REMOVAL OF METHYLENE BLUE USING IRON OXIDE PREPARED THROUGH SOLID AND WET SOLUTION ROUTE

NUR AQILAH BINTI SAMSUKAMAL

UNIVERSITI SAINS MALAYSIA

2017

REMOVAL OF METHYLENE BLUE USING IRON OXIDE PREPARED THROUGH SOLID AND WET SOLUTION ROUTE

by

NUR AQILAH BINTI SAMSUKAMAL

Thesis submitted in partial fulfilment of the requirement for the degree of Bachelor of Chemical Engineering

June 2017

ACKNOWLEDGEMENT

Alhamdulillah, thanks to Allah s.w.t. for His blessings, with the strength and patience that He had given to me, I managed to finish this Final Year Project. Million thanks to my inspiring supervisor, Dr. Ing. Noorashrina A. Hamid and understanding coordinator, Associate Professor Dr. Mohd Azmier Ahmad who helped me through the ups and downs in completing the project. I also would like to dedicate my special gratitude to my lovely mother, Siti Rozaimah Sheikh Abdullah, my supportive father, Samsukamal Sulong, my sisters and my brothers for the endless prayer, moral support and advice in whatever I am doing throughout my life. Last but not least, I would like to thank my friends especially Azahirah Azhari and Tai Ming Li, staffs, technicians and others who have not been mentioned here for the help and support throughout the times.

Nur Aqilah binti Samsukamal

May 2017

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOL

Symbol	Meaning	Unit
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Highest initial adsorbate concentration	mg/L
C_t	Dye concentration at time, t	mg/L
m	Mass of iron oxide samples	g
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed at time, t	mg/g
T	Time	h
V	Solution volume	L

LIST OF ABBREVIATIONS

AC	Activated carbon
ASAP	Accelerated Surface Area and Porosimetry System
BET	Brunauer-Emmett-Teller
BOD	Biological oxygen demand
C_2H_5OH	Ethanol
C.I.	Colour index
CNT	Carbon nanotube
COD	Chemical oxygen demand
D	Mean particle size
$Fe(NO_3)_3.9H_2O$	Iron (III) nitrate nonahydrate
Fe_2O_3	Iron (III) oxide
Fe_3O_4	Iron (II, III) oxide (magnetite)
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene blue
MG	Malachite green
MMWCNT	Magnetic multi-wall carbon nanotube
MMMWCNT	Magnetic-modified multi-walled carbon nanotubes
MnP	Iron oxide magnetic nanopowder
PAA	Polyacrylic acid
pH	Potential of hydrogen
pH_{pzc}	Point of zero charge
REC	Rectorite

rpm	Rotation per minute
TSS	Total suspended solids
UV-Vis	Ultraviolet–visible
XRD	X-ray diffraction

PENYINGKIRAN METILENA BIRU MENGGUNAKAN FERUM OKSIDA YANG DIHASILKAN MELALUI SINTESIS PEPEJAL DAN LARUTAN BASAH

ABSTRAK

Dua jenis ferum oksida yang disediakan melalui kaedah keadaan pepejal dan kaedah larutan basah telah dicirikan dan diuji sebagai penjerap untuk penyingkiran metilena biru (MB) daripada larutan akueus. Sifat-sifat penjerap telah dicirikan menggunakan pembelauan sinar-X (XRD) dan pengukuran luas permukaan BET. Penjerap tersebut terdiri daripada ferum oksida (hematit). Kajian ini telah dijalankan untuk mengenalpasti kapasiti penjerapan penjerap dengan mengkaji kesan kepekatan awal pewarna (25-300 mg/L), masa sentuhan (0-24 jam) dan suhu larutan (30, 45 dan 60^{o}C) terhadap penyingkiran pewarna MB. Walau bagaimanapun, oleh kerana data keseimbangan yang diperolehi bagi penjerapan pewarna MB tidak konsisten untuk semua parameter yang dikaji, keadaan ini menunjukkan bahawa ferum oksida yang dihasilkan dalam kajian ini tidak sesuai untuk digunakan sebagai penjerap bagi penyingkiran pewarna MB. Oleh itu, hasil yang optimum untuk penjerapan pewarna menggunakan penjerap tersebut tidak dapat ditentukan dalam kajian ini.

