REMOVAL OF METHYLENE BLUE DYE BY POLYVINYL ALCOHOL/MULTI-WALLED CARBON NANOTUBES ADSORBENTS

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by

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LIST OF SYMBOLS

	Symbols	**Unit**
b	Langmuir adsorption constant	mL/mg
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Initial concentration of adsorbate	mg/L
C_t	Concentration of adsorbate at certain time	mg/L
K_F	Freundlich isotherm constant related to capacity	$mg/g(L/mg)^{1/n}$
n_f	Intensity of adsorption constant Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent	mg/g
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time, t	mg/g
qm	Maximum adsorption capacity of adsorbent	mg/g
Q_o	Rate of adsorption	mg/g
R^2	Linear regression correlation coefficient	-
R_L	Separation factor	-
t	Time	hr
V	Volume dye solution	mL
W	Mass of adsorbent	g

LIST OF ABBREVIATIONS

MWCNT	Multi-walled carbon nanotubes
MB	Methylene blue
PVA	Polyvinyl alcohol
PVA/MWCNT	Polyvinyl alcohol/Multi-walled carbon nanotube
UV	Ultraviolet

PENYERAPAN METILENA BIRU OLEH PENJERAP POLIVINIL ALKOHOL/ NANOTIUB KARBON BERBILANG DINDING

ABSTRAK

Pada masa ini, pencemaran air menjadi masalah serius di kebanyakan negara disebabkan oleh pembangunan industri di seluruh dunia. Industri tekstil merupakan sektor popular yang menggunakan pewarna telah menyebabkan kebanyakan air yang dibuang adalah tercemar. Dalam kajian ini, penjerap PVA dan PVA/MWCNTs yang digunakan untuk penyingkiran pewarna metilena biru (MB) disintesis dengan menggunakan kaedah penyongsangan fasa. Beberapa parameter seperti kepekatan awal, masa hubungan dan, kuantiti penjerap dikaji untuk menilai prestasi penjerap. Penjerap PVA/MWCNTs mampu menyingkiran 46.58% MB sementara penjerap PVA dapat menyingkiran 44.71% MB pada keadaan keseimbangan dengan kepekatan awal adalah 2 mg/L. Oleh itu, penjerap PVA/MWCNTs didapati lebih berkesan untuk menghilangkan MB berbanding dengan penjerap PVA. Daripada data keseimbangan, terdapat dua jenis model yang digunakan untuk mengambarkan isoterma penjerapan iaitu Langmuir dan Freundlich. Dalam kajian ini, didapati bahawa Langmuir model adalah sesuai untuk menerangkan penjerapan MB di dalam process ini yang menunjukkan bahawa penjerapan satu lapisan telah terbentuk pada penjerap. Semenatara, kajian model kinetik menunjukkan bahawa urutan pseudo-kedua terlibat yang mengambarkan bahawa proses penyerapan kimia mengambil bahagian dalam proses penjerapan ini. Tambahan lagi, ini dapat dibuktikan dengan kapasiti penjerapan yang diperoleh menggunakan model ini lebih hampir dengan hasil experimen.

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ABSTRACT

Nowadays, water pollution becomes a serious issue in most of the country due to the development industry around the world. Textile industries is a popular sector that uses dyes that cause lots of water removed are contaminated. In this study, PVA and PVA/MWCNTs adsorbent were synthesized by using the phase inversion method to be used as an adsorbent to remove the methylene blue (MB) dye. Several parameters such as initial concentration, contact time and, the adsorbent dosage were studied to evaluate the performance of adsorbents. Based on the results, PVA/MWCNTs adsorbents was able to remove 46.58% of MB while the PVA adsorbents was able to eliminate 44.71% of MB at equilibrium state with an initial concentration is 2 mg/L. Hence, PVA/MWCNTs adsorbent was found to be the more efficient to remove the MB compare to the PVA adsorbent. From the equilibrium data, the two models were used to illustrate the adsorption isotherm, which is Langmuir, and Freundlich isotherm. In this experiment, it was found that the Langmuir models were suitable to explain the adsorption of MB dye in this process that shown a single layer adsorption was formed on the adsorbents. While the kinetic studies showed that the pseudo-second-order kinetic models were involved that describes that the chemisorption process has taken place in this adsorption process. In addition, it can be proven with the adsorption capacity obtained by using this model more closely to the experimental result.

