DEVELOPMENT OF VARIOUS MODIFIED MAIZE COB AS ADSORBENTS FOR METHYLENE BLUE DYE WASTEWATER TREATMENT

by

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Thesis submitted in fulfillment of the requirements

for the degree of

Master of Science

JULY 2013

PENGHASILAN PELBAGAI PENJERAP BERASASKAN TONGKOL JAGUNG TERUBAHSUAI DALAM RAWATAN AIR SISA BIRU METILEN

oleh

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Tesis yang diserahkan untuk

memenuhi keperluan bagi

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JULAI 2013

ACKNOWLEGEMENT

First of all, I would like to offer my sincere thanks to my supervisor, Associate Professor Dr. Norhashimah Morad for her guidance, instructions and encouragements on this project. Her kindness and time for discussion enable me to develop an understanding of the subject.

Besides, I am heartily thankful to my co-supervisors, Professor Teng Tjoon Tow and Associate Professor Dr. Norli Ismail for their precious assistance and guidance. I would like to sincerely thanks to Dr. Panneerselvam for his suggestions and guidance on the nanoparticles fields.

A great appreciate to all the academic members, lab assistance, especially Madam Teh Siew Hong and staff of School of Industrial Technology for their technical support in using the lab instruments and kind cooperation.

I would like to express my heartful appreciation to USM Fellowships of the financial support. Besides, I would also like to gratefully acknowledge Han Khim, Kean Weng, Khai Ern, Ling Wei and Soke Kwan for their kindly guidance and suggestion.

Lastly, I would like to thanks my parents for their kind support on my study in University.

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LIST OF ABBREVIATIONS

AMMC	Acid modified maize cob
AMMC-Fe_3O_4	Acid modified maize cob impregnated with ferric oxides
ANOVA	Analysis of variance
BBD	Box behnken design
BOD	Biological oxygen demand
CCD	Centre composite design
COD	Chemical oxygen demand
C.I.	Color index
DOE	Design of experiments
EDX	Energy dispersive X-ray
$FeCl_2.4H_2O$	Iron (II) chloride 4-hydrate
$FeCl_3.6H_2O$	Iron (III) chloride 6-hydrate
Fe_3O_4	Ferric oxide
HCl	Nitric acid
H_2SO_4	Sulphuric acid
KBr	Potassium bromide
MB	Methylene blue
NaOH	Sodium hydroxide
NH_4OH	Ammonium hydroxide solution
RMC	Raw maize cob
RMC-Fe_3O_4	Raw maize cob impregnated with Fe_3O_4
RSM	Response surface methodology
SEM	Scanning electron microscopy
TDS	Total dissolved solid

TS	Total solid
TSS	Total suspended solid

LIST OF SYMBOL

Symbol	Description	Unit
A	Arrhenius factor	-
b	Temkin constant which related to heat of adsorption	J/mol
C_o	Initial dye concentration	mg/L
C_t	Dye concentration at time, t	mg/L
E_a	Arrhenius activation energy	kJ/mol
ΔG^o	Standard free energy change	kJ/mol
ΔH^o	Standard enthalpy change	kJ/mol
k_1	Pseudo-first-order rate constant	min^{-1}
k_2	Pseudo-second-order rate constant	g/mg.min
k_{dif}	Rate constant of intraparticle diffusion model	$mg/g.min^{1/2}$
k_{ext}	Rate constant of external diffusion model	min^{-1}
K_f	Freundlich isotherm constant	$(m/g)(L/mg)^{1/n}$
K_L	Langmuir constant	L/mg
K_T	Temkin equilibrium constant	L/g
n	Coefficients of Freundlich isotherm	-
R	Universal gas constant (8.314)	J/mol.K
R_L	Equilibrium parameter	-
S_f	Equilibrium concentration of COD	mg/L
S_i	Initial concentration of COD	mg/L
ΔS^o	Standard entropy change	J/mol.K
T	Absolute temperature	K
V	Volume of dye solution	L
W	Weight of adsorbent	g
q_e	Amount of equilibrium of dye uptake	mg/g

q_m	Monolayer adsorption capacity at equilibrium	mg/g
q_t	Amount of dye adsorbed at any time	mg/g
x_1	Adsorbent dosage	g/100 mL
x_2	pH	-
x_3	Initial dye concentration	mg/L
x_4	Contact time	min
x_5	Temperature	^oC
x_k	Coded values	-
y_1	Percentage of dye concentration removal	%
y_2	Percentage of COD reduction	%
λ_{max}	Maximum wavelength	nm
β_o	Offset term	-
β_i	Linear effect	-
β_{ii}	Square effect	-
β_{ij}	Interaction effect	-