REMOVAL OF METHYLENE BLUE USING IRON OXIDE PREPARED THROUGH SOLID AND WET SOLUTION ROUTE

ABSTRACT

Two types of iron oxide prepared through two simple synthesis routes (i.e. solid state method and wet solution method) were characterized and tested as adsorbents for methylene blue (MB) removal from aqueous solution. The properties of the adsorbents were characterized by X-ray diffraction (XRD) and BET surface area measurement. The adsorbents composed of iron oxide particles (hematite). Experiments were carried out to determine the adsorption capacity of the adsorbents by studying the effect of initial dye concentration (25-300 mg/L), contact time (0-24 hours) and solution temperature (30, 45 and 60^{o}C) on the removal of MB dyes. However, since the obtained equilibrium data for the MB dye adsorption was not consistent for all the studied parameters, it is suggested that the iron oxide is not suitable to be used as adsorbents for MB dye removal. Therefore, the optimum results for the dye adsorption using iron oxide adsorbents is unable to be determined.

CHAPTER 1

INTRODUCTION

1.1 Research background

Colour is the first pollutant in wastewater that can be identified by eyes and it greatly influences the public perception on water quality. Even at concentration of less than 1 ppm, they are highly visible and undesirable. Dyes are vastly used for product colouring in industries such as textile, paper and plastic. These industries consumes huge volume of water for this purpose and as a result, substantial amount of coloured wastewater is generated to the environment (Crini, 2006).

The discharge of dye wastewater without proper treatment is very harmful to the aquatic life. Dyes can reduce light penetration and interfere photosynthetic processes. Under anaerobic conditions, some dyes may decompose into carcinogenic aromatic amines which could pose serious threat to humans and animals (Gupta and Suhas, 2009, Santhi et al., 2016). Methylene blue (MB) dye, for example, can cause eye burns which may lead to permanent injury to the eyes of human and animal. If it is inhaled, the affected individual may have difficulty in breathing and if it is ingested orally, it may cause burning sensation, nausea, vomiting and mental confusion (Rafatullah et al., 2010). Hence, it is necessary to treat such effluents due to its harmful impacts to the environment and health.

Despite that, the treatment for wastewater containing dyes is very difficult to be implemented due to the recalcitrant behaviour of the dyes. Dyes have complex molecular structure, making them resistant to aerobic digestion and stable to light, heat and oxidation (Crini, 2006). Hence, numerous approaches such as flocculation, coagulation, ion exchange and adsorption have been studied for finding the best way to remove dyes from wastewater. Among them, adsorption has been proven to be the most effective technique to treat the effluents. The technology is simple, cheap; and capable of treating concentrated solutions and regenerating adsorbent for reuse (Păcurariu et al., 2015). Thus, from now onwards, this study will focus on the adsorption technology for dye removal from wastewater.

1.2 Problem statement

The main challenge in the adsorption technology is to find the best adsorbent for a particular application. In the case of wastewater treatment, the most popular adsorbent used is activated carbon. Activated carbon has an excellent adsorption ability owing to its high surface area and well defined microporous structure. Unfortunately, its application is restricted by constraints such as expensive production, regeneration problems, poor mechanical properties and phase separation issues (Păcurariu et al., 2015). Due to these facts, the development of alternatives and low cost adsorbents has received much attention in recent years.

One of the suggested low cost adsorbents is iron oxides. Iron oxides are considered as potent adsorbents due to their cheapness, strong adsorption capacity, low toxicity, chemical stability, easy separation and regeneration capability (Păcurariu et al., 2015). They are known to have unique properties, such as large surface area-volume ratio, diminished consumption of chemicals, and no secondary pollutant. Although iron oxide materials seems to be promising adsorbents for dye removal, the unique properties cannot be achieved if the synthesis method is ineffective. Adsorption capacities of adsorbents are determined by the availability of surface areas on the adsorbents. The higher the surface area of the adsorbents, the higher their capacities. This performance can be achieved by decreasing of the particle size of adsorbents. So, it is crucial to choose an appropriate method that can produce adsorbents with proper particles sizes for dye wastewater treatment. It is also a great advantage if the synthesis method is inexpensive, simple, and fast as it can further reduce the production cost (Cheng et al., 2012).

There are several methods that can be used to produce iron-oxide-based nanomaterials. These methods include hydrothermal synthesis, thermal decomposition, co-precipitation, sol-gel method, and colloidal chemistry method (Cheng et al., 2012). Among these methods, sol–gel is the most suitable because it is simple and only requires small quantity of low-cost precursors and low-temperature (Kayani et al., 2014). Similar to sol gel method, the solid state method is also preferable due to its simplicity and low costs.

Based on the current literature review, the synthesis of iron oxide based materials by solid-state method and sol-gel method towards the removal of cationic dye application have yet to be explored. Hence, in this study, an attempt was made to produce iron oxide adsorbents by simple and low cost methods i.e. solid state and sol gel method, in order to examine the effectiveness of the synthesized adsorbents for the removal of MB dyes.

