

**STUDY ON THE CHARACTERISTICS AND
ADSORPTION BEHAVIOR OF NATURAL RUBBER –
HALLOYSITE NANOTUBES FILMS TOWARDS
METHYLENE BLUE**

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UNIVERSITI SAINS MALAYSIA

2019

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ADSORPTION BEHAVIOR OF NATURAL
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TOWARDS METHYLENE BLUE**

by

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**Thesis submitted in fulfillment of the requirements
for the Degree of
Master of Science**

May 2019

ACKNOWLEDGEMENT

This work was carried out in the School of Chemical Sciences, Universiti Sains Malaysia under the supervision of Assoc. Prof. Dr. Noor Hana Hanif Abu Bakar. First and foremost, I would like to express my ultimate gratitude to my main supervisor, Assoc. Prof. Dr. Hana for her patient guidance and encouragement throughout this strenuous research which have really challenged my mental and physical endurance. I also want to thank her for sharing her valuable knowledge with me and correcting my writing skills which have made this research a success. Secondly, I would like to show great appreciation to my second supervisor, Prof. Dr. Mohamad Abu Bakar for his useful advices and constructive recommendations which have improved this research a lot. Next, I would like to offer my special thanks to the laboratory staff, En. Kamarul for his assistance and patience in helping me with my problems throughout the research. Besides, I am particularly grateful for the assistance given by all the staffs in SEM, XRD and TGA analyses Labs as well as the other staffs in School of Chemical Sciences. My special thanks are extended to the Universiti Sains Malaysia authority for giving me permission to use the laboratories and instruments during my research. Also, I wish to thank my family for their support and encouragement throughout my study and finalizing my research within the limited time frame. Last but not least, I wish to extend my appreciation to my labmates, Liza, Irma, Farhana, Nazrina, Asmaa, Izzana, Najwa and Fatin for their help during my research study.

TAN YEE CHIEN

2019

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LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated total reflectance fourier transform infrared spectroscopy
CNT	Carbon nanotubes
DTG	Thermogravimetric derivative
HNT	Halloysite nanotubes
LOI	Limited oxygen index
MB	Methylene blue
NR	Natural rubber
NR-HNT	Natural rubber – halloysite nanotubes
PZC	Point of zero charge
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

LIST OF SYMBOLS

α	Equilibrium binding constant of Temkin isotherm
b	Heat of adsorption of Temkin isotherm
$^{\circ}\text{C}$	Degree celcius
C_a	Amount of adsorbed MB
C_d	Amount of desorbed MB
C_e	Concentration of MB at equilibrium
C_i	Initial concentration of MB
C_t	Concentration of MB at any time t
ΔG°	Change in Gibbs free energy
ΔH°	Change of enthalpy
ΔpH	Difference in the pH
ΔS°	Change of entropy
g_{hnt}	Mass of HNT
g_{NR}	Mass of NR
h	Initial adsorption rate
K	Equilibrium constant
K_F	Rate constant of Freundlich isotherm
K_L	Rate constant of Langmuir isotherm
K_{bv}	Rate constant of Bhattachara-Venkobachar equation
K_{nk}	Rate constant of Natarajan-Khalaf equation
K_{pf}	Rate constant of pseudo first-order
K_{ps1}	Rate constant of type 1 pseudo second-order
K_{ps2}	Rate constant of type 2 pseudo second-order
n	Freundlich isotherm constant

%D	Percentage of MB desorption
%R	Percentage of MB removal
q_e	Amount of MB adsorbed at equilibrium
q_m	Maximum adsorption capacity
q_t	Amount of MB adsorbed at any time t
R	Universal gas constant
R_L	Dimensionless separation factor
T	Absolute temperature
T_{onset}	Temperature where degradation starts
T_{max}	Temperature where maximum decomposition occurs
t	Time in min
UV-Vis	Ultraviolet-visible
V	Volume of MB solution
W	Mass of HNT
wt%	Weight percentages

