ADSORPTION OF METHYLENE BLUE USING CHITOSAN MEMBRANE EMBEDDED WITH MULTI-WALLED CARBON NANOTUBES

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ADSORPTION OF METHYLENE BLUE USING CHITOSAN MEMBRANE EMBEDDED WITH MULTI-WALLED CARBON NANOTUBES

by

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Symbol	Description	Unit
C	Highest concentration of dye	mg/L
C_0	Initial concentration of dye	mg/L
C_e	Equilibrium concentration in the solution	mg/L
C_t	The concentration of dye at time	mg/L
K_L	Langmuir adsorption equilibrium constant	L/mg
K_F	Freundlich constants	mg/L
k_1	The equilibrium rate constant of pseudo-first order model	1/min
k_2	The equilibrium rate constant of the pseudo second order model	g/mg min
M	Mass of the adsorbent	g
Q_0	The maximum adsorption capacity	mg/g
q_e	Amount of adsorption equilibrium	mg/g
q_t	Amount of adsorption at time	mg/g
R_L	Separation factor	-
R^2	Regression coefficient	-
V	Volume of solution	L
Wt.%	Mass fraction in percentage	%
$1/n$	Adsorption intensity	-

LIST OF ABBREVIATIONS

AR183	Acid Red 183
BA	4-hydroxybenzoic acid
BOD	Biochemical oxygen demand
CA	Hydrocaffeic acid
CNTs	Carbon nanotubes
COD	Chemical oxygen demand
CS	Chitosan
CVD	Chemical vapour deposition
DBA	3,4-dihydroxybenzoic acid
DWCNTs	Double walled carbon nanotubes
GA	Glutaraldehyde
GlcN	β-1,4-linked D-glucosamine
GlcNAc	N-acetyl glucosamine
H_2SO_4	Sulfuric acid
HiPCO	High pressure carbon monoxide
MB	Methylene blue
MMMs	Mixed matrix membranes
MWCNTs	Multi-walled carbon nanotubes
NaOH	Sodium hydroxide
PA	3,4-dihydroxyphenyl-acetic acid
PEP	Polyethylene terephthalate
SWCNTs	Single-walled carbon nanotubes
TSS	Total suspended solid

PENJERAPAN METELINA BIRU MENGGUNAKAN MEMBRAN KITOSAN TERANGKUM TIUB NANO KARBON DINDING BERLAPIS

ABSTRAK

Dalam kajian ini, kitosan (CS) dan CS terangkum tiub nano karbon dinding berlapis (CS/MWCNTs) membran dihasilkan dengan mengunakan kaedah penuangan larutan. Membran tersebut digunakan untuk mengkaji penjerapan metilena biru (MB) dari segi masa sentuhan, kepekatan awal MB dan suhu. Kesan masa sentuhan dilakukan dari 60- 240 minit pada suhu 25 ° C dan kepekatan MB 4 mg/L. Untuk mengkaji kesan kepekatan MB, pewarna MB yang berlainan kepekatan dari 1 mg/L hingga 4 mg/L telah dilakukan pada masa dan suhu yang ditetapkan pada 25 °C dan 240 minit. Kesan suhu dikaji dari 25 °C hingga 40°C pada kepekatan MB iaitu 4mg/L selama 240 minit. Ujian penjerapan menunjukkan membran CS/MWCNTs memberikan kapasiti penjerapan dan kecekapan penyingkiran yang lebih tinggi terhadap MB berbanding membran CS tanpa MWCNTs. Kapasiti penjerapan maksima dan kecekapan penyingkiran ialah 0.0160 mg / g dan 93.8% dan 0.0019 mg /g dan 12.5% masing-masing untuk membran CS/MWCNTs dan CS tanpa MWCNTs pada suhu 40°C, masa sentuhan 240 minit dan kepekatan MB 4 mg/L. Keseimbangan isoterma telah dianalisis menggunakan model Langmuir dan Freundlich. Penjerapan untuk MB sesuai dengan model Freundlich. Analisis kinetik dijalankan menggunakan tertib pseudo-pertama dan pseudo-kedua. Keputusan kajian menunjukkan penjerapan MB sesuai dengan perintah pseudo-kedua.

ADSORPTION OF METHYLENE BLUE USING CHITOSAN MEMBRANE EMBEDDED WITH MULTI-WALLED CARBON NANOTUBES

ABSTRACT

In this study, the chitosan (CS) and CS embedded with multi-walled carbon nanotubes (CS/MWCNTs) membrane were synthesized using solution casting method. The resultant membranes were used to study the adsorption of methylene blue (MB) in terms of contact time, initial MB concentration and temperature. The effect of contact time was conducted from 60-240 minutes at temperature of 25°C and MB concentration 4 mg/L. For study of the effect of MB concentration, different dye concentrations ranging from 1 mg/L to 4 mg/L at were conducted while the temperature and the contact time was maintained at 25 °C and 240 minutes, respectively. The effect of temperature was studied from 25°C to 40°C at MB concentration at 4 mg/L and time 240 minutes. Adsorption test showed that the CS/MWCNTs showed higher adsorption capacity and removal efficiency of MB than CS membrane without MWCNTs. The maximum adsorption capacity and removal efficiency were found to be 0.0160 mg/g and 93.8% and 0.0019 mg/g and 12.5% for CS/MWCNTs and CS membrane without MWCNTs, respectively at conditions temperature 40°C, contact time 240 minutes and MB concentration 4 mg/L. The equilibrium isotherm was analysed using Langmuir and Freundlich model. Adsorption for MB follows Freundlich model. Kinetic analysis was conducted using pseudo-first order and second order. The results showed the adsorption of MB fitted well for pseudo-second order.