1.3 Research objectives

The objectives of this research are as follows:

i) To produce iron oxide using solid state and sol-gel method for adsorption of MB.

ii) To determine the optimum parameters for adsorption of MB using the in-house adsorbent of iron oxide.

1.4 Organization of report

This report consists of three main chapters and the contents of the chapters can be described as follows:

Chapter 1 introduces the background of research, problem statement, research objectives and organization of this report.

Chapter 2 is the literature review of the research study. The review will start with the general knowledge of dyes in terms of its application, classification, impact and treatments to remove them. Then, the discussion will introduce adsorption technology as the treatment for dye removal. In this part, the factors affecting dye adsorption will be elaborated. Also, the common adsorbents for the dye removal will be presented, together with the preparation methods of the adsorbents.

Chapter 3 explains the materials and methods used in this study. This chapter describes the preparation of adsorbent, its characterization and the adsorption performance study.

Chapter 4 covers the results and discussion of the experiment. This chapter consists of two main sections, in which the first section illustrates the characterization of the adsorbents whereas the second section discusses the batch adsorption studies of the Fe_2O_3 adsorbent for methylene blue (MB) adsorption.

Chapter 5 concludes the overall findings and also the recommendations for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Dyes are widely used in various industrial applications. Unfortunately, the dyes wastewater generated from the industries creates many problems to human and environment. Many techniques in terms of biological, physical and chemical methods have been explored to treat this type of wastewater. This study will focus on adsorption by iron oxide to treat the dye wastewater. Hence, this literature review discuss the general knowledge of dyes, common methods for dye removal, adsorption technology and iron oxide as adsorbent.

2.2 Dyes

Dyes are organic chemical compounds that can attach themselves to surfaces to give colour (Yagub et al., 2014). Their molecules consists of two main components; the chromophores which are responsible for giving colour and the auxochromes which help the dyes to attach to fibres. Most dyes have complex structure and synthetic origin, making them difficult to be decolorized and decomposed biologically (Gupta and Suhas, 2009). This section will describe the general application of dyes in industries, their classification and their impacts to the environment and human health.

2.2.1 Application of dyes

Dyes are used in numerous industrial applications such as paper, pharmaceuticals, textiles, food processing and cosmetics. In Malaysia, where Batik industry is the biggest cottage textile industry, dyes are used to colour the Batik fabric. Figure 2.1 shows the picture of Batik produced in Terengganu, Malaysia. Usually, the most applied dyes for Batik are Remazol and Vinyl Sulphone fibre reactive dyes, based on process conditions such as pH, cold bath and others. The untreated wastewater from the Batik dyeing process may contain dyes, waxes, heavy metals with high COD and TSS contents (Rashidi et al., 2012).

In this study, the investigated dye is methylene blue (MB). Figure 2.2 shows the chemical structure of MB. MB which is also known as thiazine dye is a cationic dye. This dye is commonly used in printing, cosmetics and pharmaceutical (Zhang et al., 2017). It can also be applied for drying cotton, wood and silk (Rafatullah et al., 2010). Apart from that, MB has been playing important roles in microbiology and pharmacology for some time. It has been widely used to stain living organisms and to treat methemoglobinemia; a blood disorder in which an abnormal amount of methemoglobin is produced (Tardivo et al., 2005).

Figure 2.1 Batik fabric from Terengganu (Pija, 2011)

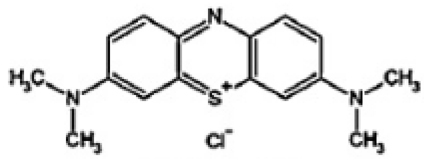

Figure 2.2 Chemical structure of methylene blue (Madrakian et al., 2011)

2.2.2 Classification of dyes

Dyes exhibit considerable structural diversity and thus are classified in several ways, i.e. in terms of their chemical structure and their application to the fibre type. The classification based on chemical structures helps in identification of group according to the characteristics properties of dyes. For instances, azo dyes are known to be strong, good all-round properties, cost-effective while anthraquinone dyes are weak and expensive. Usually, this approach is adopted by practicing dye chemists (Gupta and Suhas, 2009).

Table 2.1 summarises the classification based on application method. In this type of classification, dyes are grouped according to their specific application. The approach is often used by the dye user and the dye technologist. It is advantageous to consider the classification of dyes by use or method of application before considering chemical structures in detail because of the dye nomenclature and jargon that arises from this system. Besides, classification by application method is the principal system adopted by the Colour Index. Because the most important textile fibres are cotton and polyester, the most important dye types are those used for dyeing these two fibres, including polyester-cotton blends. Other textile fibres include nylon, polyacrylonitrile, and cellulose acetate. (Hunger, 2002).