KAJIAN MENGENAI CIRI DAN PERLAKUAN PENJERAPAN FILEM GETAH ASLI – TIUB NANO HALOSIT TERHADAP METILENA BIRU

ABSTRAK

Filem getah asli – tiub nano halosit (NR-HNT) telah disediakan dengan menambahkan tiub nano halosit (HNT) pada peratusan berat (10 – 70 wt%) yang berlainan ke dalam getah asli (NR) dan digunakan untuk menjerapkan metilena biru (MB). Sampel tersebut dicirikan dengan spektroskopi inframerah transformasi Fourier – pantulan keseluruhan dikesilkan (ATR-FTIR), pembelauan sinar x-ray (XRD), Mikroskopi pengimbasan elektron (SEM), analisis termogravimetri (TGA) dan caj takat sifar (PZC). Didapati pada wt% yang lebih rendah, HNT tersebar dengan baik. Apabila wt% HNT meningkat, ketersediaan zarah HNT yang banyak menjadikannya lebih sukar disebarkan dan menyebabkan pengagregatan HNT, yang mana menjejaskan sifat terma NR. Kajian penjerapan MB telah dijalankan untuk menyiasat keupayaan sampel untuk menyerap pewarna. Parameter yang berbeza seperti wt% HNT, kepekatan awal MB, pH, dos penjerap dan suhu telah dikaji untuk menentukan keadaan optimum untuk penjerapan MB oleh filem NR-HNT. Hasil kajian menunjuk bahawa satu keping filem 10 wt% NR-HNT (lebih kurang 2.3 x 2.6 cm) mempunyai keupayaan terbaik untuk menyerap pewarna dalam larutan dengan kepekatan awal MB = 16 mg L⁻¹ pada pH 9.7 dan 39 °C. Kinetik dan isotherm penjerapan juga disiasat untuk lebih memahami hasil kajian ini. Didapati data eksperimen berjaya disesuaikan ke dalam model kinetik pseudo tertib kedua jenis 1. NR dan 50 wt% NR-HNT lebih sesuai dengan isotherm Temkin manakala 10 wt% NR-HNT sesuai dengan isotherm Langmuir. Kajian termodinamik juga disiasat dan mencadangkan bahawa proses penjerapan MB ialah proses fizikal spontan dan

endotermik. Akhirnya, HNT boleh digunakan semula sehingga 5 kitaran penjerapan tetapi 10 wt% NR-HNT hanya boleh digunakan semula sehingga 3 kitaran disebabkan ketersediaan tapak penjerapan yang lebih rendah. Namun begitu, 10 wt% NR-HNT boleh menjerap dan juga menyahjerap pewarna berbandingkan HNT yang hanya boleh menjerap pewarna.

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ABSTRACT

Natural rubber – halloysite nanotubes (NR-HNT) films were prepared by incorporating different weight percentages (10 – 70 wt%) of halloysite nanotubes (HNT) into natural rubber (NR) and were used to adsorb methylene blue (MB). The samples were characterized using attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), x-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and point of zero charge (pzc). It was found that at lower wt%, the HNT was well-dispersed. When the wt% of HNT was increased, it made it harder to be dispersed and caused aggregation of the HNT, which affected the thermal properties of the NR. MB adsorption studies were carried out to investigate the ability of the samples to adsorb dye. Different parameters such as the wt% of HNT, initial concentration of MB, pH, adsorbent dosage and temperature were studied to determine the optimum conditions for the adsorption of MB by the NR-HNT films. The results showed that one film of 10 wt% NR-HNT (approximately 2.3 x 2.6 cm) has the best ability to adsorb dye in aqueous solution with the initial concentration of MB = 16 mg L⁻¹ at pH 9.7 and at 39 °C. The adsorption kinetics and isotherms were also investigated to further understand these results. It was found that the experimental data are successfully fitted into type 1 pseudo second-order kinetic model. The NR and 50 wt% NR-HNT best fit Temkin isotherm while the 10 wt% NR-HNT fits Langmuir isotherm. The thermodynamic studies were also investigated and the results suggested that the MB adsorption

process is a spontaneous physical process and is endothermic. Finally, while HNT can be reused up to 5 adsorption cycles, the 10 wt% NR-HNT can only be reused up to 3 cycles due to the lower availability of adsorption sites. Nonetheless, 10 wt% NR-HNT can adsorb as well as desorb dye compared to HNT that can only adsorb dye.

