# BIOSORPTION OF IRON (II) AND METHYLENE BLUE USING TEA WASTE

**NUR IZDIHARR BINTI ZAINOL**

**UNIVERSITI MALAYSIA PAHANG**

**TABLE OF CONTENT**

## LIST OF TABLE

## LIST OF FIGURE

## LIST OF ABBREVIATION

| | |
|---|---|
| MB | - Methylene Blue |
| TW | - Tea Waste |
| UV | - Ultra Violet |
| INN | - International Nonproprietary Name |
| µm | - micrometer |

## LIST OF APPENDICES

# BIOSORPTION OF IRON (II) AND METHYLENE BLUE USING TEA WASTE

**NUR IZDIHARR BINTI ZAINOL**

**A thesis submitted in fulfillment of the**

**requirements for the award of the degree of**

**Bachelor of Chemical Engineering (Biotechnology)**

**Faculty of Chemical & Natural Resources Engineering**

**Universiti Malaysia Pahang**

**DISEMBER 2010**

I declare that this thesis entitled " Biosorption of Iron (II) and Methylene Blue using Tea Waste" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and not concurrently submitted in candidature of any other degree.

| | | |
|---|---|---|
| Signature | : | …………………………..... |
| Name | : | Nur Izdiharr Binti Zainol |
| Date | : | 3rd December 2010 |

Special dedication of this grateful feeling yo my

**Beloved father and mother:**

Mr. Haji Zainol Bin Haji Saad and Mrs Hajjah Amah Binti Lazim

**Loving brothers and sisters:**

Ili Ajlaa, Muizz Zaffan, Ahmad Amzaar Palem and Siti Zulfa Palem

**Supportive Aunty:**

Miss Noorsiah Binti Lazim

For their loves, supports and best wishes.

## ACKNOWLEDGEMENT

In the Name of Allah, the Most Gracious, the Most Merciful

First of all, Alhamdulillah, praise to Allah S.W.T, The Sustainer of this world. With all His blessing I had completed my final year project with smoothly and successfully. With this chance, I would like to show my deepest gratitude and thankful to my supervisor Dr. Ir. Said Nurdin for his guidance, inspiration, patiet and support in my final year project.

Furthermore, I would like to thank my lovely family for their helps and supports. They were very supportive and always be a helpful person if I needed someone.

Besides that, I want to express my sincere appreciation to Mr. Zaki Bin Sahad and technical academics for guiding me during my experiment for my research at the laboratory. I also would like to thank all my friends especially my roommates, my classmates and UMP staffs that help me to finish this project.

**ABSTRACT**

The used of tea waste as a low-cost natural biosorbent for the removal of heavy metals and dyes had been investigated. The high concentration of Iron (II) and methylene blue caused environment problem. The purpose of this study is to investigate the capability of tea waste as the biosorbent in removal of Iron (II) and methylene blue from aqueous solution in laboratory scale. Batch experiments were conducted to determine the effects of varying biosorbent dosage, pH and contact time of adsorption.. Tea waste was prepared by dried with 60°C for 24 hours, blended and sieved into 400µm. This experiment was carried out in conical flasks within initial concentration for methylene blue is 10mg/L and Iron (II) solution is 500mg/L. Then agitated in orbital shaker CERTOMAT S-II with oscillation 200rpm. For methylene blue, UV-Vis Spectrophotometer had been used to measure the absorbance while HACH Spectrophotometer DR/2400 was used to measure the final concentration of the Iron solution. The biosorption was found to be maximum dosage is 1.0g for both solution. For parameter contact time, the biosorption started to be constant at 330 minutes for iron solution and 180 minutes for methylene blue. By varying pH range of 1 – 12, the optimum removal of Iron (II) achieved at pH 6 and methylene blue at pH 8. As the conclusion, tea waste can remove 95% - 99% Iron(II) and 85% - 99% Methylene Blue. Tea waste can be very suitable for development as an efficient biosorbent in removing Iron(II) and methylene blue for wastewater treatment.