CHAPTER 1

INTRODUCTION

1.1. Nature of textile effluent

In textile industries, the waste that releases into the environment caused contamination of ground and water that danger to marine life and human beings. About 17-20% of the river pollution is caused by textile industries. Annually during the manufacturing of the textile product, estimation 10-15% of total dyestuffs that equivalent to 280,000 tons of dyestuffs that released into the environment (Gonawala and Mehta, 2014). The textile effluents usually consist many types of dyes, detergents, solvents and salts depend on the particular textile process such as dyeing, printing, bleaching and so on. Table 1.1 shows that the characteristics of wastewater from the effluents of the textile dyeing process that consist of several types of component.

Table 1.1: Components of wastewater from a textile industries (Marcucci et al., 2003)

Aspect/component	Value
Concentration, mg/L	50-5000
COD, mg/L	50–5000
BOD, mg/L	200–300
TSS, mg/L	50–500
Organic nitrogen, mg/L	18–39
Total phosphorus, mg/L	0.3–15
Total chromium, mg/L	0.2–0.5
Colour, mg/L	>300

1.2. Dye classification

Dyes usually can be categorized correspond to their application, structure, colour and the charge of the particle simultaneously dissolution in the aqueous solution such as anionic (acid, reactive, and direct dyes), cationic (all basic dyes), and non-ionic (dispersed dyes) as shown in Table 1.2.

Table 1.2: Types of dye and applications (Tan et al., 2015)

Dyes	Example	Properties
Acidic	Acid red 183, acid orange 10, acid orange 12, acid orange 8, acid red 18, sunset yellow, acid green 27, methylene orange, amido black 10B, indigo carmine	Water soluble, anionic
Cationic	Methylene blue, janus green, basic green 5, basic violet 10, rhodamine 6G	Water soluble, releasing coloured cationic in solution. Some dyes show biological activity
Disperse	Disperse orange 3, disperse red, disperse 1, disperse yellow 1	Water-insoluble, non-ionic: for hydrophobic aqueous dispersion
Direct	Congo red, direct red 23, direct orange, direct blue 86	Water soluble, anionic, enhance was fastness by chelating with metal salts
Reactive	Reactive black 5, reactive green 19, reactive blue 4, reactive red 195, reactive red 198, reactive blue 19, reactive red 120	Extremely high washed fastness due to covalent bond formation with fiber, this dye more brighten than direct dyes
Vat	Vat blue 4, vat green 11, vat orange 14, vat orange 28, vat yellow 20	Use soluble leuco salts after reduction in alkaline bath sodium hydroxide (NaOH)

Many industries use dyes in manufacturing their product to provide colour such as paper, dye stuff, plastic, printing, textile, carpet, cosmetics, and food. The waste of dyes in these industries usually release into the environment (Rajabi et al., 2017). Most of the dyes are carcinogenic, that required effective treatment for dyes in the wastewater effluent. Table 1.3 shows the classification to the dyes and their toxicities according to the application.

Table 1.3: Applications and toxicities of various dyes (Tan et al., 2015)

Dye	Application	Toxicity
Acidic	Nylon, wool, silk, paper, leather, ink-jet printing	Carcinogen and malignant
Cationic	Paper, polyacrylonitrile, modified nylons, modified polyesters, antispectic	Carcinogen and malignant
Disperse	Polyester, nylon, cellulose, cellulose acetate, acrylic fibres	Allergenic, carcinogen
Direct	Cotton, paper, leather regenerated cellulose,	Bladder cancer
Reactive	Cotton, wool, nylon, ink-jet printing for textile	Dermatitis, allergic conjunctivitis, rhinitis occupational asthma
Vat	Cellulosic fibers	-

1.3. Adsorption process

Adsorption is a common treatment method using particulate adsorbent for the removal pollutants such as dyes from industrial wastewater. However, some weaknesses using particulate adsorbent such as lower adsorption, lower regeneration ability and lower selectivity. Because of that, many researchers are done to seek for another technology to overcome those problems. One of the examples is membrane adsorbent that was developed in mid-1980. As shown in Figure 1.1 the targeted pollutants are selectively adsorbed to the functional group of membrane adsorbent. Once the polluted water passed through the membrane, the functional active binding sites will attach to the target pollutants and the polluted remove from the drinking water with higher adsorption rate and capacity because of the contact distance is very short at a submicron-scale level between the target pollutants to the adsorbed active binding site of the membrane adsorbents (Zheng et al., 2015).

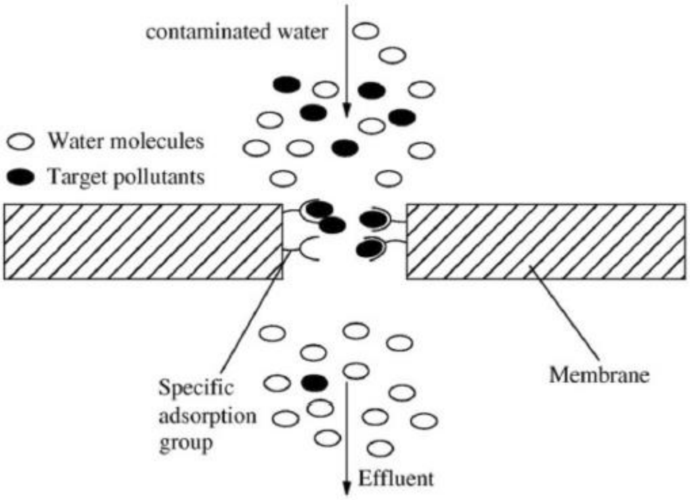

Figure 1.1: The principle of membrane adsorbent (Khulbe and Matsuura, 2018)

The polymeric membrane usually embedded with commercial filler particles such as ion-exchange resins, clays, chitosan beads, functionalized silica particles, metal ion charged bead, nanoparticle and plant waste. Generally, these filler particles comprise ionic groups that could offer charge interaction with pollutant species. The most popular mode of adsorption is ion exchange mode. This because its interaction rate is usually faster as compared to other adsorption modes. Moreover, ion exchangers are usually cheaper if compare with the specific affinity adsorbents. Since adsorption is a surface phenomenon, so by embedding the filler into the membrane could increase the total surface area of adsorption is larger that which will increase the adsorption efficiency (Suen, 2015).