CHAPTER 1

INTRODUCTION

1.1 Brief Overview

Water pollution is one of the world's most concerned issues nowadays. Majority of humans' activities require clean water, ranging from basic daily life to medical and industrial fields. Despite so, humans' activities especially in industrial sites is the main reason contributing to water pollution. Organic contaminants such as dyes are extensively used in industries such as textile, cosmetic, leather, rubber, carpet, paper and printing (Ali et al., 2017). It is approximated that the total dye used in textile industries worldwide is at least 10, 000 tons per year, and 10 – 15% of these dyes are discharged as effluents in the dyeing process (Dawood & Sen, 2014). Most dyes are clearly visible even at low concentration. If released to the environment without proper management, these effluents can generate potential damage to human beings, aquatic life, microorganisms as well as the environment. Thus, a lot of effort has been focused on dye removal from wastewater over the past decades. Several dye removal techniques including photocatalyst, degradation, membrane filtration, coagulation, chemical and physical activation, ion exchange, and adsorption have been introduced (Dawood & Sen, 2014). All of these methods have their own pros and cons. However, adsorption is considered to be a very effective method in terms of convenience of operation, simplicity of design, ability to treat dyes from wider range and higher concentrations without producing harmful substances (Dawood & Sen, 2014; Yagub et al., 2012). Above all, adsorbents are abundantly available with little or no value.

1.2 Problem Statements

Over the years, researches have been focusing on finding low cost and sustainable adsorbents. Among the wide range of selections, nanomaterials have been the favorite option for adsorbents because of their high ratio of surface area to unit mass (Kiani, 2014). In the recent years, halloysite nanotube (HNT), a unique naturally occurring aluminosilicate nanotube has gained growing interests not only for its versatility in many applications (Yuan et al., 2015), but also it is abundantly available and highly accessible, which resulted in its much lower cost when compared to other nanoadsorbents like carbon nanotubes (CNT), magnetic nanoparticles and titanium oxide (Chiew et al., 2016). It was reported that HNT costs only \$4 per kg which is a great price as compared to CNT that costs \$500 per kg (Yuan et al., 2015). However, just like any other nanoadsorbents in free powder form, recollection and reusing after adsorption is difficult and the sedimentation process has added more steps to the procedures. Besides, potential release of nanoparticles to the environment may have possible risk to the ecosystem and human health (Zhao et al., 2011). Hence, the use of host materials have come to the rescue. Literature shows that most of the host materials used to immobilize nanoparticles or clays are synthetic polymers, the use of natural polymers is infrequent (Zhao et al., 2011). In this study, natural rubber (NR), a natural polymer is used as the host material for HNT. Literature has reported the fabrication of NR-HNT nanocomposites by adding HNT as filler or additive to NR to reinforce the properties of NR (Ismail et al., 2013; Jia et al., 2014). However to our best knowledge, NR-HNT nanocomposite has never been used for dye adsorption.

1.3 Objectives of Study

This study focuses on the adsorption of MB by NR-HNT films by varying several parameters. The objectives of this study are:

1. To prepare NR-HNT and to investigate the properties of the composites.
2. To study the effect of various parameters on the adsorption of MB by the NR-HNT composites.
3. To investigate the reusability of the NR-HNT composites in comparison to the pristine HNT.

1.4 Scope of Study

This research focused on the study of MB adsorption by NR-HNT composites. The experimental procedures are divided into two main parts – the characterization of the composites and adsorption studies. To identify the ideal dosage of HNT to be incorporated into NR for the best performance of MB adsorption, different weight percentages (wt%) of HNT in NR were prepared. The resulting samples were characterized with attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), x-ray diffraction (XRD), scanning electron microscope (SEM) and thermogravimetric analysis (TGA). Finally, point of zero charge (pzc) was carried out to determine and compare the pzc of the samples. Moving on to the adsorption studies, several parameters such as the initial concentrations and pH of MB solutions as well as the effect of dosage of NR-HNT composites and temperature were investigated. Last but not least, reusability test was performed on HNT and NR-HNT samples.

1.5 Thesis Layout

This thesis consists of five chapters. The first chapter gives a brief overview of the research background and the introduction of this study. Chapter two covers works that have been done across the years which are related to the topic of this study. Chapter three presents the materials and methods used in the experimental procedures. Chapter four focuses and discusses thoroughly on the results obtained from this study. Lastly, chapter five concludes the results of this study and recommends suggestions for future work of this field.

