}{q_e}t \tag{3.6}$$

where,

k_2= equilibrium rate constant pseudo-second-order (g/mg hr)
h ($k_2 {q_2}^2$) = initial sorption rate (mg/g hr)

Equation that describe intraparticle diffusion model:

$$q_t = k_{id} t^{1/2} + C \tag{3.7}$$

where,
k_{id} = intraparticle diffusion rate constant (mg/g min$^{1/2}$)
C = intercept related to the thickness of the boundary layer.

3.6 Experiment Design

The whole experiment design in the present study is shown in Figure 3.1.

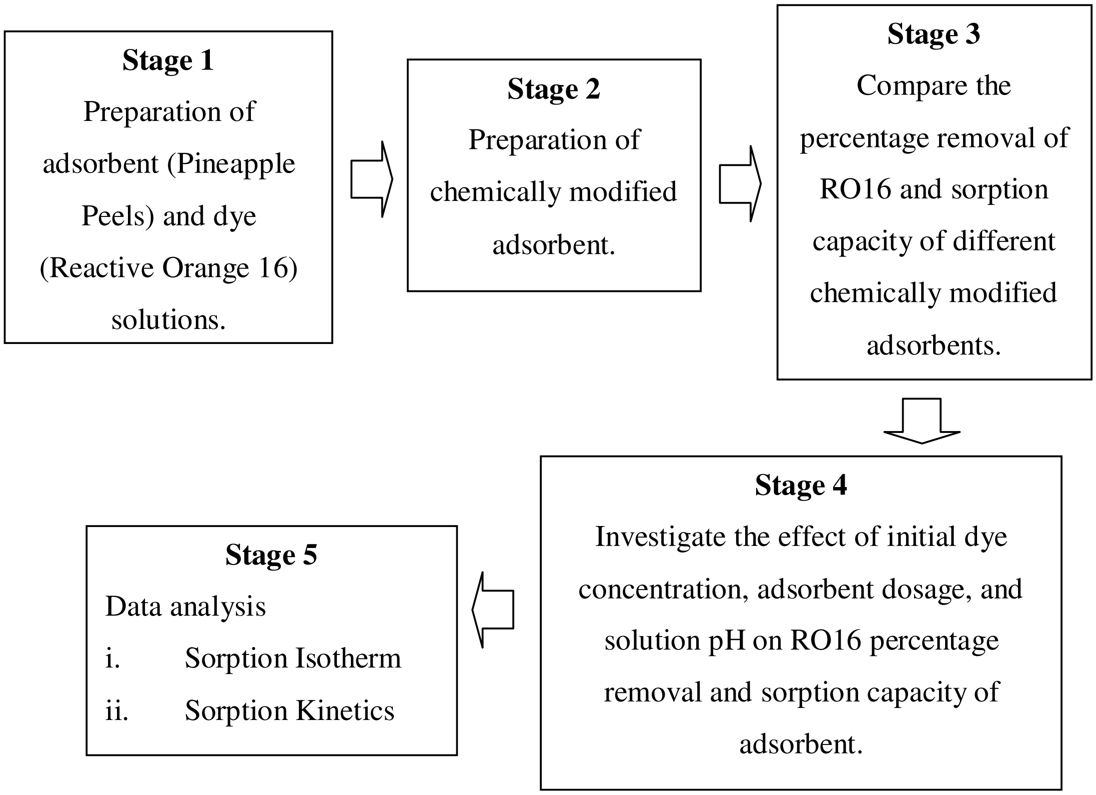

Figure 3.1: Flow Chart of the Experiment Design.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Effect of Chemical Treatment on Pineapple Peels for RO16 Removal

Effect of chemically modified adsorbent on Reactive Orange 16 (RO16) removal were investigated by pre-treating the pineapple peels with five different chemicals, namely 0.1 M hydrochloric acid (HCL), 1.2M nitrilotriacetic acid (NTA), 0.2 M calcium chloride ($CaCl_2$) solution, 0.1 M formaldehyde, and 0.1 M sodium hydroxide (NaOH) solution. Table 4.1 and Figure 4.1 present the performance of each pretreatment technique on pineapple peel in removal of RO16 from synthetic dye solution.

Table 4.1: Dye Percentage Uptake and Sorption Capacity of Chemically Treated Adsorbent at Equilibrium.

Chemical Used for Pretreatment	Percentage Uptake (%)	Sorption Capacity (mg/g)
Hydrochloric Acid (HCL)	0.37	0.04
Nitrilotriacetic Acid (NTA)	15.70	1.62
Natural	19.14	2.12
Calcium Chloride ($CaCl_2$)	29.08	2.94
Formaldehyde	50.59	5.18
Sodium Hydroxide (NaOH)	66.97	6.65

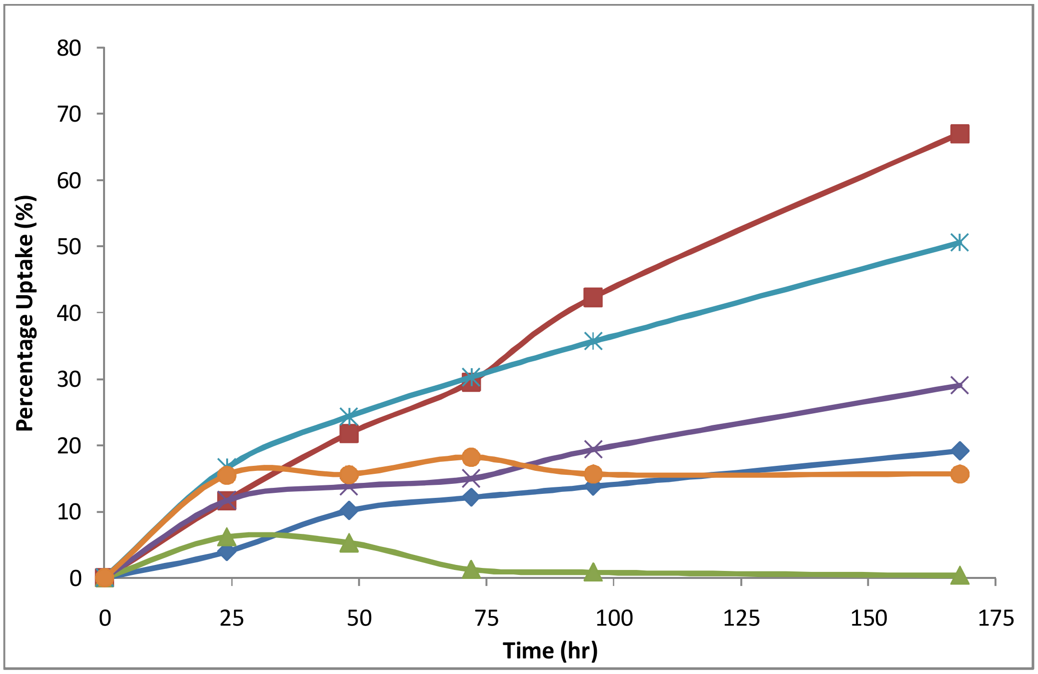

Figure 4.1: Percentage Uptake of RO16 by Chemically Modified Pineapple Peels.