1.4. Problem statement

In textile, paper, leather, cosmetic and plastic and industries, they use chemicals and dyes to colour their products. Several of pollutants release from these industrial activities into the water resources such as heavy metal, dyes, pesticides and detergents. The most problematic pollutant produce in these industries are synthetic dyes that cause problem to human health and the marine ecosystem. The presence of a small amount of dye in the water could affect the changes colour of water, which can delay the photosynthesis process of aquatic organisms because the dye reducing sunlight penetration (Panic et al., 2013). Moreover, dye also can cause skin irritation, cancer and mutagenic (Farghali et al., 2013).

There are various techniques for removing the dye such as adsorption, coagulation, flocculation (Namasivayam et al., 1996), and oxidation or ozonation. Among those techniques adsorption is preferable for dye removal process because it is economical, high efficiency, simplicity, and insensitivity to toxic substances (Wu, 2007, Panic et al., 2013). In adsorption, different types of adsorbents were used for example activated carbon, resin, zeolites and nanomaterial such as carbon nanotubes, graphene, ferric oxide, manganese oxide, titanium oxide, magnesium oxide and zinc oxide. In wastewater treatment technology the selection of adsorbent based on various characteristic for example the adsorbent must environmentally friendly, higher sorption capacity and higher selectivity towards the pollutants, ease removal of pollutants from the surface and easy for regeneration. Many researchers have verified that nanomaterial fulfil most of these requirements (Machida et al., 2006, Ali, 2012, Sadegh et al., 2017, Sharma et al., 2009).

However, in the batch process using particulates adsorbents might cause many problems such as consumption of energy for particle mixing, maintaining uniform particle suspension at a large vessel and difficult for solid-liquid separation that required filtration or centrifugation that required additional cost. Adsorption of cationic dye was studied by Lin et al. (2015) using composite membrane comprised polyethylene terephthalate (PEP) as polymeric matrix and water bamboo husk particles as the fillers.

1.5. Research objective

The main objective of this study is:

I. To synthesis CS and CS/MWCNTs membranes via solution casting method
II. To study the adsorption capacity and removal efficiency of dye at different temperature, contact time and initial MB concentration
III. To study the equilibrium isotherm and kinetic of MB adsorption on the resultant membrane

1.6. Study scope

The aims of this study was to synthesis the CS membrane with and without MWCNTs that used for removal of MB. The CS membrane were cross-linked with glutaraldehyde (GA) to increase the rigidity and stability. The membranes were prepared by solution casting method. The experiments were done in a batch system to evaluate the percentage of MB dye removal efficiency and the adsorption capacity of adsorbent. The adsorption of MB was studied with respect to initial MB concentration, contact time, and temperature. The adsorption isotherm was studied by using the Langmuir and Freundlich isotherm models, and the kinetic isotherm was determined by pseudo-first order and pseudo-second order.

CHAPTER 2

LITERATURE REVIEW

2.1. Adsorption

Adsorption is known as surface phenomenon where the accumulation of gas or liquid solute on the surface of the adsorbent. The general term of adsorbent is the adsorption of the adsorbate onto the adsorbent surface in which the adsorption occur. Figure 2.1 shows the overview of the adsorption process. In adsorption, there are five steps that occurs firstly, the diffusion of the solute to the active sites of the surface of the adsorbent. Next, the adsorption of one or more reactants onto the surface followed by surface reaction. Then, the removal of the adsorbent from the surface known as desorption. Finally, the diffusion of product away from the adsorbent surface.

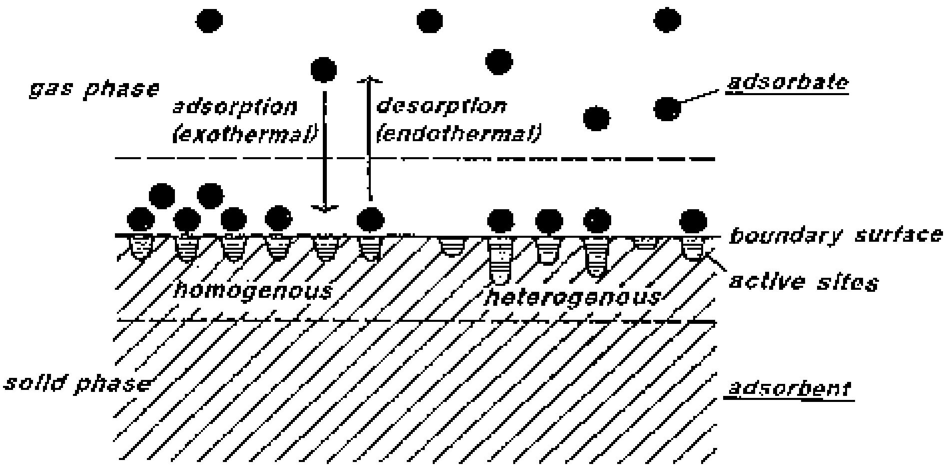

Figure 2.1: Adsorption process (Sarkar, 2013)

Adsorption may categorize into physical and chemical adsorption. The comparison between physical and chemical adsorption are shown in Table 2.1. Physical adsorption is caused by the weak Van der Waal’s interaction forces between the adsorbate molecule and adsorbent surface. This process occurs rapidly at lower temperature that forms multi-molecular layer. Physical adsorption possesses a lower heat of adsorption between the ranges of 20-40 kJ/mol and it is an exothermic process. The efficiency and capacity of adsorption are inverse proportional to the temperature, as the temperature in adsorption efficiency and capacity decrease. Physical adsorption is a rapid process that does not require activation energy and not specific in the nature of the all gases adsorbed on all solid.