PENGHASILAN PELBAGAI PENJERAP BERASASKAN TONGKOL JAGUNG TERUBAHSUAI DALAM RAWATAN AIR SISA BIRU METILEN

ABSTRAK

Penjerapan pewarna alkali, biru metilen (MB) ke atas tongkol jagung mentah (RMC), tongkol jagung yang dirawati dengan asid (AMMC), ferik oksida (Fe_3O_4), tongkol jagung mentah yang dirawati dengan oksida ferik (RMC-Fe_3O_4) dan AMMC yang dirawati dengan oksida ferik (AMMC-Fe_3O_4) telah dikaji dalam kajian ini. Kesan pH, dos penjerap, kepekatan awal pewarna, tempoh pergaulan dan suhu ke atas penyingkiran kepekatan pewarna dan pengurangan COD telah dikaji melalui proses saringan dan dioptimumkan oleh kaedah gerak balas permukaan (RSM). Semua pembolehubah yang dikaji didapati signifikan secara statistik. Penjerapan dengan menggunakan AMMC-Fe_3O_4 adalah lebih berkesan berbanding dengan empat penjerap yang lain. Proses penjerapan dengan AMMC-Fe_3O_4 menunjukkan peratusan penyingkiran kepekatan pewarna tertinggi (99.63%) dan pengurangan COD yang tertinggi (99.48%) dalam keadaan optimum, iaitu 0.75 mL g/100 dos adsorben, pH 10.31 dan 156 mg/L kepekatan awal pewarna selama 36 minit di bawah 38.40 ^{o}C. Data ujikaji kinetik (kinetic experimental data) dianalisis dengan menggunakan empat persamaan kinetik, iaitu model pseudo-tertib-pertama (pseudo-first-order-model), pseudo-tertib-kedua model (pseudo-second-order-model), model resapan luaran (external diffusion model) dan model resapan intrapartikal (intraparticle diffusion model) untuk menentukan mekanisme penjerapan dan langkah potensi pengawalan kadar. Kelima-lima penjerap adalah bersesuaian dengan model kinetik pseudo-tertib kedua. Data keseimbangan eksperimen diuji pada tiga

model isoterma, iaitu isoterma Langmuir, isoterma Fruendlich, dan isoterma Temkin. Kelima-lima penjerap menunjukkan penyesuaian yang lebih tinggi dengan isoterma Langmuir dalam proses penjerapan MB. Semua data ujikaji telah dikaji dengan lebih lanjut dalam kajian termodinamik dan keputusan menunjuk bahawa proses penjerapan dalam kajian ini adalah endotermik untuk kelima-lima adsorben kerana ΔH^{o} mereka menunjukkan nilai-nilai positif. AMMC-Fe_3O_4 telah dipilih untuk mengkaji rawatan air sisa pewarna tekstil. AMMC-Fe_3O_4 yang digunakan telah diregenerasi kembali oleh 0.01 M HCl dan 0.01 M NaOH, dan kaedah menggunakan 0.01 M NaOH menunjukkan regenerasi penjerap yang lebih berkesan.

DEVELOPMENT OF VARIOUS MODIFIED MAIZE COB AS ADSORBENTS FOR METHYLENE BLUE DYE WASTEWATER TREATMENT

ABSTRACT

The adsorption of basic dye, Methylene Blue (MB) onto raw maize cob (RMC), acid modified maize cob (AMMC), ferric oxide (Fe_3O_4), raw maize cob impregnated with ferric oxide (RMC-Fe_3O_4) and acid modified maize cob impregnated with ferric oxide (AMMC-Fe_3O_4) have been investigated in this study. The effects of pH, adsorbent dosage, initial dye concentration, contact time and temperature on dye concentration removal and COD reduction were investigated by screening process and optimized by response surface methodology (RSM). All the effects showed statistical significance and the adsorption process using AMMC-Fe_3O_4 showed the highest effectiveness among the five adsorbents. The adsorption process using AMMC-Fe_3O_4 obtained the highest percentage of dye concentration removal (99.63%) and COD reduction (99.48%) at the optimum conditions with 0.75 g/100 mL of adsorbent dosage, pH 10.31, 156 mg/L of initial dye concentration for 36 minutes under 38.40 ^{o}C. The kinetic experimental data were analyzed using four kinetic equations which include pseudo-first-order model, pseudo-second-order model, external diffusion model and intraparticle diffusion model to determine the mechanism of adsorption and potential rate-controlling step. All five adsorbents showed the best fit with pseudo-second-order kinetic model. The experimental equilibrium data were tested on three isotherm models which included Langmuir isotherm, Fruendlich isotherm, and Temkin isotherm. All five adsorbents showed

that the Langmuir isotherm exhibited better fit to the MB adsorption process using the five adsorbents. All the experimental data were further analysed based on thermodynamic characteristics and the adsorption process was found to be endothermic for all five adsorbents since their ΔH^o showed positive values. AMMC-Fe_3O_4 was chosen further to be investigated in the textile dye wastewater treatment. The spent AMMC-Fe_3O_4 was regenerated by 0.01 M of HCl and 0.01 M of NaOH. The regeneration method using 0.01 M of NaOH showed effective regeneration of spent adsorbent.

CHAPTER ONE

INTRODUCTION

1.1 Background of Project

In this century, many textile industries are being introduced daily to meet world demand for fabrics due to population growth. To increase the market ability of products, not only textile industries, but also other industries such as food, leather, ceramic, paper, printing, plastic and etc. are using dyes to color their products, which require substantial volumes of water. As a result, these industries generate a large amount of dye wastewater (Raghuvonshi et al., 2005; Chandra et al., 2007). There are more than 10,000 different dyes that are available commercially. It is estimated that over 7×10^{8} kg of dyestuffs produced annually (Nigam et al., 2000; Doğan et al., 2008).

There are a large number (up to 50 %) of dyes from textile industries that discharge their wastewater directly into natural stream due to inefficiencies in dyeing techniques (Robinson et al., 2002). According to Raghuvonshi et al. (2005), the effluent discharged from these industries are hot and contain low BOD, high COD, highly colored and also contain a high amount of dissolved solid. Hence, treatment of dyes from textile and related industries effluent is considered as a global environmental issue since it can cause serious environmental impact because of the toxicity of reactive dyes, chorolignin residues and dark coloration (Hameed, 2009).