[Symbols: (■) – NaOH-treated; (✳) – Formaldehyde-treated;
(×) – CaCl$_2$-treated; (◆) – Natural; (●) – NTA-treated;
(▲) – HCl-treated]

Based on Table 4.1 NaOH-pretreated peels yields the best result among the pretreatment technique employed. It shows the highest percentage of dye uptake and biosorbent sorption capacity at equilibrium. This is followed by formaldehyde, calcium chloride, natural (non-treated), nitrilotriacetic acid, and lastly hydrochloric acid-pretreated peels.

As observed from Figure 4.1, pineapple peels pretreated with acid solution exhibited poor adsorption result while base treatment performed better. According to Sung, Sun, & Yeoung (2006), the primary group responsible for RO16 bindings are amine group which contributes to negative charges of RO16. Therefore, RO16 molecules are likely to attract to positive charged adsorbent. This reflects that acid treatment which usually provides positive H$^+$ to adsorbent surface would gives a better result and this is in contrary with results achieved in the present study.

This suggest that the natural binding site on pineapple peels might suffer from corrosive effect of acid treatment as reported by Huang, C. & Huang, C.P. (1996) in their adsorption study, thus causing the poor adsorption process of acid treated pineapple peels. On the other hand, base treatment such as NaOH may introduce Na^+ ions to the adsorbent surface, thereby improving the overall adsorption performance.

Further explanations on these findings required detail understanding on the functional group and surface charges of pineapple peels which requires certain analysis such as Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). However, these equipments were unavailable at the time of experiment. Therefore, future works are required in order to provide more detail information regarding the functional group and adsorption mechanism that occur on the surface of pineapple peels before and after chemical modification.

From this point onwards, the experiment was conducted using chemically modified pineapple peels which yield the best result in RO16 removal. In view of satisfactory performance of NaOH-pretreated peels in adsorption of RO16, it was used as key biosorbent for subsequent study.

4.2 Effect of Initial Dye Concentration of RO16

Figure 4.2 and Figure 4.3 shows effect of initial dye concentration of Reactive Orange 16 (RO16) on percentage uptake of dye and sorption capacity of the NaOH-pretreated pineapple peels towards RO16. Table 4.2 exhibits overall performance of NaOH-treated pineapple peels in solution containing various initial concentration of RO16.

Figure 4.2 exhibits a decreasing trend of percentage uptake with increasing of initial dye concentration. As the initial dye concentration used increasing from 20 to 170 mg/L, the equilibrium % uptake of Reactive Orange 16 (RO16) decreased from 66.32% to 54.58%. The lower uptake at higher concentration may be attributed to an increase in ratio of initial number of moles of dye to the available surface area. For a given adsorbent dose, the total number of available adsorption sites is fixed, thereby adsorbing almost the same amount of dye, thus resulting in a decrease in the percentage removal of the dye corresponding to an increase in initial dye concentration (Yeddou-Mezenner, 2010).

Table 4.2: Performance of NaOH-treated Pineapple Peels in Solution with Different Initial Dye Concentration at Equilibrium Condition.

Initial Dye Concentration (mg/L)	Percentage Uptake (%)	Sorption Capacity (mg/g)
40	66.32	2.56
80	64.04	5.07
100	63.51	6.31
120	62.54	7.70
170	54.58	9.30

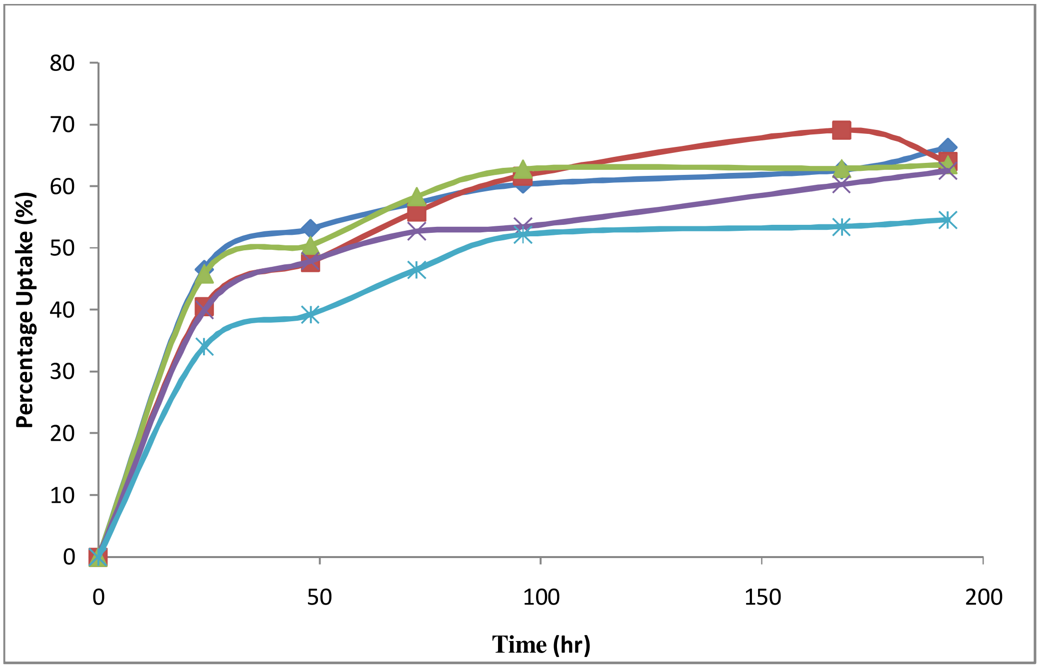

Figure 4.2: Percentage Uptake of RO16 at Equilibrium in Different Initial Dye Concentration.