Table 2.1 Dyes classification based on application (Yagub et al., 2014, Gupta and Suhas, 2009)

Class	Substrate	Method of application	Chemical types
Acid	Nylon, wool, silk, ink-jet printing, leather and food	Applied from neutral to acidic bath	Anthraquinone, xanthene, azo (including premetallised), nitro, and triphenylmethane.
Basic (cationic)	Paper, modified nylon and modified polyester	Applied from acidic dye baths	Hemicyanine, cyanine, diazahemicyanine, triarylmethane, acridine and oxazine.
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or a little alkaline bath containing additional electrolyte	Phthalocyanine, polyazo compounds, oxazine, and stilbene.
Disperse	Polyamide, polyester and nylon	Fine aqueous dispersion is applied by high temperature/pressure or lower temperature carrier methods	Benzodifuranone, azo, anthraquinone, nitro, and styryl.
Reactive	Wool, cotton, silk and nylon	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH	Anthraquinone, formazan, phthalocyanine, azo and oxazine
Sulphur	Rayon and cotton	Aromatic substrate vatted with sodium sulphide and reoxidised to insoluble sulphur-containing products on fibre	Indeterminate structures
Vat	Wool and cotton	Water-insoluble dyes solubilised by dropping in sodium hydrogen sulphite, then exhausted on reoxidised and fibre	Indigoids and anthraquinone.

Dyes also may be categorized based on their solubility: soluble dyes and insoluble dyes. Soluble dyes include acid, mordant, metal complex, direct, basic and reactive dyes; while insoluble dyes include azoic, sulphur, vat and disperse dyes (Gupta and Suhas, 2009). Other than that, they can be classified based on their particle charge upon dissolution in aqueous application medium: cationic (basic dyes), anionic (direct, acid and reactive dyes) and non-ionic (dispersed dyes) (Yagub et al., 2014).

2.2.3 Impact of dyes on environment and health

The usage of dyes in industries has generated large volume of wastewater annually. As a result, this event has caused serious problems to human and aquatic life. Dyes are usually composed of chromium, metals and aromatics which is carcinogenic. These compounds can bring serious health effects to kidney, reproductive systems, brain and central nervous system of human. They are also mutagenic and teratogenic in various microbiological, fish species (Yagub et al., 2014).

Azo dyes are harmful because of the presence of toxic amines in the dye wastewater. Some dyes such as basic dyes give intense colour to water body which may reduce the penetration of light. This phenomenon will disturb the photosynthetic activity in aquatic ecosystem. Besides, anthraquinone dyes and reactive dyes are likely to pass the treatment plants untreated because these dyes are resistant to degradation (Yagub et al., 2014). Disperse dyes have low acute ecological impact due to their poor water solubility (less than 1 mg/L). The acute toxicity to aquatic life is generally low. However, according to the European chemicals legislation, disperse dyes are categorized as substances, that may cause long-term adverse effects to aquatic life, because they are not easily biodegradable and suspected of being potentially bioaccumulative due to their hydrophobicity (Hunger and Sewekow, 2002). Therefore, currently, many researches concentrate on finding the most suitable method or technology for dye wastewater treatment, which will be elaborated more in the next section.

2.3 Treatment methods for dye removal

There are many methods to eliminate dyes from wastewater. Table 2.2 shows some of the treatment methods which are available for dye removal. The methods can be categorized into three classes: physical, chemical and biological. Each of them has its own limitations.

Table 2.2 Summary of dye removal methods (Crini, 2006, Yagub et al., 2014)

Types	Methods	Advantages	Disadvantages
Biological treatments	Decolourisation by white-rot fungi	White-rot fungi are capable of degrading dyes using enzymes	Enzyme production is unreliable, necessary to create optimum condition
	Adsorption by living/dead microbial biomass	Some dyes have a particular affinity for binding with microbial species	Not effective for all dyes
Chemical treatments	Coagulation-flocculation	Simple and economically feasible	High sludge production, handling and disposal problems
	Oxidation	Rapid and efficient process	High energy cost, chemical required
	Photochemical	No sludge is produced and foul odours are greatly reduced	Formation of by-products
Physical treatment	Membrane filtration	Remove all dye types	Concentrated sludge production, expensive, incapable of treating large volume
	Ion-exchange	Regeneration of adsorbent	Not effective for disperse dyes
	Adsorption by activated carbon	Good removal of wide variety of dyes, produce high quality effluents	Regeneration is expensive, results in loss of adsorbent

2.3.1 Biological treatment

Biological treatment is the most common method to treat dye bearing effluent. It involves living organisms using organic or, in some instances, inorganic substances for food. There are three modes of biological treatment; aerobic (in presence of oxygen), anaerobic (without oxygen) and combined aerobic – anaerobic.