Discharging dyes wastewater into natural stream will block sunlight which is necessary for many photo-initiated chemical reactions such as photosynthesis, which are required for aquatic life (Rauf et al., 2009). The incomplete bacterial degradation of some dyes will produce toxic amines which is harmful to human health (Khan et al., 2004). Hence, treatment of dyes wastewater is an area of research receiving increasing attention by many researchers.

Dyes wastewater is usually treated by physical or chemical process. These include flocculation, precipitation, electro-flocculation, membrane filtration, ozonation, electrochemical destruction, ion exchange, and Katox treatment method, which involve the use of activated carbon and irradiation. However, these techniques are costly, forms hazardous by-products, cannot widely treat dye wastewater, and require intensive energy requirement (Garg et al., 2004a; Tan et al., 2008). Hence, this has prompted a growing research interest in the cheaper alternative dye wastewater treatment methods.

1.2 Nanotechnology

Nanoscience and nanotechnology refer to the control of matter at dimension around 1 to 100 nanometer. 1 nm is one-billionth of a meter. Nanoscale materials with particle size of 1 to 100 nm can have different properties since it increase the relative surface area per unit mass which can increase physical strength and chemical reactivity. On the other hand, the influence of quantum effects at the nanoscale size will also change the basic material properties (Seller et al., 2009). Based on the developed ability to measure, manipulate and organize nano-size material, nanotechnology offers a revolution in science and technology (Rieth, 2003). Many fields including textiles, paintings, electronics, coatings, pharmaceuticals, and personal care products have revolutionize and optimize their products to utilize the unique properties of the nanoscale materials (Seller et al., 2009). Currently, the nanotechnology is also applied in environmental science and many wastewater treatment methods using these nanoscale matreials have been proposed (Ngomsik et al., 2005).

1.2.1 Magnetic Nanoparticles-Fe_3O_4

Pierre Weiss was the first who suggested the theory of magnetism in solids in which magnetic atoms are exposed to a molecular field due to magnetic interaction with the neighbor atoms. According to his theory, the temperature dependence of the magnetization gives rise to magnetic ordering below a critical temperature. Pierre Weiss theory was further developed by Werner Heisenberg in year 1928 due to the classical magnetic dipole fields from neighboring atoms were very far too small to explain magnetic ordering in solids at ambient temperature. Werner Heisenberg stated that exchange interaction between electrons give rise to an effective interaction between electron spins. This means that magnetic ordering in solids under ambient temperatures has a quantum mechanical origin (Mørup et al., 2011).

In year 1930, it was believed that ferromagnetic with all atomic magnetic moments were assumed parallel were strongly magnetic material. However, Louis Néel pointed out that very small particle of magnetic materials may be superparamagnetic at finite temperature which means that the magnetization direction may fluctutate because of thermal agitations (Mørup et al., 2011).

In recent years, magnetic nanoparticles are widely used in drug or gene release, DNA, biomolecules separation, magnetic resonance imaging, information storage, catalysis, biomedical, hypothermal treatment of tumours and water purification. Many scientific communities have shown interest to investigate other potential uses of this material. Water purification using magnetic materials was reported by only a few papers and it can be considered as a new research subject in this field (Li et al., 2011; Indira and Lakshmi, 2010). There is a paper from Yang et al. (2008) that reported the treatment of dyes by using magnetic Fe_3O_4-activated carbon nanocomposite particles.

1.3 Dyes and Pigments

People have been using color since prehistoric times. For example, people used the natural organic or inorganic colorants in decorating their bodies and in coloring the furs and skins that they wore. In those days, the colorants used were derived from natural sources such as plants, trees, roots, seeds, nuts, fruit skins, berries and lichens, crushed insects or molluscs (Christine, 2001). However, Mauve as a synthetic dye was discovered by William Henry Perkin in year 1865. There are several million different colorants that have been synthesized after the first synthetics dye was discovered and about 10000 of these were or produced on an industrial scale (Zollinger, 1987).

According to Zollinger (1987), colorants are characterized by their ability to absorb visible light within 400 to 700 nm of wavelength of light. Colorants can be classified in two main groups- dyes or pigments, based on their solubility characteristics (Christine, 2001; Zollinger, 1987).

Dyes will give color to a material as they bind with the material. Dyes are ionic and aromatic organic compounds with aryl rings structure and their color are due to the presence of a chromophore group which is a radical configuration consisting of conjugated double bonds containing delocalized electron. The chromophoric configurations include azo (-N=N-), nitroso (-NO or N-OH), carbon (=C=C=), carbonyl (=C=O), sulphur (C=S) and nitro ($-NO_2$ or =NO-OH) (Allen and Koumanova, 2005). According to Christine (2001), dyes are generally required to dissolve in water as they are almost invariably applied to the textile material from an aqueous medium. Acid dyes, direct dyes, cationic dyes and reactive dyes are completely and very readily dissolve in water.

Pigments are colored, black, white, or fluorescent particulates organic and inorganic solids. They are usually essentially physically unaffected by the substrate and insoluble in the substrate in which they are incorporated. It will retain a crystal or particulate structure throughout the coloration process (Bamfield, 2001). Pigments are abundant in nature such as rocks. There are two types of pigments which are inorganic pigments and organic pigments. Inorganic pigments such as charcoal, iron oxides and manganese dioxide were first colorants used for cave painting. However, beginning of the 19th century, inorganic pigments were produced from industries. Organic pigments were not only can obtained from rock but also from plants, animals and man. The major property of inorganic and organic pigments which is difference from dyes is their insolubility in the media in which they are used (Zollinger, 1987).