[Symbols: (◆) – 40 mg/L; (■) – 80 mg/L; (▲) – 100 mg/L; (×) – 120 mg/L; (✳) – 170 mg/L]

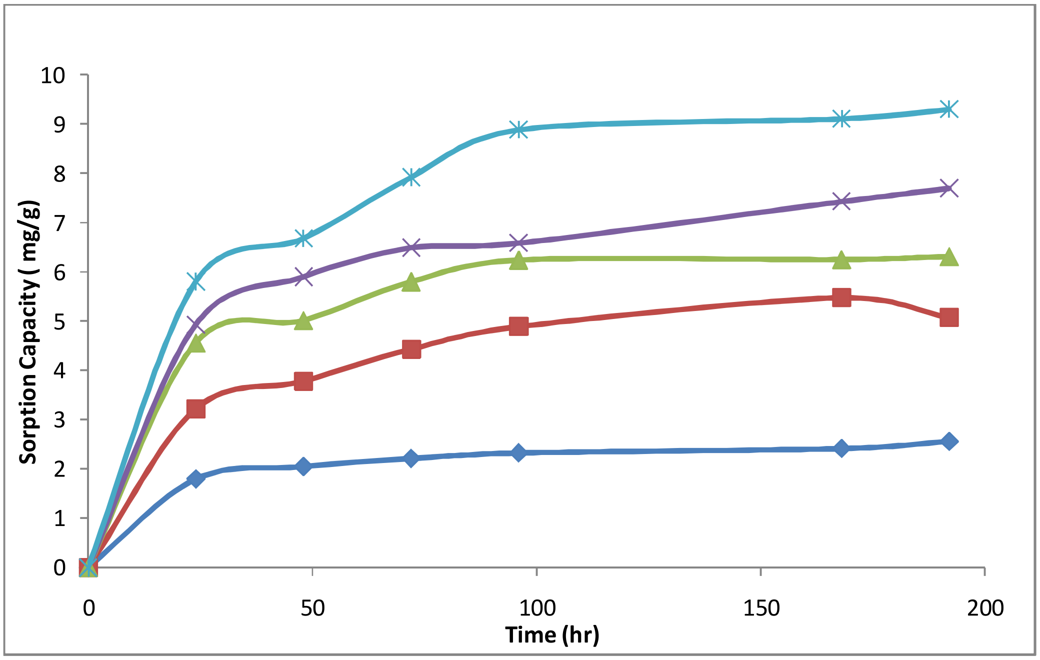

Figure 4.3: Sorption Capacities of NaOH-Treated Pineapple Peels at Equilibrium in Different Initial Dye Concentration.
[Symbols: (◆) – 40 mg/L; (■) – 80 mg/L; (▲) – 100 mg/L; (×) – 120 mg/L; (✳) – 170 mg/L]

On the other hand, Figure 4.3 shows that the sorption capacity of the adsorbent is directly proportional to the initial dye concentration. The sorption capacity of the peels increased from 2.559 mg/g to 9.299 mg/g as the initial dye concentration increased from 40 to 170 mg/L. The increment in sorption capacity of the biosorbent may be due to the increase of dye quantity which resulted in higher concentration gradient of the dye, thus leading to higher sorption capacity (Yeddou-Mezenner, 2010).

The trend in Figure 4.3 and Figure 4.4 also indicates a rapid adsorption rate of RO16 at the beginning which decreased gradually with time. The variation in the extent of adsorption may be attributed to the fact that initially all sites on the surface of the sorbent were vacant and the dye concentration gradient was relatively high. Consequently, the adsorption rate decreases significantly with the increase of contact time due to the decrease in the number of vacant sites on the surface of the adsorbent. Furthemore, as time goes by, the remaining vacant sites are difficult to occupy due to the repulsive forces between the dye molecules on the adsorbent surface (Hamdaoui, Saoudi, Chiha, & Naffrechoux, 2008).

4.3 Effect of Adsorbent Dosage on RO16 removal

The amount of NaOH-treated pineapple peels used to remove Reactive Orange 16 (RO16) were varied from 1 g to 3 g for investigation of the relationship between adsorbent dosage and dye removal performance. Figure 4.4 exhibits the effect of adsorbent dosage on the percentage uptake of RO16 while overall performance of the process is illustrated in Table 4.3.

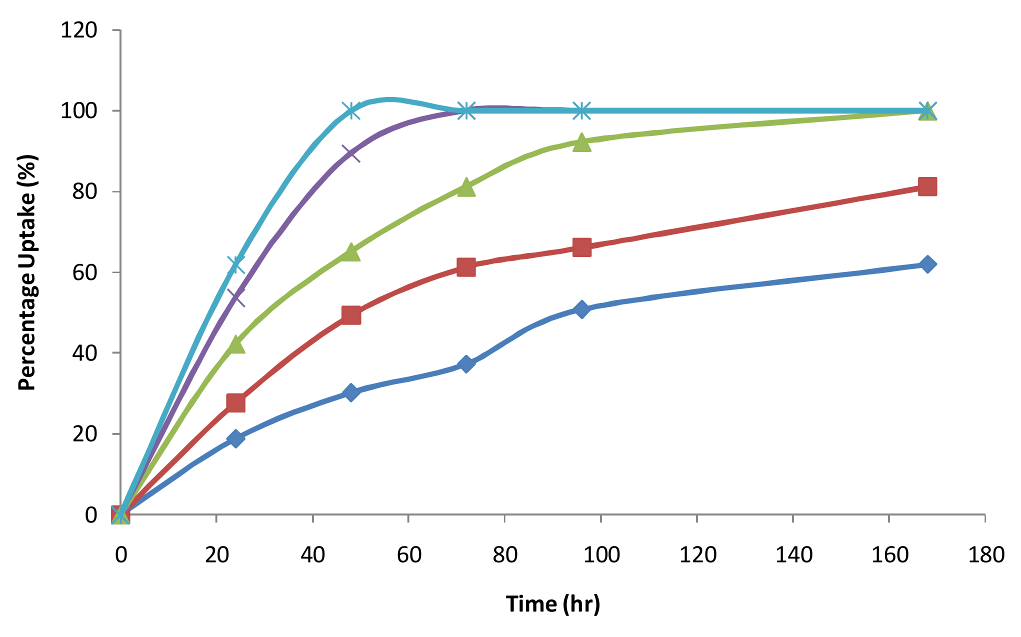

Figure 4.4: Percentage Uptake of RO16 at Equilibrium for Different Adsorbent Dosage.

[Symbols: (◆) – 1 g; (■) – 1.5 g; (▲) – 2 g; (×) – 2.5 g; (✳) – 3 g]

Table 4.3: Dye Percentage Uptake and Sorption Capacity of Biosorbent at Equilibrium Condition Using Different Adsorbent Dosage.