In aerobic conditions, enzymes secreted by bacteria that present in the wastewater will break down the organic compounds. As for anaerobic treatment, dyes wastewater can be decolourised with the efficient and cheap removal of BOD levels. In combined aerobic–anaerobic treatment, complete mineralization is often achieved in the treatment due to the synergistic action of different organisms. Generally, concentration of dyes, initial pH and temperature of the effluent will affect the decolourisation process. Even though biological treatment is suitable for variety of dyes and cost-competitive, the treatment faces the following problems; low biodegradability of the dyes, less flexibility in design and operation, larger land area requirement and longer times required for decolourisation-fermentation processes. Eventually, the method is unable to remove dyes from effluent on a continuous basis in liquid state fermentations (Gupta and Suhas, 2009).

2.3.2 Chemical treatment

Chemical treatment of is one of the best methods for dye removal. The method removes dyes by chemical reactions that involve exchanging or sharing electrons among atoms (Woodard et al., 2006). Examples of this treatment include coagulation or flocculation, combined with flotation and filtration, electroflotation, electrokinetic coagulation, conventional oxidation methods and electrochemical processes (Crini, 2006). Basically, the method is economical but it may become expensive because of the cost of chemicals. The advantage of this process is its ability to remove disperse, sulfur and vat dyes satisfactorily. However, at the end of the process, accumulated sludge is produced in large quantities even though the dyes are removed. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use (Gupta and Suhas, 2009).

2.3.3 Physical treatment

Physical methods of wastewater treatment accomplish removal of substances by use of naturally occurring forces, such as gravity, electrical attraction, and van der Waal forces, as well as by use of physical barriers. In general, the mechanisms involved in physical treatment do not result in changes in chemical structure of the target substances (Woodard et al., 2006). In dye wastewater treatment, physical methods including membrane filtration processes and adsorption techniques are widely used. Membrane processes usually face the problems of limited time before fouling and expensive maintenance whereas adsorption is reported to be one of the most effective techniques to produce a high quality treated effluents as it is flexible and insensitive to toxic pollutants (Crini, 2006). Further explanation on adsorption method will be described in the following section.

2.4 Adsorption technology

2.4.1 Theory of adsorption

Adsorption refers to a process where a substance is accumulated at the interface between two phases either at liquid-solid interface or gas-solid interface. The substance that concentrates at the interface is called the adsorbate, whereas the solid which is adsorbing, is known as the adsorbent (Yagub et al., 2014, Gupta and Suhas, 2009, Ali et al., 2012).

There are two types of adsorption; chemisorption and physisorption. Chemisorption occurs when strong chemical bonds are formed between molecules or ions of adsorbate and adsorbent surface due to the exchange of electrons. Physisorption involves the weak van der Waals intraparticle bonding between adsorbate and adsorbent. Usually, adsorption on most adsorbent is controlled by physical forces with some exception of chemisorption (Yagub et al., 2014). The physical forces includes van der Waals forces, hydrophobicity, hydrogen bonds, polarity, steric interaction and dipole induced dipole interaction (Ali et al., 2012).

Adsorption has been proven to be the most effective method for removing various type of pollutants in wastewater. The technique is inexpensive, simple, capable of generating high-quality effluents and has low maintenance cost (Sehlleier et al., 2016). It can remove up to 99.9% of soluble and insoluble organic pollutants (Ali et al. 2012). It also does not result in the formation of dangerous products (Rafatullah et al., 2010). Therefore, this method has been applied to removal of wide range of contaminants such as dyes.

2.4.2 Factors affecting adsorption of dye

The adsorption of dyes may be influenced by several factors such as temperature, solution pH and initial dye concentration. It is a necessary to optimize these parameters as they can give effects to the performance of dye adsorption.

2.4.2.1 Effect of solution pH

Solution pH is one of the common factors that can affect the adsorbent capacity in the wastewater treatment. As the solution pH varies, the degree of ionization of the adsorptive molecules and the surface properties of adsorbent will change accordingly. Point of zero charge (pH_{pzc}) is an important parameter to determine the adsorption ability of the surface and the type of surface active centres. It is the pH where the surface charge is zero. Cationic dye adsorption is favoured at $pH>pH_{pzc}$ due to the presence of OH^- functional group. Meanwhile, anionic dye adsorption is favoured at $pH<pH_{pzc}$ when the surface is positively charged (Yagub et al., 2014).