Colorants can be classified according to their chemicals structure or according to the method of application. However, the society of Dyers and Colorists, Bradford, England had produced a publication of Color Index (C.I.) to classify the dyes and pigments. The Color Index provides information regarding the methods of application and the range of fastness properties of dyes and pigments. Each colorant is given a C.I. Generic Name which incorporates its application class and a number which simply reflects the chronological order (Christine, 2001).

1.3.1 Textile Dyes

Textile dyes contain substituted aromatic and heteroaromatic groups. The dyes are classified into acid, reactive, direct, basic, disperse, metal complex, vat, mordant and sulphur dyes with regard to method and domain of usage of dyes. Reactive and direct dyes are commonly used for cotton and viscose-rayon and disperse dyes are used for polyster dyeing (Valh and Le Marechal, 2009).

The wastewater which is collected from the textile industry contains vat dyes. Indigoids and antraquinone are two main groups of vat dyes. Vat dyes are very popular and largely applied on cellulosic fibers such as cotton. This type of dye is carcinogenic and can affect health and cause environmental concerns (Balan and Monteiro, 2001).

1.3.2 Methylene Blue (MB)

Methylene blue (MB) is a basic dye and its chemical name and synonyms are 3,7-bis(dimethylamino)phenothiazinylium chloride, and methylthioninium chloride respectively. It is the most common phenothiazinium dye which primarily used in histology for staining (Zimcik and Miletin, 2009). Nowadays, MB also applied in dyeing cotton, wood and silk (Rafatullah et al., 2010). MB shows a strong absorption band within the range of 550-700 nm with the maximum at 664 nm (Zimcik and Miletin, 2009).

1.4 Textile Industries in Malaysia (Penang)

The top three export earners of manufactured goods for Malaysia is textile and apparel. Penang is one of the prominent locations for textile and apparel in Malaysia. During industrialization era which started to take place in the early 1970s, textile and apparel is a pioneering industry leader that set their foothold in Penang. Examples of textile and apparel manufacturers which still in operation in Penang since 1970s are Penfabric, Penfibre, The Eastern Garment Manufacturing, and South East Garment. In year 2006 there were 52 textile and apparel establishments in Penang.

1.4.1 Regulations and Laws for Textile Dye Wastewater in Malaysia

It is commonly noted that releasing the dyeing effluents to the natural streams will cause harm to human health, aquatic life and also polluted the natural streams. Therefore, the environmental authorities regulate the permissible limits. In Malaysia, the effluent discharged from industry must comply with the Fifth Schedule in Environmental Quality (Industrial Effluent) Regulation 2009 which is shown in Table A1.1. A total 30 parameters including color must be monitored on the discharging effluents before being released to any natural streams. The acceptable conditions for the containing COD of the discharging industrial effluent are listed in Table A1.2 (Environmental Quality Act and Regulation, 2009).

1.5 Dye Wastewater Treatments

In recent years, the control of water pollution has become increasing important due to the importance of water for human life, sustainable ecosystem and economical development. Dyes cause a lot of problems in the environment. Therefore, an efficient and cost-effective of dyes wastewater treatment is needed.

Dyes wastewater can be treated by chemical, biological and physical method. Applications of physical forces are in required the physical treatment method. The physical methods include precipitation, sedimentation, adsorption, nanofiltration, reverse osmosis, filtration and ultrafiltration (Valh and Le Marechal, 2009).

However, chemical treatment methods involve the addition of chemicals or by chemical reactions. The chemical treatment methods include reduction, oxidation, compleximetric methods, ion exchange and neutralization (Valh and Le Marechal, 2009).

Biological treatment methods are widely used in the dye the wastewater treatment in recent years. This technique provided many advantages such as inexpensive, low running cost and the end products of complete mineralization not being toxic. This process can be carried out in presence of oxygen (aerobic), without oxygen (anaerobic) or combined both aerobic and anaerobic process (Gupta and Suhas, 2009).

The adsorption process is one of the efficient methods to remove dyes from effluence among all of the dye wastewater treatment methods. The adsorption process is a post-treatment method in the dye wastewater treatment plant.

1.6 Adsorption Process

In eighteen century, Scheele and Fontana carried out the experiment of the ability of porous solids to reversibly adsorb large volumes of vapor. However, the application of adsorption in industrial process streams is a more recent development. There has been a significant increase in both the range and scale of the industrial process stream during 1970s. Activated carbon or silica gel adsorbents were used in the earlier adsorption (Ruthven, 1984).

Adsorption process is collecting soluble substances in solution on a suitable interface. Adsorption of dyes wastewater is depended on the high affinity of many dyes for adsorbent materials. The physical and chemical factors which will influence the dyes wastewater adsorption process are including adsorbent surface are, pH, temperature, dye-adsorbent interaction, particle size and contact time (Valh and Le Marechal, 2009).

Adsorption can produce high quality water and also is an economical process. There are two mechanisms (physical adsorption and chemical adsorption) which occur in the adsorption process. Physical adsorption is easily reversible due to the weak interparticle bonds (van der Waals, hydrogen and dipole-dipole) between the adsorbate and adsorbent. In contrast, there is a strong interparticle bonds (ionic and covalent bonds) present between the adsorbate and adsorbent due to an exchange of electron (Allen and Koumanova, 2005).