Adsorbent Dosage (g)	Percentage Uptake (%)	Sorption Capacity (mg/g)
1.0	62.01	6.48
1.5	81.17	5.64
2.0	100	5.03
2.5	100	4.11
3.0	100	3.39

From Figure 4.4, it can be seen that the % uptake of RO16 is directly proportional to adsorbent dosage. The more amount of adsorbent use, the higher the percentage uptake of RO16 where the percentage uptake of RO16 increase from 62% at 1 g to 100% at 2 g and above. The reason for such behavior may be attributed to greater surface area and large number of vacant biosorption sites thus favoring more dye biosorption (Gong, Ding, Li, Yang, Liu, & Sun, 2005). From the study, 2 g adsorbent dosage was sufficient to achieve maximum removal of dye from a solution of 100 mg/L and further increase in the biosorbent concentration did not affect the percentage of RO16 removal.

As observed from Table 4.3, sorption capacity of sorbent decreased with increasing of adsorbent dosage, from 6.48 mg/g at 1g of sorbent to 3.39 /g at 3g sorbent. This may be due to the increase in vacant sorption site to dye molecules ratio with increasing biosorbent dosage (with dye concentration fixed at 100 mg/g) while the amount of adsorbent dosage increased. Similar findings were reported by Ozer, Akaya, & Turabik (2006).

4.4 Effect of pH

Effect of pH on the removal of Reactive Orange 16 (RO16) dye were investigated by varying the pH of the dye solution using 5M NaOH and 5M H_2SO_4. The pH chosen for studies are pH 1, pH 3, pH 5, and pH 7. At pH above 8, the colour of RO16 change irreversibly indicating an alteration in the structure of RO16 molecules (Sung, Sun, & Yeoung, 2005). Therefore, pH above 8 cannot be used for this experiment since the solution that changed colour was no longer RO16. The effect of pH on percentage uptake of RO16 and sorption capacity of pineapple peels were shown in Figure 4.5 while Table 4.4 provides information on both the parameters at equilibrium condition.

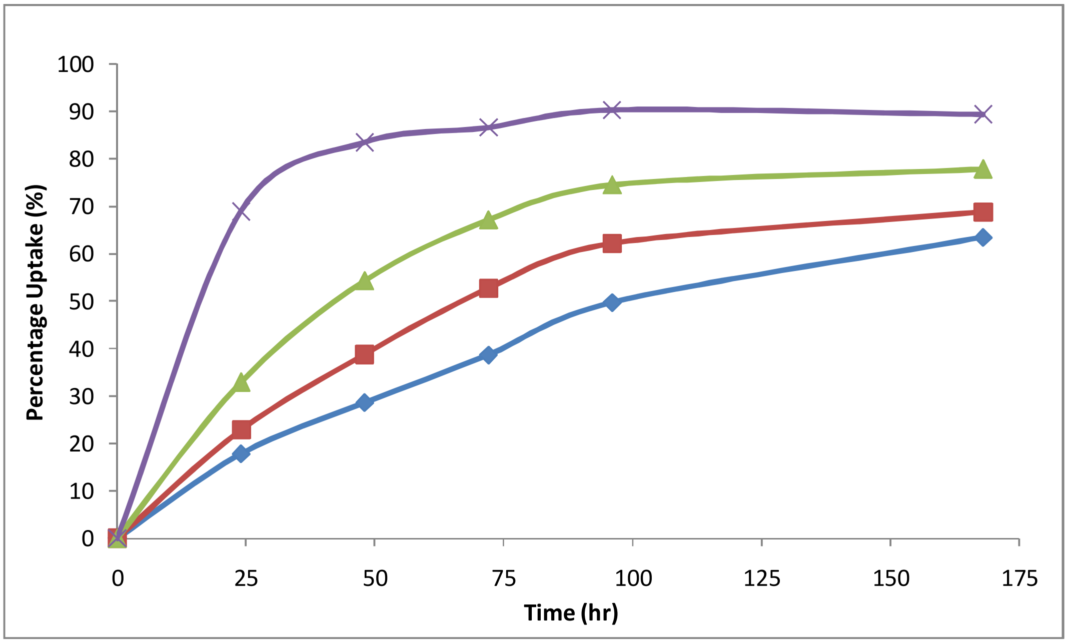

Figure 4.5: Percentage Uptake of RO16 at Different pH.
[Symbols: (◆) – pH 7; (■) – pH 5; (▲) – pH 3; (×) – pH 1]

Table 4.4: Dye Percentage Uptake and Sorption Capacity of Biosorbent at Equilibrium Condition Using Different pH.

pH	Percentage Uptake (%)	Sorption Capacity (mg/g)
1	89.35	8.89
3	77.84	8.00
5	68.77	7.16
7	63.44	6.65

Figure 4.5 shows that the percentage uptake of Reactive Orange 16 (RO16) is inversely proportional to solution pH. The highest % uptake of RO16 is 89.35% and the highest sorption capacity is 8.89 mg/g occurs at pH 1. Therefore, it can be concluded that acidic pH boost the performance and efficiency of RO16 removal.

Similar trend was reported by previous researcher as well. By using Fourier transform infrared spectroscopy (FTIR), Sung, Sun, & Yeoung (2005) reported that primary amine groups were likely to have been responsible for RO 16 binding. As the pH of solution decreases, the number of binding sites for negatively charged amine increased and, thereby, the uptake of RO 16 increased.

4.5 Adsorption Isotherm

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Equilibrium studies in adsorption give the capacity of adsorbent. It is described by adsorption isotherm characterised by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. In this study, the equilibrium data obtained experimentally were fitted to two most common models, the Langmuir and Freundlich isotherm model.

The Langmuir theory assumes that biosorption occurs at specific homogeneous sites within the biosorbent. The linearised form of Langmuir isotherm (as shown in Equation 4.1) was used to characterise the adsorption process of RO16 onto pineapple peels. A Langmuir isotherm plot of $1/q_e$ against $1/C_e$ is shown in Figure 4.6.

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{bq_{max}}\right)\left(\frac{1}{C_e}\right) \tag{4.1}$$

where,

q_e = Equilibrium dye concentration on adsorbent at any time (mg/g)

q_{max} = maximum of Langmuir monolayer adsorption capacity (mg/g)

b = Langmuir constant (L/mg)

C_e = Equilibrium dye concentration in sample (mg/L)

The Freundlich isotherm (Freundlich, 1906) is the earliest known relationship describing the sorption equation. It gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies (Emin, Colgecen, & Donat, 2004). Equation for Freundlich isotherm is given by Equation 4.2. The plot of log q_e versus log C_e is shown in Figure 4.7

$$log q_e = log k_f + \left(\frac{1}{n}\right) log C_e \tag{4.2}$$

where,

q_e = Equilibrium dye concentration on adsorbent at any time (mg/g)

k_f = Freundlich constant (mg/g $(1/\text{mol})^{1/n}$)

1/n = exponential constant

C_e = Equilibrium dye concentration in sample (mg/L)

All the corresponding values of interest for Langmuir and Freundlich isotherm were calculated and tabulated in Table 4.5.