In contrast, chemical adsorption is a slow process that involves the formation of chemical bonds between adsorbent and adsorbate, it is a monolayer often released higher heat of adsorption between range 40-400 kJ/mol. Chemisorption from a gas commonly takes place only at temperatures more than 200°C. It is highly specific in nature that happens just when there is some possibility of the compound formation between the solid adsorbent and adsorbed gas. This process generally required activation energy and it is irreversible process (Paul, 2016, Seader et al., 2011).

Table 2.1: Comparison between chemical and physical adsorption

Physical	Chemical
▪ Lower heat of adsorption 20-40 kj/mol	▪ Higher heat adsorption 40-400 kj/mol
▪ Formation of Van der Waal's forces	▪ Formation of chemical bond forces
▪ Reversible	▪ Irreversible
▪ It is not very specific	▪ It is highly specific
▪ Forms multi-molecular layer	▪ Forms monomolecular layer
▪ Does not require activation energy	▪ Required activation energy
▪ Occur at low temperature	▪ Occur at higher temperature

2.2. Carbon nanotubes (CNTs)

In 1991, carbon nanotubes (CNTs) were discovered by Iijima, CNTs made up entirely of carbon and can be divided into single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and MWCNTs. SWCNTs is the simplest structure consist of a single layer cylindrical arrangements of graphene sheets and individual carbon structure. The diameter range of SWCNTs is between 0.4-3 nm. While DWCNTs having diameter in range 2-4 nm. MWCNTs are multiple concentric tubes having a diameter of 10–200 nm (Sudhakar et al., 2010). There are several methods to produce CNTs such as arc discharge, high pressure carbon monoxide (HiPCO), chemical vapour deposition (CVD) and excimer laser ablation.

As the CNTs exhibit excellent electrical, mechanical, thermal and magnetic properties, so there are several potential application in the development of CNTs-based membrane (Qian et al., 2000), photovoltaic devices, superconductor, electrochemical capacitors, nanowires, nanoelectronic, nanocomposite materials, removal of heavy material and dye technology. Qian et al. (2000) reported that by adding 1 wt.% of MWCNTs into polystyrene could increase the stress about 25% and the elastic modulus by 35%-45% as compared to blank polystyrene.

Selen et al. (2016) reported that MWCNTs particles can be used for removing of MB from the wastewater at optimum pH 10 with the maximum adsorption capacity 95.30 mg/g. Prola et al. (2013) reported that the percentage removal of mixtures dye from the textile effluents is 99.87% for MWCNTs and 97% for activated carbon. The MWCNTs is more economical adsorbent because it can be reused for several time and can be regenerated. CNTs is a good adsorbent for removing of organic and inorganic substance from the contaminant aqueous solution as compared to the common adsorbent like activated carbon. CNTs have the unique characteristic which are high selectivity, large specific area and high aspect ratio (l/d), consist of smaller in size with hollow and layered structure offer for the higher adsorption capacity compared to the activated carbon (Prola et al., 2013).

The surface modification of CNTs has the greater impact on enhancing their performance and the ability in adsorbing the synthetic dyes from aqueous solution due to higher the number of binding sites and also the formation of new functional groups.

Oxidation is the most popular method for surface modification because it is an easy method for introducing hydroxyl and carbonyl groups to the sidewalls of CNTs. The removal of methylene red and MB were found effective by using oxidized MWCNTs than un-oxidized MWCNTs (Ghaedi and Kokhdan, 2012, Ghaedi et al., 2012). Shahryari et al. (2010) studies on the same batch experiments on MWCNTs having larger surface area 280 m^2/g compared to that of CNTs 160 m^2/g that used by Yao et al. (2010) and stated a higher MB adsorption was 132.6 mg/g at 37°C larger adsorbent surface area provide higher MB adsorption capacity.

2.3. Mixed matrix membranes (MMMs)

MMMs consisting by inorganic particles dispersed onto polymer, as shown schematically in Figure 2.2. Various module types of MMMs for example flat shape, hollow fiber, disc holder, cylindrical tube, spiral-wound module, and cartridge. Among them, the most common module used is a flat shape and hollow fiber. The bulk phase (phase A) usually is a polymer and the dispersed phase (phase B) is inorganic particles such as zeolite, carbon molecular sieves and nanoparticle. Based on its structure, MMMs can be divided into dense and porous structure. For dense structure it is used in gas separation, pervaporation, and fuel cell and so on while, for porous structure usually used for adsorption. In separation, MMMs can achieve higher selectivity, permeability, higher separation by the dispersion of inorganic particle. Several benefits, dispersion of inorganic particle could offer a pathway for target species to pass through and also the void volume fraction in the MMMs can be optimised. In addition, the chemical composition of inorganic particle surface can acts as facilitated transport carrier (Chung et al., 2007).

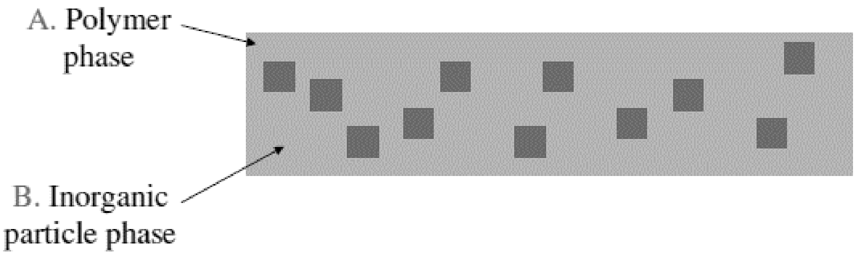

Figure 2.2: Schematic diagram of mixed matrix membrane (Chung et al., 2007)

Generally, many benefits in the adsorption process using MMMs which are, least membrane fouling, lower flux decline, energy saving, simple and flexible for large-scale operation such as natural gas separation, hydrogen recovery, and removal of volatile organic compound from effluent stream. Over the years, the researchers still explore various ways to improve the performance of MMMs in terms of material used and the operation such as by choosing environmentally friendly polymer, using smaller fillers to reduce the intra-filler diffusion limitation, using the same functional group of polymer and filler to optimize the adsorption ability of the MMMs and selecting the suitable cylindrical configuration in order to longer the residence time (Suen, 2015).