1.6.1 Activated Carbon

Activated carbon is the main adsorbent used in industry. The different physical forms of activated carbon are produced according on their application. For an example, granular activated carbon (GAC) is to be used in adsorption columns and powder activated carbon (PAC) is to be used in batch adsorption (Allen and Koumanova, 2005).

According to Ruthven (1984), activated carbon is made by thermal decomposition of carbonaceous material. It is then activation with steam or carbon dioxide at high temperature (700-1100 ^{o}C). The structure of carbon consists of elementary microcrystallites of graphite which are stacked together in random orientation. This will cause the space between the crystals which form the micropores.

Physical and chemical activation methods are the two basic activation methods. Physical activation required high temperature (600-1200 ^{o}C) and it consumed more times for activation process. However, chemical activation method required a through washing due to the use of chemical agents (Gupta and Suhas, 2009).

1.7 Problems Statement

Many researchers have reported that adsorption by solids is a most effective method and an attractive alternative for dyes aqueous solution removal (Hameed and Khaiary, 2008). The most widely used adsorbent for adsorption of dyes, chemical pollutants, herbicides, etc. is activated carbon (Zohra et al., 2008). However, adsorption of activated carbon is limited to certain dyes due to the high operational charges related to its activation and regeneration (Al-Ghouti et al., 2003). Although activated carbon provides good efficiency in dyes wastewater treatment, this adsorbent is expensive and difficult to regenerate after use (Sakkayawong et al., 2005). Therefore, production of relatively low cost adsorbents which can be applied to water pollution treatment is needed to be carried out (Zohra et al., 2008).

Nowadays, many studies on the development of low-cost adsorbent by using agricultural waste materials is needed for an effective process that efficiently remove pollutants from wastewater (Dias et al., 2007). There are a number of studies regarding the preparation of activated carbon from biomass by-products including almond shells, coconut shell, hazelnut shells, rice husk, bagasse pith, orange peels, eucalyptus leaves and etc. (Husseien et al., 2009; Bagheri and Abedi, 2009).

The maize cobs are the by-product of processing maize and the total yield of it was estimated at 6.1×10^8 ton in year 2001. This showed that the resources of maize cobs are rather abundant (Cao et al., 2006). Some studies on extracted xylan from maize cobs which is applicable as additive in papermaking, textile printing and the pharmaceutical industry was reported by Hromádková et al. (1999). The fermentable hydrolysate was prepared from maize cobs by Rivas et al. (2002). Aggarwal and Dollimore (1997) reported preparing activated carbon from maize cobs by chemical activation methods. However, there are less reports on the preparation of activated carbon from maize cobs with large surface area. Hence, to develop a new approach that is more effective utilizing the maize cobs, it is necessary to increase the value of products by adjusting the structure of the products.

Magnetic nanoparticles are used frequently in water purification field in recent years. Dye wastewater treatment by using impregnated magnetic materials onto activated carbon is a new research subject in this field (Li et al., 2011).

The chemical oxygen demand (COD) is usually used to measure the amount of organic pollutants in water or wastewater but many previous studies on dye wastewater treatment do not consider the COD measurement and they just emphasized on the decolorization of dye aqueous solution. In this study, COD is considered as a crucial parameter to be reduced throughout the adsorption process.

Methylene blue which can cause eye burns, difficult breathing, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (Rafatullah et al., 2010) was chosen as adsorbate in this study due to its harmful impacts on receiving water.

In this study, maize cobs obtained as waste from the sweet corn seller were used to form activated carbon. The internal structure of the maize cobs was modified by two methods. One is known as acid activated which using concentrated sulphuric acid as an activation agent. Another method is impregnated magnetic nanoparticles (Fe_3O_4) onto the maize cob. The surface morphology of the activated materials was then examined using scanning electron microscopy (SEM) and the functional group of the activated material was then examined by FT-IR. The adsorption kinetics, isotherm model and thermodynamics were studied under various experimental conditions.

1.8 Objectives

The objectives of present study as below:

(a) To characterize the various adsorbents used in this study using SEM, BET, FT-IR, TEM and EDX.

(b) To determine the efficiencies of dye concentration removal and COD reduction of methylene blue aqueous solution and textile dye wastewater by using various modified maize cobs.

(c) To determine the effects of pH, initial dye concentration, adsorbent dosage, time, and temperature on the dye concentration removal and COD reduction throughout the adsorption process.

(d) To determine the optimal conditions of adsorption process by using design of experiment (DOE) and response surface methodology (RSM) and the kinetics and mechanisms that are involved in the adsorption processes.

(e) To determine the efficiencies of dye concentration removal and COD reduction of real industrial textile wastewater using the effectiveness adsorbent and the best regeneration method of used adsorbent.

CHAPTER TWO

LITERATURE REVIEW

2.1 Nanotechnology

Nanotechnology has various definitions and concepts, but the simplest definition is nanotechnology is a technology at the nanoscale which is considered to cover the range from 1 to 100 nm of particle size of a material. Nanotechnology offers possibility of creating nanamaterials by its novel combinations of properties. The functional of material will be enhanced by nanotechnology with reducing the characteristic dimensions. Nanotechnology also offers a universal fabrication technology (Ramsden, 2011).