Sehlleier et al. (2016) investigated the adsorption of methylene blue by iron-oxide/polymer nanocomposite and they found out that higher adsorption of MB was obtained at higher pH values due to the electrostatic attractions between the positively charged MB dye cations and the negatively charged hydroxyl groups on the surface of the iron oxide/polymer composite. Santhi et al. (2016) demonstrated the effect of pH on the adsorption of MB and MG dyes by *A. squmosa* seed and they noticed that the removal efficiency of 75.66% for MG and 24.33% for MB were achieved at pH 6.0.

2.4.2.2 Effect of contact time and initial dye concentration

The effect of initial dye concentration is another parameter that will influence the efficiency of dye adsorption. Basically, this parameter depends on the correlation between the concentration of the dye and the availability of sites on the adsorbent surface. The percentage of dye removal will decrease as the initial dye concentration increases because the sites on the adsorbent surface might have been saturated with dye molecules. On the other hand, due to the high driving force for mass transfer at a high initial dye concentration, the capacity of the adsorbent will increase as the initial concentration increases (Yagub et al., 2014).

Ai et al. (2011b) studied the adsorption of MB by magnetite loaded M-MWCNTs and noticed that during the initial adsorption phase, the adsorption capacity and percent removal of MB onto the M-MWCNTs significantly increase. Then, the adsorption capacity and percent removal continue to increase at a relatively slow speed with contact time until a state of equilibrium is achieved after 120 min. These occurrences may due to the high availability of vacant sites for adsorption at the early stage, but after some times, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Besides that, it was observed that the adsorption capacity of MB increases but the percent removal of MB decreases with the increase in initial concentration. Such trend was also reported on the adsorption of MB on papaya seeds (Hameed, 2009a).

2.4.2.3 Effect of temperature

The adsorption capacity of an adsorbent can be affected by surrounding temperature. An adsorption is considered as endothermic if the amount of adsorption increases with increasing temperature, resulting from the high mobility of dye molecules and the increase of adsorption active site at increasing temperature. An exothermic adsorption is indicated by the decrease of adsorption capacity with increasing temperature. This may due to the decrease of adsorptive forces between the dye molecules and the active sites on the adsorbent surface (Yagub et al., 2014). A study by Păcurariu et al. (2015) had explored the effect of temperature on the adsorption of MB by iron oxide magnetic nanopowder (MnP) and they found out that the adsorption capacity decreases as the temperature decreases, which indicated that the adsorption of the MB onto MnP is an exothermic process.

2.4.2.4 Effect of adsorbent dosage

The amount of adsorbent used in dye removal is also significant in determining the capacity of an adsorbent. Normally, the percentage of dye removal from wastewater increases as the amount of adsorbent increases. This is because, the amount of active sites increase with increasing adsorbent dosage. From economical point of view, adsorbent dosage is important to be studied because the smallest amount of adsorbent required to adsorb dye from wastewater can be determined and hence the adsorbent cost can be reduced (Yagub et al., 2014).

Hameed (2009a) reported in his study that the percent removal of MB dye increases from 34.67% to 80% as the adsorbent dose was increased up to 0.4 g but then the percentage remained constant despite the adsorbent dose was further increased to 1.0 g. The reason behind this may due to the increase of available adsorption surfaces which contributes to the increase of adsorption sites availability.

2.4.3 Adsorbents for dye removal

A good adsorbent should has porous structure which results in high surface area for adsorption so that it can remove dye from wastewater in shorter time (Sehlleier et al., 2016, Gupta and Suhas, 2009). Normally, the pore structure and sizes can be classified according to the IUPAC definition as microporous when the pore size is below 2 nm, as mesoporous if the pore size is between 2 and 50 nm and microporous when the pore size is above 50 nm (Sehlleier et al., 2016).

There are various kind of adsorbents that can be used for dye removal as shown in Figure 2.3. Many of them have been examined and proposed for dye removal. Some of the adsorbents' adsorption capacity for MB dye removal are tabulated in Table 2.3. The most popular adsorbent is activated carbon (AC). AC is a carbonaceous material which exhibits a high degree of porosity and extended inter particulate surface area (Ali et al., 2012). This material has great capacity to adsorb dyes due to its large surface area and its characteristics that can be easily modified by chemical treatment. However, it is expensive, non-selective and ineffective against disperse and vat dyes. Its regeneration is also expensive and results in loss of adsorbent (Crini, 2006). These problems has led many research to find more economic adsorbents for dye removal.