2.3.1. Solution casting method

Solution casting is typically used to prepare a small sample of a single layered membrane for research purposes. Nevertheless, this method also suitable for fabrication of multi-layered dense/porous membrane by coating the multi-solution on the glass support. In this method, the polymer and all other necessary components dissolve in common solvent to obtain homogenous solution followed by casting the solution into petri dish or flat glass plate and left for several days for evaporation. Once, the evaporation of solvent complete, the dried membrane peeled off from the petri dish. The steps of membrane preparation are shown in Figure 2.3.

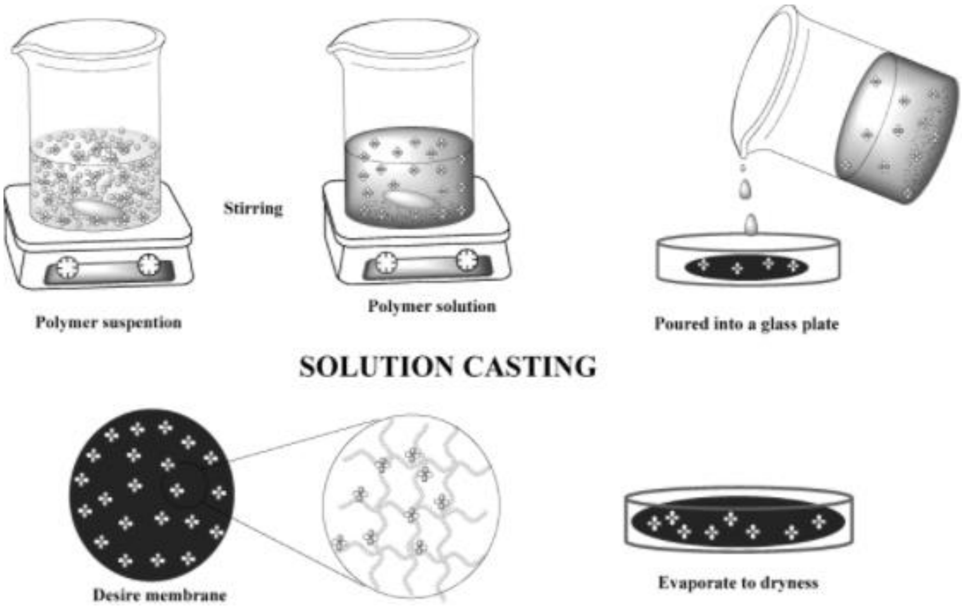

Figure 2.3: Preparation of membrane by solution casting (Roy and Singha, 2017)

In order to prevent the solution running over the casting plate, so the polymer solution that used in this method should be adequately viscous, polymer concentrations usually in the range of 15–20 wt.% (Baker, 2004). In fact, the selection of solvent in this method is important to synthesis the good membrane. The most suitable solvent is moderately volatile liquid such as acetone, ethyl acetate, and cyclohexane. Avoid solvent with high boiling point and low volatility such as dimethyl formamide or N-methyl pyrrolidone. Moreover, highly volatile solvents such as methylene chloride causing gelation of the polymer because of the rapid evaporation solvent. However, rapid evaporating solvent can use to synthesis smooth membrane by lowering the evaporation rate that can be obtained by covering the cast membrane with glass plate elevated 1-2 cm above the membrane (Roy and Singha, 2017, Baker, 2004).

2.4. Chitosan

Chitosan (CS) is a natural biopolymer that usually obtained from chitin by the deacetylation reaction under alkaline condition, consists of linear β-1,4-linked D-glucosamine (GlcN) and N-acetyl glucosamine (GlcNAc) unit. Figure 2.4 shows the structure of CS. Several advantages of CS such as biocompatibility, biodegradability, non-toxicity, economical because chitin is the second-most abundant polymer in nature following to cellulose and good adsorption capacity (Jafari Sanjari and Asghari, 2016). CS is a widely used as adsorbent in the wastewater treatment technology for removal of heavy metal and dye because of the presence of functional group on chitosan chain which are hydroxyl (-OH) and amino ($-NH_2$) play as reaction sites (Wu et al., 2001). Ravi Kumar (2000) reported the amino groups of CS can be cationized, once they adsorb anionic dye strongly in acidic condition by electrostatic attraction but CS is very sensitive to changes of pH. The CS performance as the adsorbent can be optimized by crosslinking reaction using formaldehyde, GA, glyoxal, epichlorohydrin, ethylene glycon diglycidyl ether and isocyanates. Crosslinking reaction can stabilize CS in acidic medium solution that give the enhancement for pore size distribution, mechanical resistance, chemical stability and adsorption/desorption (Wan Ngah et al., 2011).

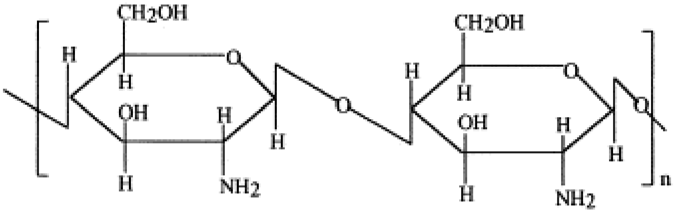

Figure 2.4: The structure of chitosan (Orrego and Valencia, 2008)

Chao et al. (2004) reported modified CS by enzymatic grafting of carboxyl groups onto chitosan can increase the adsorption capacity for adsorbing the cationic dye. In their study four different types derivatives of phenol were used as substrates of tyrosinase to graft onto chitosan which are, 4-hydroxybenzoic acid (BA), 3,4-dihydroxybenzoic acid (DBA), 3,4-dihydroxyphenyl-acetic acid (PA), and hydrocaffeic acid (CA). They reported that the modified chitosan gel was found to be effective in the adsorption of cationic dyes crystal violet (pH 7) and bismarck brown Y (pH 9) at 30°C. The isotherm follows Langmuir type and the maximum adsorption capacities for both dyes were increased with the following order CS-CA > CS-PA > CS-DBA > CS-BA.