Nanotechnology has many potential rewards and many researchers believe that it may offer substantial advantages. According to the U.S. Environmental Protection Agency (U.S. EPA), use of nanotechnology could reduce the energy consumption. For example, uses of nanotechnology-based lightweight composites and thinner paint coatings can reduce the weight of airplanes and automobiles. Hence, it will reduce their fuel usage. On the others hand, nanotechnology also offers the potential to decrease the cost producing solar cells. This had enabled more widespread use of solar power (Seller et al., 2009).

In environmental protection, many engineers and researchers use nanomaterials in wastewater treatment and environmental remediation. Not only in wastewater treatment, there are many researchers also studying the use of nanotechnology to treat air pollution. Nanotechnology also applied in some sensors to detect some chemical contaminated in wastewater or air pollution (Seller et al., 2009).

Researchers are studying nanomaterial use in medical imaging especially drug delivery. Nanotechnology can detect and monitor changes within cells without destroying the cells. For example, biosensing technologies use nanotechnologies to make our understanding of fundamental understanding of cells and a host of disease-specific phenomena (Ashby et al., 2009; Seller et al., 2009).

2.2 Nanoscale Materials or Nanoparticles

Nanoparticles or nanoscale materials are nanoscale form of well-known materials such as gold, silver, platinum, iron and others (Ashby et al., 2009). During the middle of the 19th century, there are different types of nanoparticles in fabrication have been well established. For example, ferric hydroxide nanoparticles produce by Thomas Graham's method (Ramsden, 2011).

Nanoparticles or nanoscale materials can exist in many ways. Some of nanoscale materials such as viruses and volcanic ash are occur naturally. Some of them also can be made of element carbon, carbon-based compounds, metals or metals oxides, or ceramics. These types of nanoscale materials have many shapes and structures which include particles or crystals, tubes, wires, or rods, branched structures, composites and etc. However, National Institute for Occupational Safety and Health (NIOSH) has defines the nanoscale materials into eleven categories which are agglomerated sphere, colloids, crystalline, films, nanohorns, nanorods, nanotubes, nanowires, quantum dots, spherical and others (Seller et al., 2009).

There is several nanoscale materials are widely use in recent year. They are including titanium dioxide, zero-valent iron, silver, carbon black, carbon nanotube and fullerene (Seller et al., 2009).

2.2.1 Titanium Dioxide

Titanium is commonly found in the minerals rutile, or also known as titania (TiO_2) and ilmenite ($FeTiO_3$). Titanium oxide, TiO_2 has been widely used by manufacturers as a pigment due to its ability to absorb or reflect light of different wavelengths. Coatings which containing TiO_2 can provide protection from photochemical degradation due to the TiO_2 can absorb UV radiation. Besides that, the TiO_2 also well known in welding electrodes, ceramics and catalyst (Seller et al., 2009).

2.2.2 Carbon Black

Carbon black is one of the oldest nanoscale materials in widely commercial used. An impure form of carbon black was manufactured by Chinese with burning vegetable oils in lamps since 3500 years ago. However, modern manufacturers still produce carbon black by incomplete combustion or thermal decomposition.

Carbon black consists of more than 97 % element carbon and its products are characterized by their structure, size, surface area, surface activity and particles size (Seller et al., 2009). Carbon black consists of carbon particles ranging in size from a few to several hundred nanometer, but it present in form of bigger particles due to the large quantity of the mass (Ramsden, 2011). Carbon black not only serve as a strengthening or reinforcing filler in rubber products, but it also used in plastics, coatings and inks (Seller et al., 2009).

2.2.3 Carbon Nanotubes

According to Ramsden (2011), Iijima was first reported the characterization and synthesis of carbon nanotubes in year 1991. The actual nature of carbon nanotubes with seamlessly rolled up tubes of graphere was established relatively recently. However, multiwalled carbon nanotubes commonly consist of several concentric tubes of graphere nested inside each other. The structure of the both single walled carbon nanotube and multiwalled carbon nanotubes shows in Figure A4(a) and A4(b) in section Appendix B (Ramsden, 2011).

The characteristics of carbon nanotubes depend on their composition, size, and orientation. Carbon nanotubes are neither insoluble in water nor solvents. It has a great physical strength and flexibility which are approximately 200 times as strong as steel. Carbon nanotube is light in weight and the density is 2.6 g/cm^3 which about one-third the density of steel. Carbon nanotubes can conducts electricity very well if the carbon atoms arranged in straight lines along the length of the tube. However, the nanotube is a semiconductor when the carbon atoms are arranged in a spiral. It is also high thermal conductivity and high storage of chemical substances within the hollow cylinder (Seller et al., 2009).

The carbon nanotubes were widely used in chemistry applications, medicine or life science tools, electronics and information technology and also capacitors in solar cell to store energy due to its unique properties (Seller et al., 2009).

2.2.4 Fullerenes

Fullerenes are also known as buckyballs and it normally exist as C_{60}, C_{70}, etc. (Ramsden, 2011). It is a spherical particle and mostly comprising 60 carbon atoms which arranged as 20 hexagons or 12 pentagons which shown in Figure A5 in section Appendix B (Seller et al., 2009).

The fullerenes present in several of structures which including endohedral or incarfullenes, multi-walled or nested fullerenes and heterofullerens. The fullerenes commonly present in C_{60} form followed by C_{70}. However, the higher fullerenes are included C_{74}, C_{76}, C_{78}, C_{80}, C_{82}, C_{84}, C_{86} and C_{96}. The structure, derivatization, and degree of agglomeration will influence the properties of fullerenes. Pure fullerenes are normally have low solubility in water, but it will form polymorphic hexagonal until cell agglomerates in water referred to as nano-C60 (approximately 25 to 500 nm) under certain conditions. Fullerenes are widely used in catalyst and sensors, sports equipments, cosmetic and photochemistry application (Seller et al., 2009).