CHAPTER 1

INTRODUCTION

This chapter will provide some introduction of the removal of methylene blue dye by using the polyvinyl alcohol/multi-walled carbon nanotubes as an adsorbent. The discussion will focus on the research background of the dye and adsorbent, problem statement, and objectives of this research project.

1.1 Research Background

The growth of the dye industry rapidly increased due to its potential that has been used in many types of products such as food, textile, cosmetics, paper, paint, printing, and pharmaceutical (Gholivand et al., 2015). There are many types of dyes used in industries including azo, indigo, and aniline dyes. Furthermore, about 70% of azo dye was used in most of the industry (Hassaan & El Nemr, 2017). In general, the aim of using the dye is to make the products become more attractive and look new (Stothers, 2019).

Unfortunately, the application of the dyes in the industry will create serious issues that affect the quality of water. The direct discharge of this component into the environment has shown negative impacts on aquatic life and humans. For example, it will cause insomnia, cancer, vomiting, coughing, and headache (Sadegh et al., 2016). It is due to the hazardous component such as toxic ion in the dye that risks human health when they exposure for a short or long time to these components (Hassaan & El Nemr, 2017).

Therefore, several technologies have been developed to overcome this problem. There are many methods were discussed by several researchers to remove the dye such as reduction, adsorption, oxidation, membrane filtration, and ion exchange. Based on these methods, adsorption was selected as a method that has a great potential to remove the dye effectively because it is easy to operate and required low cost. It is also able to reduce biological and chemical waste (Zulfiqar et al., 2020).

Nowadays, the use of polymeric nanocomposite as an adsorbent to adsorb the contaminant from wastewater showed excellent capability compare to the activated carbon due to its behavior that is suitable for various applications. Where the activated carbon usually was difficult to separate with water and cause produce secondary pollution (Moosavi et al., 2020). While, polyvinyl alcohol (PVA) grew attention as a polymeric adsorbent because it has great tunable physicochemical properties, structural diversity, long lasting, and provides high selectivity. It also provides other benefits such as high durability, biocompatibility, excellent tensile, and degradability (Mok et al., 2020). Therefore, this type of adsorbent has great potential to remove a large amount of contaminants from wastewater (Sadegh et al., 2016).

1.2 Problem Statement

Nowadays, the uses of dyes show great potential in various industries such as textile, pharmacy, and cosmetics. This industry will generate a large amount of dye wastewater with 85% of dye effluent will be removed from the dyeing process (Kant, 2012). Improper management of the dye removal into the water stream will create serious water pollution. The synthetic dye usually has a toxic effect due to the presence of hazardous compounds such as sulphur, naphthol, vat dyes, and nitrates that will increase toxicity in effluent removal and could create pollution and harm to human health (Samchetshabam et al., 2017).

Thus, several technologies have been performed to remove the dye from wastewater through biological, chemical, and physical method such as enzyme degradation, advanced oxidation process, oxidation, adsorption, ion exchange, coagulation and flocculation (Katheresan et al., 2018). The adsorption method was found to be the most effective method to remove the dye because it requires low cost, simple and economical (Alhujaily et al., 2020). While the traditional method such as coagulation and flocculation were not effective since it generate a large amount of sludge, limited to specific of dyes and require additional chemicals (Katheresan et al., 2018).

To remove the dye from wastewater, carbon nanotubes (CNTs) have shown excellent results as adsorbents due to its characteristics that have a high specific surface area, and high thermal stability. By using the multi-walled carbon nanotubes (MWCNTs) as an adsorbent, the adsorption ability could be improve by introducing other functional groups onto their surface such as polyvinyl alcohol (Wu et al., 2017). These polymers are synthetic water-soluble biopolymers that show good thermal and mechanical properties (Abdullah & Dong, 2019). The phase inversion method also was introduced to prepare the adsorbent because it was able to control the morphological of the adsorbent that suitable for various applications (Kausar, 2017). Therefore, this research was conduct on the synthesis of PVA/MWCNTs by using the phase inversion method as an adsorbent to remove the methylene blue (MB) dye.

1.3 Objectives

The objectives of this study are set out as below:

I. To synthesis, PVA/MWCNTs adsorbent to remove the methylene blue dye using phase inversion method.

II. To determine the effects of the initial concentration of methylene blue, contact time and adsorbent dosage for the removal of MB.