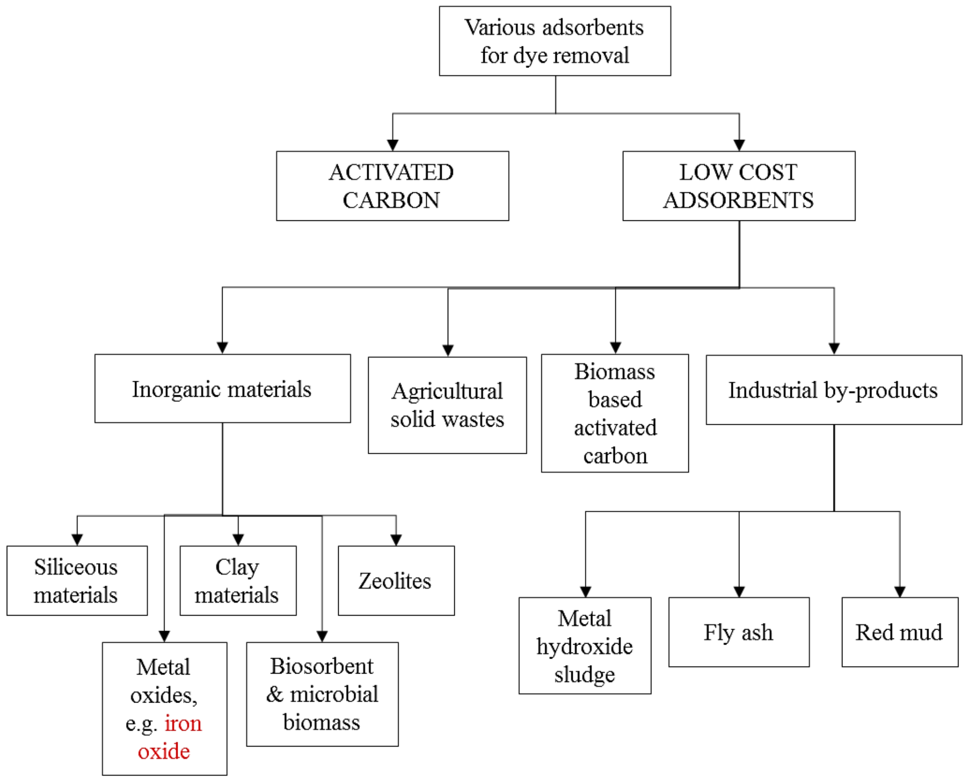

Figure 2.3 Various adsorbents that can be used for dye removal (Yagub et al., 2014)

Table 2.3 Adsorption capacities (mg/g) of various adsorbents in MB dye removal

Adsorbent	**Adsorption capacity (mg/g)**	**References**
Commercial AC	980.3	Kannan and Sundaram (2001)
Sewage sludge	114.94	Otero et al. (2003)
Brown alga	38.61	Caparkaya and Cavas (2008)
Jackfruit peels	285.713	Hameed (2009b)
Papaya seeds	555.557	Hameed (2009a)
CNTs and iron oxide composed nanocomposite	15.74	Gong et al. (2009)
Graphene and magnetite composite	43.82	Ai et al. (2011a)

Basically, a low cost adsorbent is a material which requires little processing and is abundant in nature or waste product from another industry which has lost its economic or is a by-product or further processing values. This sort of adsorbent offers two benefits at one time, which are water treatment and waste management. Examples of the adsorbent include agriculture solid wastes, biomass solid waste based AC adsorbent, industrial by-products and inorganic materials (Yagub et al., 2014).

2.5 Iron oxide as adsorbent

2.5.1 Iron oxide

Iron oxide is one of the inorganic materials that can be used as adsorbent. It can exist in many forms in nature; magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) (Xu et al., 2012). Among them, α-Fe_2O_3 is the most stable iron oxide under ambient conditions which is widely used in catalyst, pigment, sensor, gas purification and water treatment (Chizari Fard et al., 2017).

Figure 2.4 shows the XRD patterns of the α-Fe_2O_3 prepared by the solid-state reaction technique from Cao et al. (2013) work. It can be seen that all of the diffraction peaks could be indexed to α-Fe_2O_3 (JCPDS No. 33-0664). The average crystallite size (D) was determined from the X-ray line broadening using Scherrer's formula, $D = 0.89\lambda/\beta\cos\theta$, where λ is the wavelength (Cu-Kα_1), β is the full width at the half maximum (fwhm) of the (1 0 4) or (1 1 0) line (in radian) and θ is the diffraction angle of the peak.

According to the Scherrer's equation, the mean crystallite size of the three samples was calculated to be about 9 nm, 23 nm and 65 nm, respectively. The sizes, BET area, pore diameter and total pore volume of the samples are listed in Table 2.4. It is noted that S1 exhibited the smaller size and the bigger surfaces (Cao et al., 2013).