# ABSTRAK

Kajian tentang kegunaan hampas teh sebagai biosorben berkos rendah untuk menghilangkan logam berat dan pewarna telah dijalankan. Penyelidikan ini dapat memberikan cara alternatif untuk menghilangkan logam berat dan bahan pewarna yang telah menyebabkan pada pencemaran alam sekitar. Objectif kajian ini adalah untuk mengetahui kemampuan hampas teh sebagai biosorben dalam pengjerapan Ferum (II) dan metilen biru dari larutan air dalam skala makmal. Eksperimen telah dilakukan untuk menentukan kesan dari beberapa parameter iaitu pH, dos dan masa penjerapan. Hampas teh disediakan dengan mengeringkan pada suhu 60 $^{0}$ C selama 24 jam, dihancurkan dan diayak untuk mendapatkan saiz 400µm. Penyelidikan ini dilakukan dengan kepekatan awal untuk biru metilen adalah 10 mg / L dan Ferum (II) adalah 500mg / L. Sampel akan dibiarkan bertindakbalas dengan serbuk teh pada ayunan kelajuan 200rpm. Alat yang digunakan untuk menganalisis sampel adalah spektrofotometer Ultra Violet dan spektrofotometer HACH model DR/2400. pH yang diubah adalah dalam lingkungan 1 hingga 12. pH yang paling sesuai untuk Ferum (II) adalan pH 5 manakala untuk metilen biru adalah pH 8. Sebagai kesimpulan yang boleh dibuat, peratusan Ferum(II) dan metilen biru yang telah berjaya diserap telah mencapai 95%-99% untuk Ferum(II) manakala 85%-99% untuk metilen biru. Oleh itu, teh adalah sangat sesuai untuk dijadikan bahan penjerap untuk merawat sisabuangan air dari industri.

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

There are too many polluted rivers, seas and others because of existence of heavy metals and dyes in the wastewater. As Malaysia is fast becoming an industrial country, many of the rivers have become polluted due to the many wastes that have been discharge into the rivers and seas. For an example, the paper making industry, it requires chemicals then it often poisonous in its production. The rivers are used as an outlet for the chemicals to drain away, in turn harming the waters and the lives that revolve around them. In Malaysia, 97 % of the effluent discharged is mainly from three industrial categories, which are food industry, chemical industry and textiles industry (Azira *et al*., 2004). Another good example is the construction of a new golf course near the waterfall at tourist attraction Fraser's Hill in the state of Pahang, causing it to become extremely murky and dirty due to the silt and sand that comes from the construction. The waterfall which has been the centre point of the hill has now lost all its attraction just because of the overwhelming need to attract more tourists to the place by building more facilities.

Among various industrial processes, dyes from textile industries produce a large amount of color effluent which is unacceptable under Malaysia environmental regulations besides other parameters such as COD, BOD, dissolved oxygen, total iron, and others (Tan *et al*., 2000). So, the most serious pollution in Malaysia nowadays is water pollution. In the present work, methylene blue is selected as a model compound in order to evaluate the capacity of the adsorbent for the removal of methylene blue from its aqueous solution. Iron(II) sulphate or ferrous sulphate is the chemical compound with the formula Fe(II), known since ancient times as copperas. It is most commonly encountered as the blue-green heptahydrate.

Adsorption of methylene blue and Iron(II) by using tea waste from aqueous solutions was studied to enable comparison with alternative commonly available absorbents. Batch experiments were conducted to determine the factors affecting adsorption and kinetics of the process. Fixed bed column experiments were performed to study practical applicability and breakthrough curves were obtained. Tea waste is capable of binding appreciable amounts of Iron(II) and Methylene Blue from aqueous solutions. The adsorption capacity was highest at solution pH range 7-8. The adsorbent to solution ratio and the metal ion concentration in the solution affect the degree of metal ion removal. Uddin *et al.* (2009) stated that the kinetic data fits to pseudo second order model with correlation coefficients greater than 0.999. Increase in the total adsorption capacity was observed when both Iron(II) and Methylene Blue are present in the solution. Higher adsorption rate and the capacity were observed for smaller adsorbent particles. Tea waste is a better adsorbent compared to number of alternative low cost adsorbents reported in literature.