The removal of azo dyes (tartrazine and amaranth) from the aqueous solutions by adsorption using CS film was studied by Rêgo et al. (2013). They reported that, the optimum adsorption of azo dyes occurred at pH 2 and the concentration of CS film at 100 mg/L. The results showed that the maximum adsorption capacities for the tartrazine and amaranth were 413.8 mg/g and 278.3 mg/g, respectively. The adsorption capacity is depended on the electrostatic interaction between the protonated amino groups of the chitosan film (NH_3^+) and sulfonated groups (SO_3^-) of the azo dyes. Nevertheless, in the desorption experiments with NaOH 0.50 mol/L, it showed that the CS film could be reused for two cycles of adsorption, and gave similar adsorption ability.

Dotto et al. (2013) investigated the removal of acid red 18 and FD&C blue no. 2 dyes from the aqueous solution in batch operation system using CS films. At 25 °C the maximum adsorption capacities of acid red 18 and FD&C blue no. 2 were 2194.6 mg/g and 154.8 mg/g, respectively. After adsorption process, the CS films structure is retained and easily separated from the liquid phase.

2.5. Methylene blue

MB was selected in this study because of the strong adsorption onto solids. MB is a cationic dye that considered not very toxic dye but it can cause health problem. There are some harmful effects for instance difficulty breathing, nausea, vomiting, diarrhea, jaundice and gastric. The structure of MB is shown in Figure 2.5 (Ndi Nsami and Ketcha Mbadcam, 2013).

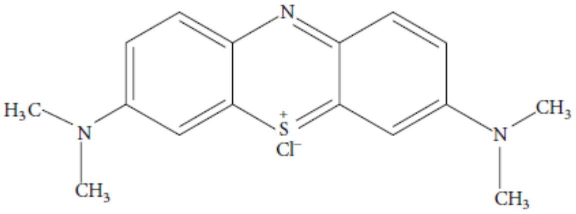

Figure 2.5: The structure of methylene blue (Selen et al., 2016)

Wang et al. (2012) studied the adsorption of MB and acid red 183 (AR183) using MWCNTs from the aqueous solution in single and binary dye systems. In single dye systems, the maximum adsorption capacity of MB and AR183 were 59.7 mg/g and 45.2 mg/g, respectively. The adsorption capacity for MB is higher compared to AR183 because MB forms strong π-π bonds. In binary-dye systems both dyes also promote adsorption on MWCNTs, MB and AR183 presented a synergistic effect at lower AR183 concentrations 10 mg/L. When increasing the concentration of AR183 resulting lower for the MB adsorption. Yao et al. (2011) studied the adsorption capacity of the anionic methyl orange dye was 27.6 mg/g lower than the cationic dye of MB studied by Wang et al. (2012) because the non-planar structure of methyl orange.

2.6. Adsorption isotherm

The adsorption isotherm is the equilibrium relationship between the concentration of adsorbate in the liquid phase and the concentration of adsorbate adsorbed on the surface of the adsorbent at equilibrium temperature. There are two most common model to describe the equilibrium of adsorption process which are Langmuir and Freundlich isotherms.

2.6.1. Langmuir isotherm

The Langmuir isotherm model indicate that no interaction between the adsorbate molecule and restricted to a monolayer adsorption onto a surface thus chemisorption estimated to this type. The Langmuir isotherm equation is expressed as (Mahmoodi and Mokhtari-Shourijeh, 2015):

$$q_e = \frac{Q_0 K_L C_e}{1+K_L C_e} \tag{2.1}$$

where,

q_e = the amount of adsorption equilibrium (mg/g)

C_e = the equilibrium concentration in the solution respectively (mg/L),

Q_0 = the maximum adsorption capacity (mg/g) and

K_L = the Langmuir adsorption equilibrium constant (L/mg).

The linear form of this isotherm equation written as (Mahmoodi and Mokhtari-Shourijeh, 2015):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \tag{2.2}$$

A plot of C_e/q_e versus C_e indicates a straight line. The Langmuir constant of Q_0 and K_L can be determined from the slope and y-intercept of the graph.

Another essential factor of Langmuir equation can be stated in terms of separation factor or equilibrium parameter, R_L as (Yao et al., 2010):

$$R_L = \frac{1}{(1+K_L C)} \tag{2.3}$$

where,

C = the highest of dye concentration (mg/L).

The R_L is important value that indicates the adsorption system to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

2.6.2. Freundlich isotherm

The Freundlich isotherm is an empirical equation used to describe the multilayer adsorption on the heterogeneous surface. The Freundlich equation is expressed as linear equation (Mahmoodi and Mokhtari-Shourijeh, 2015):

$$q_e = K_F {C_E}^{1/n} \tag{2.4}$$

where,

q_e = the amount adsorbed at equilibrium (mg/g)

C_e= is the equilibrium concentration of solution (mg/L),

$1/n$ = the adsorption intensity

K_F = Freundlich constants (mg/L).

The logarithmic form of this equation is as follow (Mahmoodi and Mokhtari-Shourijeh, 2015):

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{2.5}$$

The plot of log q_e against log C_E gives a straight line with slope of (1/ n) and the intercept of log K_F. The range value of n (2-10) indicated good adsorption, (1-2) moderately difficult and less than 1 is represent poor adsorption characteristic (Yao et al., 2010).

2.7. Adsorption kinetic

Adsorption kinetic is studies the mechanisms of adsorption that significant for the efficiency of the process. The characteristic constants of adsorption are determined using pseudo-first order equation and second-order equation (Mahmoodi and Mokhtari-Shourijeh, 2015).