Table 4.5: Parameters of Langmuir and Freundlich Isotherm Equations.

Langmuir Isotherm			**Freundlich Isotherm**		
q_{max} (mg/g)	b (L/mg)	R^2	k_f	n	R^2
26.18	0.0084	0.996	0.31	1.21	0.989

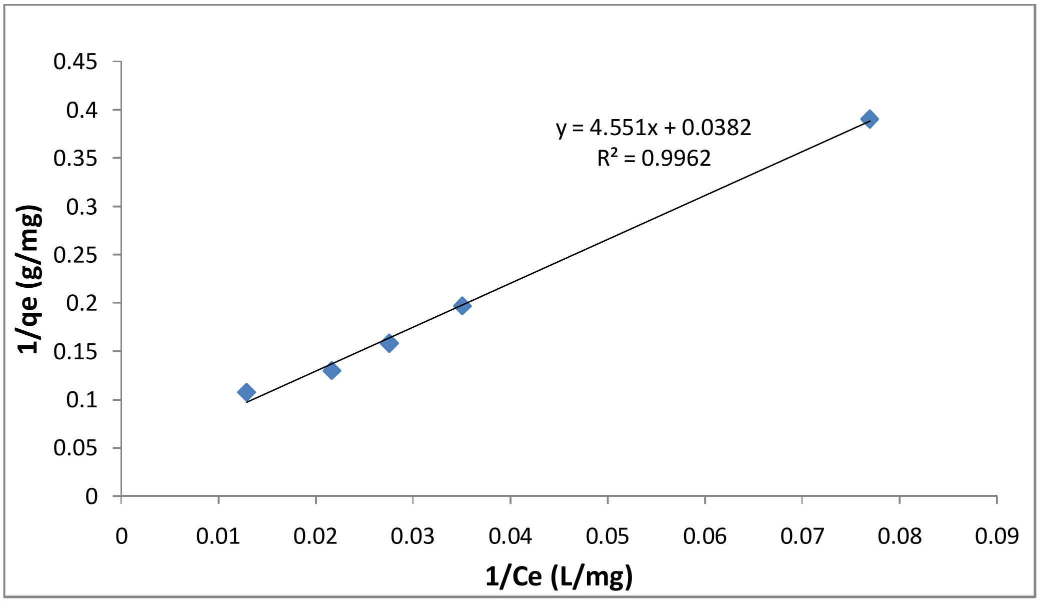

Figure 4.6: Langmuir Isotherm Plot.

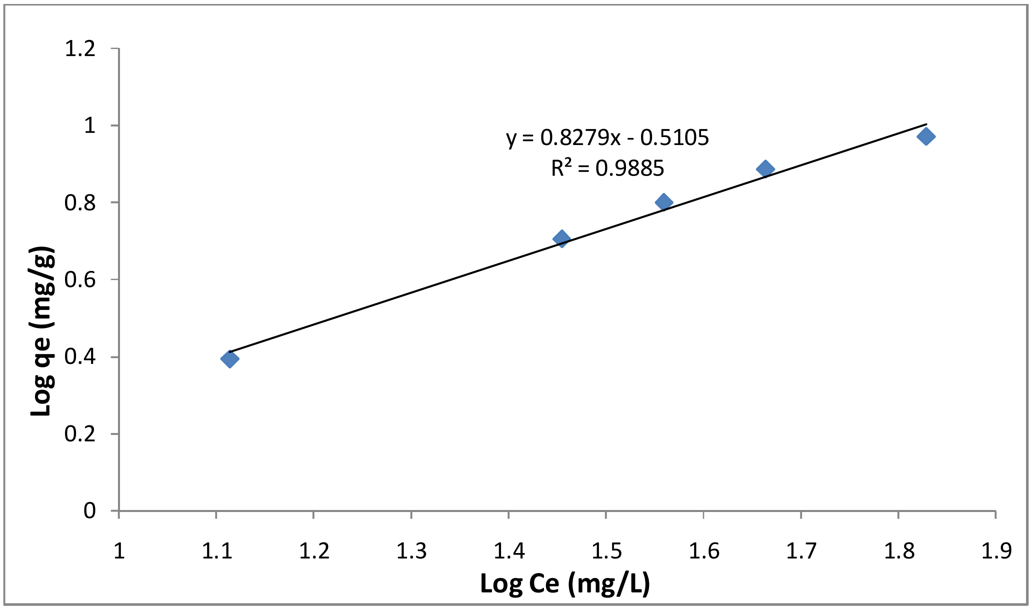

Figure 4.7: Freundlich Isotherm Plot.

Figure 4.6 and Table 4.5 shows that the adsorption process of Reactive Orange 16 (RO16) by NaOH-treated pineapple peels at different initial dye concentration fits very well with Langmuir isotherm model. The high correlation coefficient value of 0.996 suggested that the Langmuir isotherm might be a suitable isotherm model. It was thus, concluded that the biosorption process of RO16 by NaOH treated pineapple peels exhibit monolayer biosorption, and the maximum monolayer biosorption capacities were found to be 26.18 mg/g. The Langmuir constant, *b*, can be used to determine the suitability of using pineapple peels for the biosorption of RO16 using the Hall separation factor (R_L) as follows (Nadeem et al., 2008):

$$R_L = \frac{1}{1 + bC_0} \tag{4.3}$$

where C_0 is the highest initial dye concentration (mg/L). R_L value at different initial dye concentration is calculated using Equation 4.3 and tabulated in Table 4.6.

Table 4.6: Constant Separation Factor for Different Initial Dye Concentration.

Initial Dye Concentration, C_0 (mg/L)	Constant Separation Factor, R_L (dimensionless)
40	0.749
80	0.598
100	0.544
120	0.498
170	0.412

R_L is the constant separation factor (dimensionless) and can be used for interpretation of the sorption type as below (Dahiya, Tripathi, & Hegde, 2008):

$R_L > 1$, unfavorable
$R_L < 0$, unfavorable
$R_L = 1$, favorable (linear)
$0 < R_L < 1$, favorable
$R_L = 0$, irreversible

In this study, R_L values for different initial dye concentration are found in between 0.412 and 0.749, and this, along with the shape of the curve of the data

(Figure 4.6) indicates that the biosorption of RO16 by NaOH-treated pineapple peels is favorable.