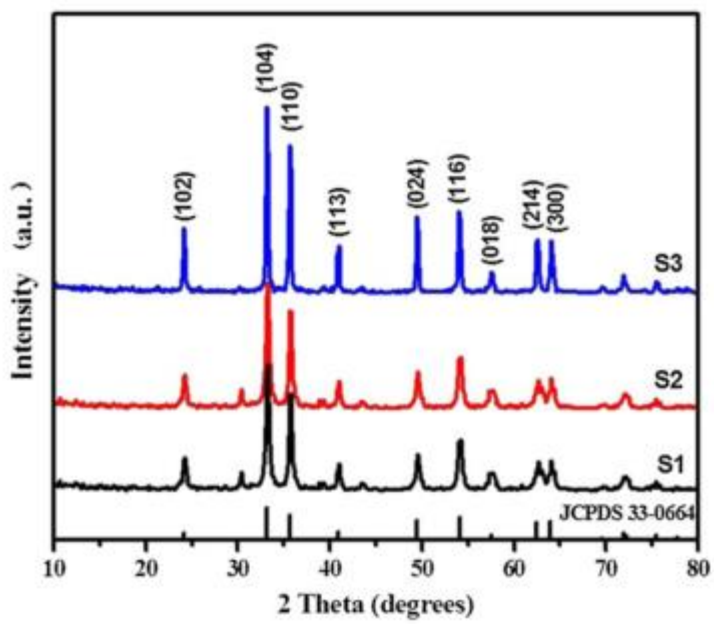

Figure 2.4 XRD patterns of samples from Cao et al. (2013) work

Table 2.4 Microstructure parameters of samples

Sample	**Size of particle (nm)**	**BET surface area (m^2/g)**	**Pore diameter (nm)**	**Total pore volume (cm^3/g)**
S1	9	102.95	7.7	0.198
S2	23	49.43	7.4	0.092
S3	65	16.27	10.7	0.044

The synthesis and utilization of iron oxides as adsorbents have been extensively studied because of their high adsorption capacity, low cost, chemical stability, low toxicity, easy separation and great recycling capability (Păcurariu et al., 2015). Figure 2.5 portrays the example of MB dye adsorption on iron oxide/polymer nanocomposite. The solution becomes clear after the adsorption and magnetic separation.

A summary of the adsorption capacity for the removal of MB dyes from wastewater, using various kind of iron oxide based materials are presented in Table 2.5. Comparing the adsorption capacity values listed in the table, it is obvious that the adsorption capacity is higher when the BET surface area is larger. The synthesized magnetic iron-oxide/polymer composite has the highest adsorption capacity compared to others due to its large surface area (890 m^2/g). However, the adsorption capacity of MB onto the MnP adsorbent by Păcurariu et al. (2015) is higher than those reported by Gong et al. (2009) using a MMWCNT ($q = 15.74$ mg/g) even though they have very similar characteristics. This was due to the fact that Păcurariu et al. (2015) worked at pH 11, which is much more favourable for the MB removal than at pH 7 by Gong et al. (2009).

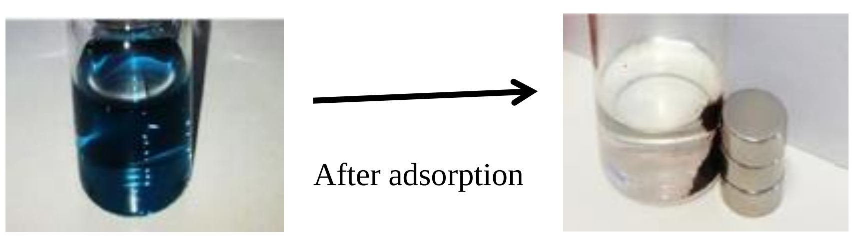

Figure 2.5 Photo of MB solution (100 mg/L). Right: After addition of iron-oxide/polymer nanocomposite adsorbent and magnetic separation (Sehlleier et al., 2016)

Table 2.5 Adsorption capacity by different iron oxide nanomaterials for the adsorption of MB dye (Păcurariu et al., 2015)

Sample	BET surface area (m^2/g)	Pore diameter (nm)	Total pore volume (cm^3/g)	Adsorption capacity (mg/g)	References
MnP	59.58	14.23	0.23	25.54	Păcurariu et al. (2015)
MMWCNT	61.74	-	0.2924	15.74	Gong et al. (2009)
MMMWCNT	144.68	-	-	48.10	Madrakian et al. (2011)
Pristine iron-oxide nanoparticle	93	-	-	6	Sehlleier et al. (2016)
Iron oxide/polymer composite	890	10-12	1.6	298	Sehlleier et al. (2016)
MPS-iron oxide	98	-	-	23	Sehlleier et al. (2016)