2.2.5 Zero-Valent Iron

Granular zero-valent iron have been used in treat chlorinated hydrocarbons and chromium in groundwater since 1900s. However, some researchers found out that the rate of reduction dechlorination of chlorinated hydrocarbons depended strongly on the surface area of the granular zero-valent iron. Hence, this had led to the development of nano zero-valent iron with 40 and 300 nm of diameter of the particles. This had increased surface area and provides greater reactivity. Nano zero-valent iron can be form by heat iron pentacarbonyl, ferric chloride reacted with sodium borohydride, and iron oxides reacted with hydrogen under high temperature and ball mill iron fillings to nano-sized particles (Seller et al., 2009). Table 2.1 shows the information about the structure and composition of the specified nanoscale materials and some of their uses.

Table 2.1. Types and uses of nanoscale material or nanoparticles (Source: Seller et al., 2009)

Structure	Composition					
	Carbon		Metals		Ceramics/Silica	
	Nanoparticles	Uses	Nanoparticles	Uses	Nanoparticles	Uses
Particle	Carbon Black	Pigment (reinforcement of rubber products)	Titanium dioxide (TiO_2)	Cosmetics (environmental remediation)	Ceramic nanoparticles	Coating on photo paper
	Nano-sized wax particles	Car wax	Zero-valent iron, nano magnetite (Fe_3O_4)	Environmental remediation		
			Silver	Antibacterial agent in wound care, athletic, clothing, washing machines		
			Zinc oxide	Cosmetics		
			Cerium oxide	Diesel additive to decrease emission		
Tube /wire	Carbon nanotubes	Electronics, sporting goods	Nanowire			
Dendrimer	G5 dendrimer	Targeted drug delivery	Iron sulfide clusters immobilized in dendrimers	Environmental remediation		
Others	Fullerence	Cosmatics	Quantum dots	Semi-conductors	Functionazied ceramic nanoporous sorbents	Water treatment

2.3 Magnetic Nanoparticles

A class of engineered particulate materials with particles size less than 100 nm and which can be manipulated under the influence of an external magnetic field is known as magnetic nanoparticles. They are usually composed of magnetic elements which included iron, nickel, cobalt, magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), cobalt ferrite (Fe_2CoO_4) and chromium dioxide (CrO_2) (Indira and Lakshmi, 2010).

A material's magnetic properties are classified due to its magnetic susceptibility (the ratio of the induced magnetization to the applied magnetic field) (Indira and Lakshmi, 2010). In ferri- or ferromagnetic materials, magnetic moments align parallel to magnetic field, coupling interactions between the electrons of the material result in ordered magnetic state. The susceptibilities of these materials depend on their external field magnetic field, temperature and atomics structure. Ferri- or ferromagnetic materials such as magnetic nanopartilces become a single magnetic domain and also maintain one large magnetic moment at small size which in order of tens of nanometer (Sun et al., 2008).

However, in the diamagnetic materials, the magnetic moment is antiparallel to magnetic field resulting in very small and negative susceptibilities (from -10^{-6} to -10^{-3}) and they do not retain magnetic properties when the external field is removed. These kinds of materials are described as paramagnetic (Sun et al., 2008).

The thermal energy is sufficient to induce free rotation of the particle at sufficiently high temperature which also known as blocking temperature. This will cause a loss of net magnetization in the absence of external field. Therefore, this enables the particles to maintain their colloidal stability and avoids aggregation.

Hence, it is making it feasible for their use in biomedical application. In the addition, the paramagnetic materials result in much lower magnetic susceptibilities than the coupling interactions in single magnetic domains (Sun et al., 2008; Indira and Lakshmi, 2010).

2.3.1 Iron Oxide Nanoparticles

Recent development of nanotechnology has shed a light on wastewater purification area. Nanoparticles have been attracting much interest due to their unique properties and potential applications.

Adsorption is a common but important separation process in the wastewater treatment. The diameters of adsorbents are mostly in the range of sub-micron to micron and they have large internal porosities to ensure adequate surface area for adsorption. However, the adsorption rate and the available capacity were decreased cause by the diffusion limitation within the particles. Hence, there is an incentive to develop a novel adsorbent with a high capacity for large solutes, a small diffusion resistance and a large surface area for adsorption (Liao and Chen, 2002).

Magnetic nanoparticles are widely use in the fields of high-density data storage, ferro-fluids, magnetic resonance imaging, wastewater treatment, bioseperation and biomedicine (Mak and Chen, 2004). Several types of magnetic nanoparticles for various applications could be tailored by using functionalized natural or synthetic polymers to impart surface reactivity (Liao and Chen, 2002).

In recent year, magnetic Fe_3O_4 nanoparticles have attracted in the area of medical care, magnetic recording and magnetic sensing. These types of magnetic nanoparticles exhibit the finite-size effect or high ratio of surface-to-volume. This was resulting in a higher adsorption capacity for the wastewater purification through adsorption process (Shen et al., 2009).

The magnetic nanostructure particles (Fe_3O_4) not only non-toxic and biocompatible but it also holds the advantages of flexibility, eco-friendly characteristics and economic in operational cost (Shen et al, 2009; Ma et al., 2007).