Freundlich isotherm model assumes that the biosorption process takes place on heterogeneous surfaces. Based on Figure 4.7 and Table 4.5, it can be seen that the adsorption of RO16 onto NaOH treated pineapple peels is also well described by Freundlich isotherm model. In this study, k_f values were found to be 0.31. The value of k_f indicates the ease of separation of RO16 dyes ions from aqueous solution (Ahalya, Kanamadi, & Ramachandra, 2005) and in this case, it is quite low. This shows that the removal of RO16 is difficult which again verified the fact that the biosorption of reactive dyes is more challenging compared to other normal dyes. $1/n$ gives an indication of the favorability of biosorption and the values of $n>1$ represent favorable biosorption condition (Vadivelan & Kumar, 2005). In this study, n values were found to be 1.21 and this indicates that the adsorption intensity is favourable over the entire range of concentrations studied.

Overall, the result of adsorption isotherm analysis indicates that the adsorption of RO16 onto NaOH-treated pineapple peels exhibit both Langmuir and Freundlich isotherm model characteristic reflecting the presence of more than one kind of adsorbent–adsorbate surface interaction.

4.6 Adsorption Kinetics and Modelling

The kinetic adsorption data were processed to understand the dynamics of adsorption process in terms of the order of rate constant (Ahmad, Hameed & Aziz, 2007). In this study, three kinetic models were used, including the pseudo-first-order model, pseudo-second-order model, and Weber-Morris intraparticle diffusion model. The pseudo-first-order rate expression is given by Equation 4.4.

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \tag{4.4}$$

where,

q_e= Equilibrium dye concentration on adsorbent at any time (mg/g)

q_t = amount of dye uptake (mg/g) at time, t (hr)

k_1= rate constant of pseudo-first-order biosorption, (hr^{-1})

A graph of log (q_e – q_t) versus t were plotted using adsorption data of RO16 onto NaOH treated pineapple peels at different initial dye concentrations and shown in Figure 4.8. On the other hand, pseudo-second-order kinetic model is expressed in Equation 4.5 and applicability of pseudo-second-order-kinetic model in this biosorption was investigated by plotting $^1/_{q_t}$ against t in Figure 4.9.

$$\frac{1}{q_t} = \frac{1}{k_2 {q_2}^2} + \frac{1}{q_e} t \qquad (4.5)$$

where,

k_2= equilibrium rate constant pseudo-second-order (g/mg hr)

h ($k_2 {q_2}^2$) = initial sorption rate (mg/g hr)

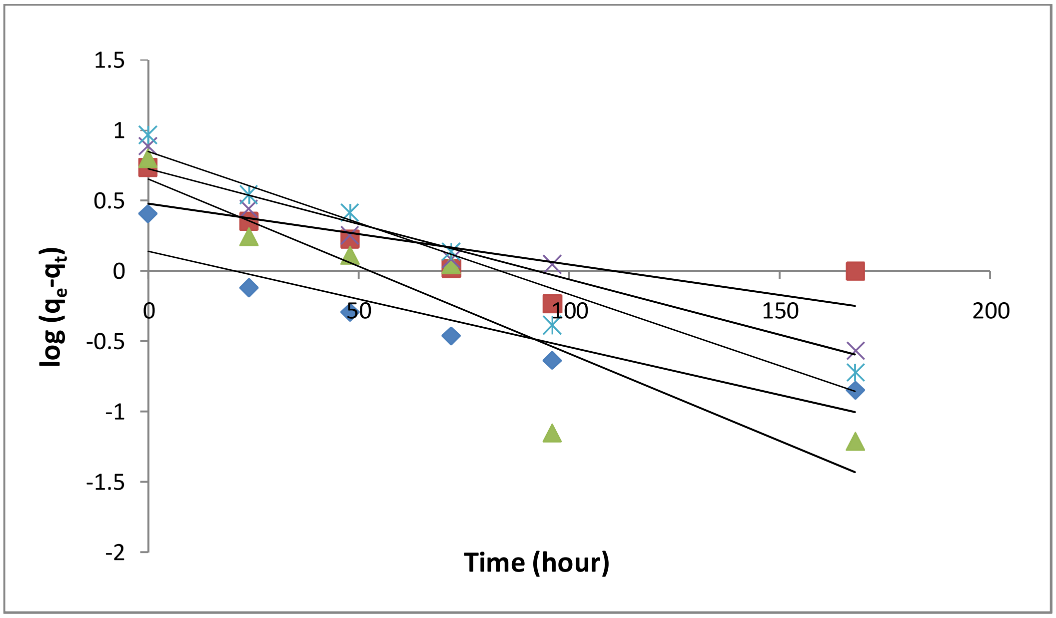

Figure 4.8: Pseudo-First-Order Sorption Kinetic Plots of RO16 Biosorption on NaOH Treated Pineapple Peels.

[Symbols: (◆) – 40 mg/L; (■) – 80 mg/L; (▲) – 100 mg/L; (×) – 120 mg/L; (✳) – 170 mg/L]