In this study, tea waste was designed to remove Iron(II) and methylene blue by varying process condition  of contact time, pH and adsorbent dosage. The most optimum condition will be apply in the existing wastewater sources in the industries in Malaysia. This process had gained importance due to its advantages over conventional separation technical such as chemical precipitation, ion exchanges, reverse osmosis, membrane filtration and activated carbon adsorption, which are used to remove toxic metals and dyes from wastewater.

## 1.2 Problem Statement

Based on the previous research, there are a lot of journals about removing methylene blue but there are none for removing Iron(II). It was easier to gather the data for physical properties of methylene blue. I have to find all the data about iron(II) by using other sources. There are a variety of sources that contribute the contamination of the environment which is increasing seriously in these years. Industries were growing in these areas of the world produce large quantities of effluents, which most are hazardous such as dye and iron from textile, fabric and plastics industry.

Most conventional adsorption systems use activated carbon which is expensive and necessitates regeneration, the high cost of activated carbon has stimulated interest in examining the feasibility of using cheaper raw materials. The researcher has been found that another material that more cheap and can get easily which can remove dye and iron in waste water. Tea waste is one of the waste that is almost as rich in potent antioxidants. It is the most effective low cost alternative to remove metals such as Iron(II) from aqueous solution. Thus, Methylene Blue and Iron (II) can be adsorb from aqueous solution during this study.

## 1.3 Objective

The objective of this study are to investigate the bioremoval efficiency of Iron (II) and methylene blue using tea waste and to investigate the effect of pH, contact time and dosage of tea waste in removal of Methylene Blue and Iron(II) from aqueous solution using tea waste.

## 1.4 Scope of Study

In order to achieve the objectives, there are some scopes that should be focused in which are in observation and investigation the effect of process condition for Iron(II) and Methylene Blue can be remove by using tea waste. The determination of the removal percentage can be obtained by analyze the result of initial concentration and final concentration for each variable: pH, Dosage of tea waste and Contact time

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Wastewater

Water contamination with heavy metals discharge from industrial activities and urbanization is very important problem in the current world which can affect the ecosystem of environment and human health. Attention had been paid to find the methods to remove heavy metals from waste water from dispose because they will cause the biological materials that have ability to accumulate heavy metals from wastewater. Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources.( Byrd *et.al.,*1984)

Sewage is correctly the subset of wastewater that is contaminated with feces or urine, but is often used to mean any waste water. Sewage includes domestic, municipal, or industrial liquid waste products disposed of, usually via a pipe or sewer or similar structure, sometimes in a cesspool emptier. Industrial wastewater treatment covers the mechanisms and processes used to treat waters that have been contaminated in some way by anthropogenic industrial or commercial activities prior to its release into the environment or its reuse.

Most industries produce some wet waste although recent trends in the developed world have been to minimize such production or recycle such waste within the production process. However, many industries remain dependent on processes that produce wastewaters. The physical infrastructure, including pipes, pumps, screens, channels etc. used to convey sewage from its origin to the point of eventual treatment or disposal is termed sewerage. ( Byrd *et.al.*,1984)

## 2.2 Heavy Metals

### 2.2.1 Iron

The production of iron from its ores involves powerful reduction reactions in blast furnaces. Cooling waters are inevitably contaminated with products especially ammonia and cyanide. Production of coke from coal in coking plants also requires water cooling and the use of water in by-products separation. Contamination of waste streams includes gasification products such as benzene, naphthalene, anthracene, cyanide, ammonia, phenols, cresols together with a range of more complex organic compounds known collectively as polycyclic aromatic hydrocarbons (PAH).