2.7.1. Pseudo-first order kinetic model

The pseudo-first-order equation was used only for the rapid initial phase. The linear pseudo-first-order equation is given by (Mahmoodi and Mokhtari-Shourijeh, 2015):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2.6)$$

where,

q_e = the amount adsorbed at equilibrium (mg/g),

q_t = the amount of dye adsorbed at time (mg/g)

k_1= the equilibrium rate constant of pseudo-first order model (1/min)

t= time (minute)

2.7.2. Pseudo-second order kinetic model

A linear form of pseudo-second order kinetic model can be expressed as (Mahmoodi and Mokhtari-Shourijeh, 2015):

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (2.7)$$

where,

q_t = the amount of adsorption at time (mg/g)

q_e = the amount adsorbed at equilibrium (mg/g).

k_2 = the equilibrium rate constant of the pseudo-second order model (g/mg min)

t= time (minute)

CHAPTER 3

MATERIALS AND METHOD

3.1. Materials

Table 3.1: List of the materials and its specification

Material	Specification	Supplier
Chitosan powder	-	Aldrich Chemistry
MWCNTs	Purity 95 wt.% with COOH content 2.56 wt.%	Timesnano
Methylene Blue	Maximum lambda 660-665nm	Sigma Aldrich (M)
Glutaraldehyde solution	Purity 25%	Fisher Scientific
Acetone	Purity 99.89%	Fisher Scientific
Sulfuric acid (H_2SO_4)	Purity 95-97%	Merck
Acetic acid	Purity 97	Sigma Aldrich
Ethanol	Purity 99.8%	Fine chemical
Sodium hydroxide pellets	-	QReC
Deionized water	N/A	Produced in lab

3.2. Membrane preparation

3.2.1. Preparation CS/MWCNTs membrane

CS and CS/MWCNTs membrane were prepared by solution casting method. CS solution was prepared by dissolving of CS powder into aqueous acetic solution. The solution consists of 3 wt.% CS, 2 wt.% acetic acid and 95 wt.% deionized water. The solution was stirred using magnetic stirrer overnight at room temperature to form homogenous solution. 1 wt.% of MWCNTs-COOH was added into a CS solution. The suspension was stirred to form homogenous solution and then, it was sonicated for 20 minutes to improve the dispersion of the MWCNTs-COOH into the polymer matrix. The CS solution and CS/MWCNTs mixed solution were casted by casting 7g of suspension onto the petri dish and left it dried for 4-5 days.

The dried CS and CS/MWCNTs membrane, were then immersed in alkaline solution overnight to convert the cationic amine groups (NH_3^+) to free amine (NH_2). The alkaline solution consisted of 3 wt.% sodium hydroxide, 45 wt.% ethanol and 50 wt.% of deionized water. Next, the CS and CS/MWCNTs membrane rinsed with deionized water and left dried at room temperature.

3.2.2. Preparation CS/MWCNTs/GA membrane

The dried CS and CS/MWCNTs membranes were chemically cross-linked by immersing it in the crosslinking solution consisting 0.5 wt.% GA, 0.05 wt.% H_2SO_4 in 80 wt.% acetone and 19.45 wt.% deionized water for 20 minutes at ambient temperature. Finally, the membranes were rinsed with deionized water to remove the residual solution.

3.2.3. Preparation of methylene blue

The stock solution of MB with concentration 1mg/L is prepared by dissolving 0.001 g of MB in 1 L of deionized water in 1 L volumetric flask. Then, similar procedures were repeated for preparing different concentrations of MB of 2mg/L, 3mg/L and 4mg/L.

3.3. Batch adsorption process

The adsorption test was performed by immersing the membrane into the MB solution. The experiment to study the effect of contact time, effect of initial MB concentration and effect of temperature for CS membrane with and without MWCNTs.

The MB adsorbance was determined with spectrophotometer (Spectro Gen 20 Vis-Thermo Scientific) at 660 nm.

The amount of MB adsorbed (mg/g) and the removal efficiency (%) were determined using following equation (Selen et al., 2016):

$$q_t = \frac{C_0 - C_t \times V}{M} \tag{3.1}$$

$$Dye\ removal(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{3.2}$$

where,

q_t = the amount of dye adsorbed at time (mg/g)

C_0 = the initial concentration of dye (mg/L),

C_t = the concentration of dye at time (mg/L),

V = the volume of the solution (L)

M = the mass of the adsorbent (g).

3.3.1. Experiment 1: Effect of contact time

To investigate the effect of contact time, the experiments were performed at MB concentration of 4 mg/L and 25°C contact period ranging from 60 to 240 minutes.

3.3.2. Experiment 2: Effect of initial MB concentration

In order to identify the effect of MB concentration, the dye concentrations were varied from the dye concentration 1mg/L, 2mg/L, 3mg/L and 4mg/L while the temperature and the contact time were maintained at 25°C and 240 minutes.

3.3.3. Experiment 3: Effect of temperature

In order to determine the effect of temperature the MB concentration and contact time were fixed at 4mg/L and 240 minutes while the temperatures were varied from 25°C, 30°C, 35°C to 40°C.

3.4. Experiment activities

The overall experiment activities carried out in this study are presented in the following schematic flow diagram.