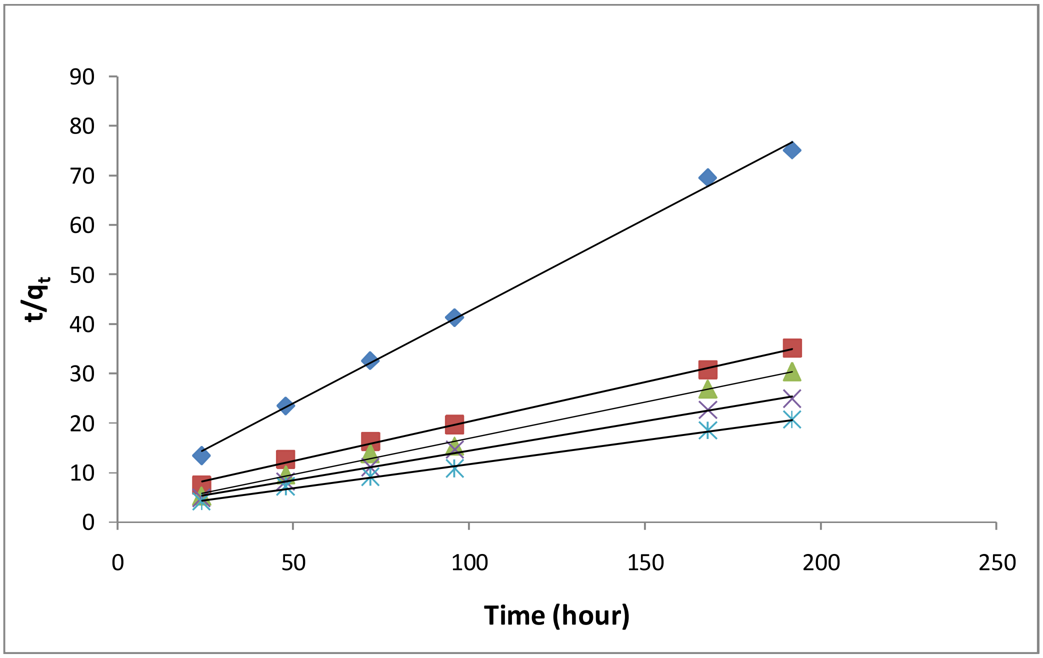

Figure 4.9: Pseudo-Second-Order Sorption Kinetic Plots of RO16 Biosorption on NaOH Treated Pineapple Peels.
[Symbols: (◆) – 40 mg/L; (■) – 80 mg/L; (▲) – 100 mg/L;
(×) – 120 mg/L; (✳) – 170 mg/L]

Pseudo-first-order rate constant (k_1), pseudo-second-order rate constant (k_2), and $q_{e,\mathrm{cal}}$ were determined from the slope and intercepts of the graph in Figure 4.8 and Figure 4.9 respectively. These parameters were then tabulated in Table 4.7.

Table 4.7: Important Paramaters of Pseudo-First-Order and Pseudo-Second-Order Biosorption Kinetic Models.

Concentration (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo First Order			Pseudo Second Order		
		k_1	$q_{e,cal}$	R^2	k_2	$q_{e,cal}$	R^2
40	2.5586	0.0157	1.3775	0.8519	0.0260	2.6882	0.9978
80	5.4740	0.0099	3.0095	0.5795	0.0057	6.2972	0.9976
100	6.3117	0.0286	4.4802	0.8347	0.0096	6.8213	0.9952
120	7.6975	0.0182	5.3272	0.9515	0.0059	8.3752	0.9973
170	9.2994	0.0233	7.0990	0.9445	0.0046	10.3199	0.9971

The suitability of a kinetic models in describing the biosorption process depends on the approximation of the $q_{e,\mathrm{cal}}$ calculated from the kinetic model plots towards $q_{e,\mathrm{exp}}$ obtained experimentally and the value of correlation coefficient (R^2). Theoretically, when R^2 value is nearer to 1.0, the fit of data is considered to be excellent.

From Table 4.7, it can be observed that the theoretical $q_{e,\mathrm{cal}}$ values calculated from pseudo-first-order kinetic model did not give reasonable values with regard to the experimental uptake ones, $q_{e(\mathrm{exp})}$. Furthermore, the R^2 value for each concentration in pseudo-first-order kinetic model are lower compared to its counterpart in pseudo-second-order kinetic model and none of it exceed 0.99 with the lowest being 0.5795 at 80 mg/L initial dye concentration while highest being 0.9515 at 120 mg/L initial dye concentration. These suggest that the present adsorption system does not follow pseudo-first-order process.

On the other hand, the theoretical $q_{e,\mathrm{cal}}$ values agree quite well with the experimental uptake value, $q_{e,\mathrm{exp}}$ in the case of pseudo-second-order kinetic model. Besides this, the correlation coefficient (R^2) for the pseudo-second-order kinetic model for each initial dye concentration is closer to unity compared to its counterpart in pseudo-first-order kinetic model, with all exceeding 0.99 suggesting that the present adsorption system can be described more favorably by pseudo-second-order process. This supports the validity of the basic assumption in pseudo-second-order kinetic model that chemisorptions or an effective electrostatic interaction plays a major role in the adsorption (Yeddou-Mezenner, 2010).

The kinetic data of Reactive Orange 16 (RO16) biosorption onto sodium hydroxide (NaOH) treated pineapple peels at different initial dye concentration was further analyzed using Weber and Morris intraparticle diffusion model. The intraparticle diffusion model proposed by Weber and Morris has been widely applied for the analysis of adsorption kinetics. According to this model, a plot of q_t versus $t^{1/2}$ should be a straight line from the origin if the adsorption mechanism follows the intraparticle diffusion process only. However, if data exhibit multi-linear plots, then the process is governed by two or more steps. The intraparticle diffusion equation is shown in Equation 4.6. Figure 4.10 shows a graph of q_t versus $t^{1/2}$ plotted using the same biosorption kinetic data mentioned above.

$$q_t = k_{id}t^{1/2} + C \tag{4.6}$$

where,

k_{id} = intraparticle diffusion rate constant (mg/g min$^{1/2}$)

C = intercept related to the thickness of the boundary layer

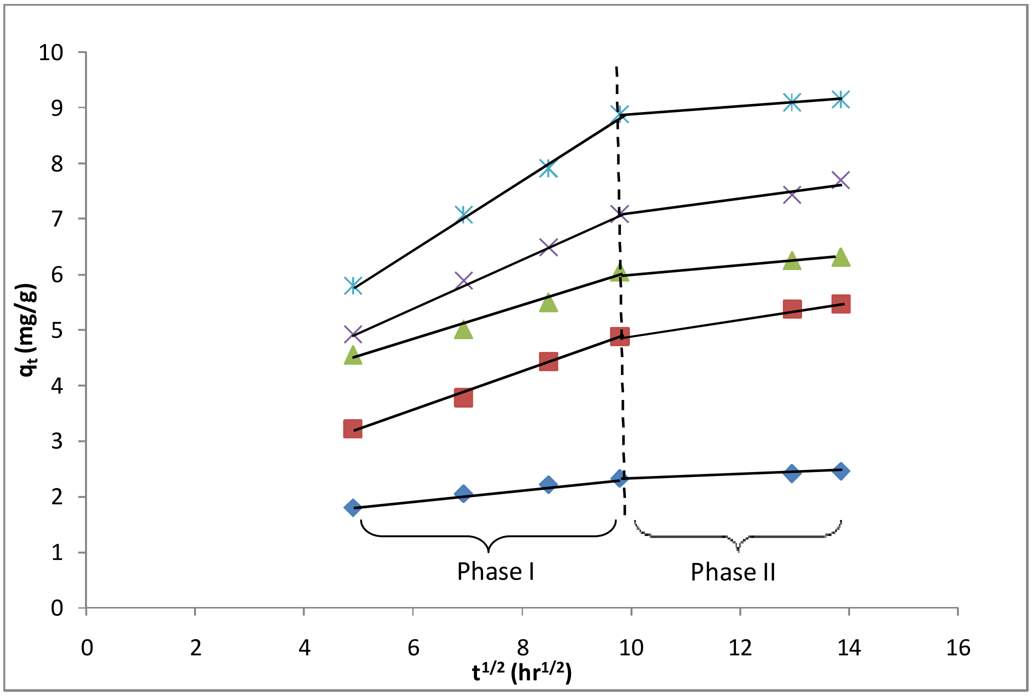

Figure 4.10:Weber and Morris Intraparticle Diffusion Model Plots of RO16 Biosorption on NaOH Treated Pineapple Peels.
[Symbols: (◆) – 40 mg/L; (■) – 80 mg/L; (▲) – 100 mg/L; (×) – 120 mg/L; (✳) – 170 mg/L]