III. To evaluate the adsorption performance of PVA/MWCNTs through adsorption isotherm and kinetic studies.

CHAPTER 2

LITERATURE REVIEW

This chapter describes the opinion and suggestions from several researchers related to the main topic of this final project**.** In addition, will summarize the general of dye substances, type of adsorbent and elaborate on the adsorption method. Besides, it will also introduce the types of adsorption isotherms and kinetics that were commonly used to evaluate adsorption performance.

2.1 Dyes

The dye is a molecule that consists of two chemical groups that are chromophore and auxochrome. The chromophore was used to provide the color while the auxochromes are responsible to ensure the dye molecule will fix on the tissue or textile (Exbrayat, 2016). Shindy (2016) has explained that the dye is aromatic compounds with the structures like aryl rings that have a delocalized electron system. Therefore, this structure is important that taking part in the absorption of electromagnetic radiation with various wavelengths that occurs in electron clouds. These phenomena actually will prove that chromophores usually making energy in the electron clouds by adsorbing the radiation within its range. While the human eyes will see the color as a result of the adsorption of dye.

There are differences between the dye and pigments such as in terms of solubility. The dye usually was dissolved in the water meanwhile the pigment is known as a colorant that is likely not soluble in the water. Besides that, the chemical composition in the dye usually is organic compounds compare with the pigment that contains inorganic compounds that consist of heavy toxic (Pachade, 2020).

Nowadays, the uses of dye were familiar in most of the industry that can be shown by 10 000 commercially available dyes were produced with more than 700 000 metric tons per year. This process also causes almost 200 000 tons of dye effluent was produce through the dyeing process (Hassaan & El Nemr, 2017). All this wastewater will discharge into the environment or water stream. Therefore, it is important to ensure this waste will be treated before being removed.

2.1.1 Methods of dye removal

Some researchers have found there were several harmful components contained in the dye. For example, Ragunathan et al. (2007) has concluded that the dye industry worker could be exposed to chromosome aberration cause changes in the number and structure of chromosomes in blood lymphocytes due to long exposure to the mixture of chemical dye. Besides that, environmental issues also have been reported due to the removal of dye colored into the water streams. Since the dyes are usually difficult to degrade, high in toxicity, thus will cause water pollution (El-Sikaily et al., 2012).

There is a high possibility that dye substances will harm to the human and the environment. Thus, several methods are needed to treat or remove the dye effluent before being discharged. This method can be categorized into three types, which are physical, chemical, and biological (Katheresan et al., 2018).

The biological or conventional method is the most commonly used by the combination of the aerobic and anaerobic processes. The advantages and disadvantages of the biological methods such as microbial biomass, algae degradation, enzyme degradation, fungal culture, and microbial cultures were shown in Table 2.1.However, biological method was familiar because it is cheap and simple (Robinson et al., 2001).But, biological methods unable to remove the hazardous components completely. It also will involve living things that need to ensure the system is stable to maintain its suitable growth rate.

The chemical dye removal methods such as advanced oxidation process, electrochemical destruction, Fenton reaction dye removal, oxidation, ozonation, and photochemical were presented in Table 2.2 along with their advantages and disadvantages. Currently, this method requires high cost and energy. In addition, excess chemicals will be produced through this method.

Katheresan et al. (2018) has stated that the physical dye removal methods, for example, are adsorption, coagulation or flocculation, membrane filtration, and ion exchange are the most efficient and simple methods compared to chemical and biological dye removals methods as shown in Table 2.3. It also more convenient to use because it does not involve any living organisms.

Table 2.1 Biological dye removal methods with its advantages and disadvantages (Katheresan et al., 2018).

Method	Description	Advantages	Disadvantages
Adsorption by microbial biomass	Mixture of organic living organisms fashioned to adsorb dye molecules.	• Selected dyes have an exceptional affinity towards microbial biomass	• Not an effective method for all dyes
Algae degradation	Algae consumes dye particle for self-growth.	• Able to consume dyes. • Cheap. Easily assessable. • Environmental friendly process.	• Unstable system.
Aerobic-anaerobic combination (conventional method)	A prepared sludge breaks down complex dye molecules.	• Able to fairly decolourize a variety of dye types. • Cheap. No foam formation.	• Does not completely eliminate all dye particles. • Formation of methane and hydrogen sulphide as by products. • Inflexible method. • Large land area requires. • Produces sludge. • Takes long time.
Enzyme degradation.	Extracted enzyme used to degrade dye molecules.	• Cheap. • High efficiency. • Non-toxic.	• Unreliable amount of enzyme production