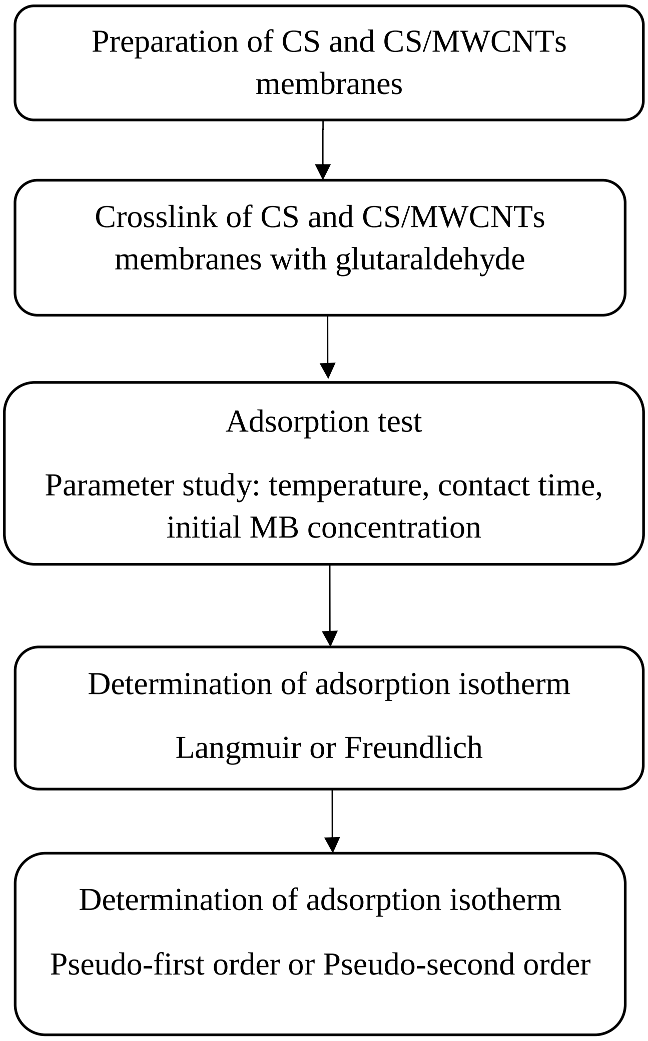

Figure 3.1: Schematic flow diagrams of experimental activities

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Calibration curve

Figure 4.1 shows the calibration curve for MB absorbance with respect to its concentration. The adsorbance was measured at different MB concentration ranging from 0.5 mg/L to 4 mg/L. Based on graph plotted in Figure 4.1, it shows that the adsorbance of MB increase when the concentration of MB increase. The relationship showed that the adsorbance directly proportional to the concentration of MB. Hence, the adsorbance of MB was highly depended on the concentration of MB. This calibration curve with a plot of absorbance against concentration can be used to determine the final concentration of MB with respect to the adsorbance after immersed with CS/MWCNTs and CS membrane with MWCNTs at several parameters for example temperature, initial concentration MB and contact time.

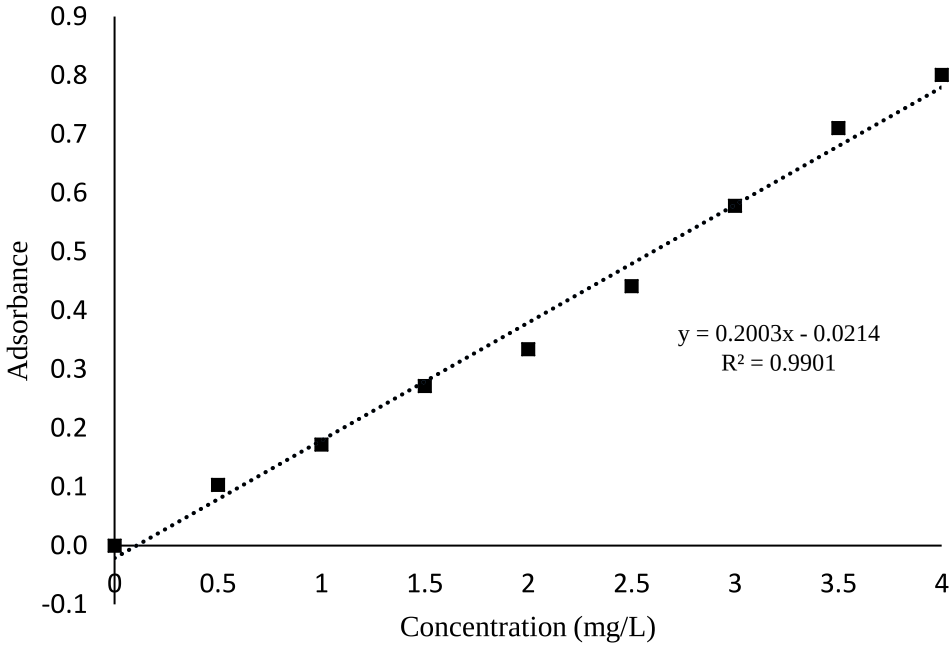

Figure 4.1: Calibration curve for MB adsorbance and its concentration

4.2. Effect of contact time

The adsorption and the removal efficiency of MB were studied at different contact time from 60 minutes to 240 minutes at constant temperature 25°C and concentration 4 mg/L. As shown in Figure 4.2 and Figure 4.3 the adsorption of MB and removal efficiency of MB increases with the increase of contact time for both CS membrane with without MWCNTs. At initial 60 minutes, the adsorption process was rapidly then the adsorption becomes slowly until achieving equilibrium. This is because at the initial stage, the higher number of vacant surface sites available for adsorption process. When the contact time is longer, the remaining number of vacant surface sites is lower because it is already occupied by adsorbate onto the surface of the membrane so, the adsorbance capacity of dye decrease (Mall et al., 2006). It observed that the adsorption and removal efficiency for MB is higher for CS/MWCNTs as compared to CS membrane without MWCNTs. The optimum adsorption and removal efficiency for MB was determined at contact time 240 minutes for CS/MWCNTs membrane, at which the amount of MB adsorbed was 0.0122 mg/g of adsorbent and the removal efficiency was 71.5%, respectively. For CS membrane without MWCNTs the adsorption and removal efficiency at 240 minutes were determined to be 0.0015 mg/g of adsorbent and 8.75%, respectively. This is because MWCNTs offer higher adsorption capacity due to the large specific area and their hollow pore size that can give another transport pathway with lower diffusion resistance.