Theoretically, Figure 4.10 would yield a straight line if the adsorption process obeyed the intra-particle diffusion model (Yeddou-Mezenner, 2010) and if these lines pass through the origin, then intraparticle diffusion is the rate controlling step (Tsai, Hsien, & Yang, 2004). When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further indicates that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously (Akar, T., Anilan, Gorgulu, & Akar, S.T., 2009). The values of the intercept, *C* give an idea about the thickness of boundary layer, where the larger the intercept, the greater the boundary layer effect.

Figure 4.10 shows that the adsorption plots of sodium hydroxide (NaOH) treated pineapple peels are not linear over the whole time range and can be separated into two linear regions. This indicates that there are two adsorption stages taking place. Lorenc-Grabowska and Gryglewicz (2007) explained such multi-linearity stages. The first linear portion (phase I) can be attributed to external surface adsorption where the dye molecules of Reactive Orange 16 (RO16) diffuses through the solution to the external surface of the adsorbent or the boundary layer diffusion of dye molecules with high adsorption rate. The second portion (phase II) illustrates the gradual adsorption stage, where slow diffusion of the dye molecules from the surface site into the inner pores occur. Apart from this, it can also be observed that the straight line did not pass through the origin. This indicates that boundary layer of certain thickness exists in the NaOH treated pineapple peels and the intraparticle diffusion was not the only rate controlling step (Yeddou-Mezenner, 2010).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

The result from this research proves that pineapple peels is a potential adsorbents for removal of Reactive Orange 16 (RO16) from aqueous solutions. Pretreatment of pineapple peels with sodium hydroxide (NaOH) shows the most promising result. The adsorption of RO16 using NaOH treated pineapple peels are affected by three parameters, namely initial dye concentration, adsorbent dosage, and pH of solutions. From the result obtained, conclusion can be drawn that percentage of dye removal is inversely proportional to initial dye concentration, directly proportional to adsorbent dosage, and acidic condition is favourable for sorption process of RO16 by NaOH-pretreated pineapple peels. Adsorption isotherms analysis indicates that the present adsorption exhibit both Langmuir and Freundlich isotherm model characteristic, reflecting the presence of more than one kind of adsorbent–adsorbate surface interaction. Thus, both monolayer and heterolayer adsorption exist on the surface of biosorbent. The adsorption kinetics data of RO16 fitted well to pseudo-second-order kinetic model with high correlation coefficient that exceeds 0.99. This indicates that chemisorptions or an effective electrostatic interaction plays a major role in the present adsorption process. Finally, plotting of adsorption kinetics data using Weber and Morris intraparticle diffusion model reveals that boundary layer of certain thickness exists in the NaOH treated pineapple peels and the intraparticle diffusion was not the only rate controlling step.

As regards to future work, the following recommendations are suggested:

a) Further study of surface functional groups before and after treatment as well as before and after adsorption process using Fourier transform infrared spectroscopy

(FTIR) and X-ray photoelectron spectroscopy (XPS).

b) Investigate the performance of pineapple peels as biosorbent for other type dyes.
c) Since real textile industries wastewater contain a mixture of dyes and other pollutants, further study should be conducted on the performance of pineapple peels in removing real dye effluents from industries.
d) Pilot-plant scale studies to check the feasibility of using pineapple peels as biosorbent for dye removal at industries level.

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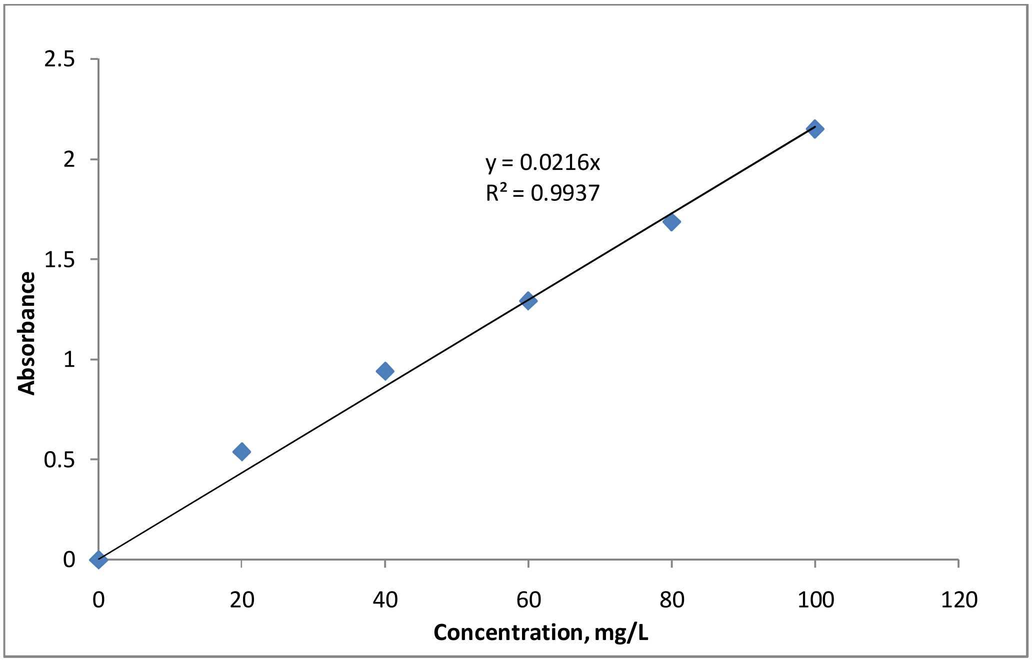
APPENDICES

APPENDIX A: STANDARD CURVE



Calibration Curve of RO16