The conversion of iron or steel into sheet, wire or rods requires hot and cold mechanical transformation stages frequently employing water as a lubricant and coolant. Contaminants include hydraulic oils, tallow and particulate solids. Final treatment of iron and steel products before onward sale into manufacturing includes pickling in strong mineral acid to remove rust and prepare the surface for tin or chromium plating or for other surface treatments such as galvanisation or painting. The two acids commonly used are hydrochloric acid and sulfuric acid. Wastewaters include acidic rinse waters together with waste acid. Although many plants operate acid recovery plants, (particularly those using Hydrochloric acid), where the mineral acid is boiled away from the iron salts, there remains a large volume of highly acid ferrous sulfate or ferrous chloride to be disposed of. Many steel industry wastewaters are contaminated by hydraulic oil also known as soluble oil. Duffus ( 2002)

**Figure2.1** : Iron(II) Sulphate powder

Heavy metals ions such as $Fe^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ are needed in plant metabolism but when they present in excess they can become extremely toxic (sungai Buloh Nature Park, 2001). Iron is one of toxic heavy metals. In plant, Iron is involved in the production of chlorophyll. Iron also one of a component of enzymes and associated with sulfur to produce other compound that can be catalyzed by other reaction. Iron applications go from food containers to family cars, from screwdrivers to washing machines, from cargo ships to paper staples. Steel is the best known alloy of iron, and some of the forms that iron tales include: pig iron, cast iron, carbon steel, and wrought iron, alloy steels, iron oxides. It also has been used in textile industry and ink manufacturing.(Lu *et.al.,* 2004)

## 2.3 Dyes

Dyes can generally be described as a colored substance that has an affinity to the substrate to which it is being applied and it can be applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments appear to be colored because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments.

Dyes and pigments are not commonly used in textile industries but also many other industries such as plastics, paper, food, cosmetics, paints, leather, art and craft, printing inks and rubber. The various treatment methods for the removal of colour and dye are coagulation using alum, lime, ferric sulfate, ferric chloride, chemical oxidation using chlorine and ozone, membrane separation processes, adsorption and so on. Among these methods, adsorption currently appears the best treatment in order to remove colour from wastewater (Walker *et al.*, 1998; Rozada *et al.*, 2003).

Dyes and colour discharged into rivers that meant for public water supply may not meet the drinking water quality standards. Dyes and their degradation products may be carcinogen and toxic if these effluents are treated inefficiently before discharging to the rivers or streams, they could bring negative impact to human health (Kadirvelu *et al*., 2003; Pala *et al.*, 2003).

Dyed flax fibers have been found in the Republic of Georgia dated back in a prehistoric cave to 36,000 BP. Archaeological evidence shows that, particularly in India and Phoenicia, dyeing has been extensively carried out for over 5000 years. The dyes were obtained from animal, vegetable or mineral origin, with no or very little processing. By far the greatest source of dyes has been from the plant kingdom, notably roots, berries, bark, leaves and wood, but only a few have ever been used on a commercial scale. Dyes are classified according to how they are used in the dyeing process.

a) Acid dyes

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 dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Most synthetic food colors fall in this category.

b) Basic dyes

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.

c) Direct or substantive dyes

Direct or substantive dyeing is 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.

d) 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 color 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.

e) 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. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.

f) 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 fibers at home or in the art studio.

g) Disperse dyes

Disperse dyes were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibres. In some cases, a dyeing temperature of 130 °C is required, and a pressurised dye bath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

h) Azoic dyes

Azoic dyeing is a technique in which an insoluble azo 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. This technique of dyeing is unique, in that the final color is controlled by the choice of the diazoic and coupling components.

i) Sulfur dyes

Sulfur dyes are two part "developed" dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chartreuse color, This is aftertreated with a sulfur compound in place to produce the dark black we are familiar with in socks for instance. Sulfur Black 1 is the largest selling dye by volume.