		• Possesses the ability to degrade dyes using enzymes. • Reusable.	
Fungal cultures	Fungus breaks down dye molecules and consumes them for self-growth.	• Can eliminate various types of dyes at once. • Flexible method.	• Lengthy growth phase. • Needs a nitrogen confined area to grow. • Requires large reactors for complete dye removal. • Unstable system.
Microbial cultures such as mixed bacterial	Bacteria mixed with chemicals or other bacteria to remove dye particles.	• Takes a maximum of 30 h in decolourization of dye wastewater, which is considered fast.	• Effective to a limited number of dyes. • Large-scale application is preferred due to high cost.
Pure and mixed culture	Mixtures of algae, bacteria or fungus with necessary chemicals to remove dye.	• Reusable. • Suitable only for azo dye removal.	• Colourless toxic by-products. • Produces sludge. • Requires conventional method as post-treatment.

Table 2.2 Chemical dye removal methods with its advantages and disadvantages (Katheresan et al., 2018).

Method	Description	Advantages	Disadvantages
Advanced oxidation process	Multiple oxidation process done simultaneously to remove dye particles.	• Can eliminate toxic materials. • Can remove dye in unusual conditions. • Good dye removal method.	• Expansive. • Not flexible. • Production of undesirable by-products. • pH dependent.
Electrochemical destruction	Electro-coagulation or non-soluble anodes are used to eat up dye molecules.	• Chemicals do not get consumed and no sludge build-up. • Fairly suitable soluble and insoluble dye removal method.	• Additional hazardous material production. • High cost of electricity. • Less effective dye removal compared to other methods due to high flow rates.
Fenton reaction	Fenton’s reagent (mixture of catalyst and hydrogen peroxide) to remove dye particles from wastewater.	• Fairly suitable dye removal method for soluble and insoluble dyes. • Removes all toxins in water. • Suitable for dyes wastewater with solid content.	• Cannot remove disperse and vat dyes. • High iron sludge generation. • Long reaction time. • Works only on low pH.
Oxidation	Oxidising agents used to treat dye effluents. Agents break down complex dye molecules to carbon dioxide and water. Usage of catalyst can further enhance the process.	• Can completely degrade dyes. • Common chemical dye removal method. • Short reaction time. • Straightforward application	• Costly. • Difficult to activate hydrogen peroxide agent. • pH dependent. • Requires catalyst for efficient removal.
Ozonation	Ozone produced from oxygen is used to eliminate	• Can be used in its gaseous state.	• Has an extremely short half-life for only 20 min.

	dye particles.	• Does not increase wastewater volume. • Effective dye removal method. • No sludge generation. • Quick reaction.	• High cost. • Produces toxic by-products. • Unstable method.
Photochemical	Fenton reaction coupled with ultraviolet light to remove dye molecules from wastewater.	• Effective dye removal method. • No foul odours production. • No sludge production.	• Expansive. Forms a lot of by-products.
Ultraviolet irradiation	Usage of UV light to decompose dye particles in wastewater.	• Hazardous chemical required. • No sludge production. • Weakens foul odours.	• Energy depletion. • High cost. • Limited treatment times.

Table 2.3 Physical dye removal method with its advantages and disadvantages (Katheresan et al., 2018).

Method	Description	Advantages	Disadvantages
Adsorption	Adsorbents fashioned from high adsorption capacity materials to adsorb dye molecules.	• Excellent removal method for a wide variety of dyes. • Re-generable adsorbent.	• Adsorbents can be costly.
Coagulation and flocculation	Coagulation/flocculation inducing agents are added to dye wastewater where dye particles clump together. Clumps can then be removed through filtration.	• Cheap. • Robust method. • Suitable only for disperse, sulphur and vat dye effluents.	• Generation of huge amounts of concentrated sludge. • Not suitable for acid, azo, basic, and reactive dye effluents. • Sometimes expansive due to requirement of special chemicals. • pH dependent system.
Ion exchange	A reversible chemical process whereby ions from the dye wastewater swaps with similar ions attached to a stationary solid surface.	• Can be regenerated. Good dye removal method. • Produces high quality water.	• Effective to a limited number of dyes.