2.3.2 Synthetic Routes of Preparation of Magnetic Nanoparticles-Fe_3O_4

Iron oxide (Fe_3O_4) nanoparticles have been produced by variety of synthesis process since many years ago. Iron oxide was started prepared by traditional wet chemistry solution-based methods. The method was then developed to more exotic techniques such as laser pyrolysis or chemical vapor deposition due to the development of sciences and technology (Sun et al., 2008).

Nowadays, many methods have been modified to prepare Fe_3O_4 magnetic nanoparticles due to the many researchers start interested on the advantages of magnetic nanoparticles. The preparation methods are including chemical co-precipitation, micro-emulsion, hydrolyzation, etc. However, Zhao et al. (2008) had pointed out the chemical co-precipitation method is the most simplicity and productivity method. This method is widely used for biomedical applications because Fe_3O_4 magnetic nanoparticles are non-hazardous materials and this method will produce large quantity of Fe_3O_4 magnetic nanoparticles (Yang et al., 2008).

In terms of medicine, chemical co-precipitation is known as specifically the precipitation of an unbound "antigen along with an antigen-antibody complex".

The reaction principle is shown in chemical reaction equation 2.1 (Indira and Lakshmi, 2010).

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \longleftrightarrow Fe(OH)_2 + 2Fe(OH)_3 \longrightarrow Fe_3O_4 + 4H_2O \quad (2.1)$$

Although chemical co-precipitation is the simplicity method to produce Fe_3O_4 magnetic nanoparticles, it was hard to get high magnetic response and uniform-sized Fe_3O_4 magnetic nanoparticles. Hence, there is need for further research on this method (Zhao et al., 2008).

According to Vergés et al. (2008), Massart and his research parents were pioneers in obtaining magnetic nanoparticles from $FeCl_2$ and $FeCl_3$ with 1:2 (ratio of Fe^{2+} to Fe^{3+}) precipitated in alkaline solutions such as NaOH, NH_3, etc. The particle sizes obtained by this method are between 6 and 7 nm, but with a poor defined morphology and large dispersion. However, several alternative routes for limiting the size dispersion have been reported and these particles have an advantage for their application in biology due to they are stable in water.

Thermal decomposition of organic iron precursors in the presence of a surfactant can produce high-quality magnetic nanoparticles with their particle sizes up to 20 nm. However, these magnetic particles are only stable in organic media and this cause they limit use for biomedical application (Vergés et al., 2008).

Finally, Matijević and her research partners had come out several procedures for preparation of magnetic nanoparticles with the particle sizes between 100 and up to 1000 nm. These methods are based on the hydrothermal reduction of Fe^{3+} complexes or on the oxidation of Fe^{2+} salts. Both of the reactions were carried out in basic media (Vergés et al., 2008).

2.4 Dyes

Chromophores which produce the color and auxochrames which enhance the affinity of dye toward the fibres are the two important components in the dye molecules. Dyes can be classified into three categories those are cationic or also known as basic dyes, anionic (disperse) dyes such as direct dyes, acid dyes and reactive dyes, and nonionic dyes (Salleh et al., 2011).

2.4.1 Anionic Dyes

Anionic dyes depend on a negative ion and it includes many compounds from many classes of dyes which differences in structure but posses as a common feature, water solubilizing and ionic substituent. For the example, azoic, anthraquinone, triphenylmethan and nitro dyes. Anionic dyes also include direct dyes and reactive dyes (Salleh et al., 2011).

Most of the acid dyes have good water solubility. Acid dyes as organic sulphonic acids and they will have a harmful effect on human beings (Salleh et al., 2011). These types of dyes are widely used with silk, wool, and modified acrylic (Salleh et al., 2011). They also used for dyeing protein and synthetic polyamide fibers (Zollinger, 1987).

On the other hand, reactive dyes with a low degree of fixation due to the hydrolysis of reactive groups in water phase will cause the environmental pollution as release them to the natural streams. Most of these dyes will interact with cotton, wool, etc. to form covalent bonds (Salleh et al., 2011).

2.4.2 Cationic Dyes

In general, the pendant cationic dyes and delocalized cationic dyes are the two important groups of cationic dyes. The structure of pendant cationic dyes are similar to dispersal dyes while the delocalized cationic dyes carry a cationic charge which is delocalized in the chromogen (Zollinger, 1987).

The chemical structures of the cationic dyes are based on the substituted aromatic groups and this group of dyes is toxic colorants and will cause allergic dermatitis, skin irritation, mutations and cancer. Cationic dyes carry positive charge in their molecules. It known as basic dyes and it is water soluble and yield colored cations in solution. Cationic functionality is found in cationic azo dyes, methane dyes, anthraquinone, di- and tri-arylcarbenium, phathalocyanine dyes, various polycarbocyclic and solvent dyes. Basic dyes are highly visible and have high brilliance and intensity of colors among the other group of dyes. There are several cationic dyes were used in intensity as a dye model in dyes adsorption studies. For the examples: Methylene blue, Basic blue 41, and Basic red 46 (Salleh et al., 2011).

2.4.3 Textile Dyes

Textile industries usually used basic dyes, acid dyes, reactive dyes, azo dyes, direct dyes mordant dyes, sulfur dyes and vat dyes. However, industries are widely used azo derivatives dyes in this recent year (Salleh et al., 2011). Table 2.2 shows the typical dyes that are used in the textile industry today.