CHAPTER 2

LITERATURE REVIEW

2.1 Clay

Clay is a naturally occurring fine-grained raw material found on earth which consists primarily of alumina, silica, water and weathered rock. Clay shows plastic properties at different water content, which will harden upon drying or firing (Uddin, 2017). Clay evenly disperses in water and forms slurry mud which can be mould into desired shapes. This property of clays has led to its wide usage in pottery and ceramics industries for the making of earthenware, plates, bowls, cups and even kids' toys. Clay is the size fraction of the soil composed of particles which have less than 2 micrometres (μm) equivalent spherical diameter. The clay fractions are commonly dominated by clay minerals or phyllosilicates (Chesworth et al., 2008). Clay minerals are composed of tetrahedral and octahedral sheets bonding together through hydrogen bonding. The tetrahedral sheet is formed by silicon-oxygen (SiO_4^{4-}) tetrahedrons connected through basal oxygen atoms, where Si atoms are partly replaced by trivalent aluminum (Al) and iron (Fe) atoms. On the other hand, the octahedral sheet is formed by octahedrons of $(\text{MO}_4(\text{OH})_2, \text{M} = \text{Al}, \text{Mg}, \text{Fe})$ linked together by apical and basal oxygen atoms. (Bujdák & Rode, 1999; Farrokhpay et al., 2016). Clay minerals can be categorized into 1:1 or 2:1 layer types. In a 1:1 layer clay, a tetrahedral sheet is connected to an octahedral sheet whereas a 2:1 layer clay consists of an octahedral sheet being sandwiched in between two tetrahedral sheets (Hussin et al., 2011). A schematic diagram as shown in Figure 2.1 was drawn by Bujdák and coworkers (Bujdák & Rode, 1999) to illustrate these clay structures. Examples for 1:1 layer type are kaolinite and serpentine while 2:1 layer type are

smectites, micas, illites, vermiculite and chlorites (Brigatti et al., 2006; Bujdák & Rode, 1999).

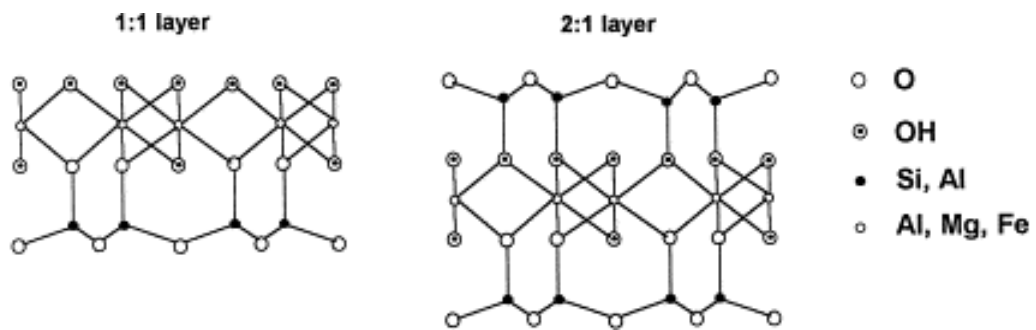


Figure 2.1: Schematic diagram for 1:1 and 2:1 layer types (Bujdák & Rode, 1999).

2.1.1 Clays as Adsorbent

In general clays have been extensively used in many applications. One of the most widespread application is as an adsorbent. This is mainly because it is low cost and can be acquired abundantly. Among the main reasons it has been classified as an excellent adsorbent is because of its high specific surface area due to its small particle sizes (Abollino et al., 2008). Clay minerals are most commonly used as adsorbents in removing heavy metals that are positively charged in aqueous solutions. Literature has reported that montmorillonite and vermiculite are used to remove As^{3+} , Cd^{2+} , Cr^{3+} , Cu^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} ions in aqueous media (Abollino et al., 2003; Malandrino et al., 2006; Saleh et al., 2016). Other clay minerals like bentonite and kaolinite are also used as adsorbents for the removal of positively-charged heavy metals (Co^{2+} , Cu^{2+} , Fe^{3+} , In^{3+} , Ni^{2+} , and Pb^{2+}) in aqueous solutions (Bhattacharyya & Gupta, 2008; Calagui et al., 2014; Futralan et al., 2011). Other than heavy metals, clay minerals are also popularly used in the removal of dyes. Previous works have reported the wide usage of different clay minerals in the removal of MB (Bilgiç, 2005; Cottet et al., 2014; Uyar et al., 2016), Basic Red 46 (Santos et al., 2016), Basic

Yellow 28 (Turabik, 2008), Remazol Violet 5R and Acid Blue 25 (Aguiar et al., 2017). Furthermore, clay minerals are also used to adsorb organic compounds like benzothiophene sulfone (Choi et al., 2017b), dibenzothiophene sulfone (Choi et al., 2017a), carboxylic acid (Silva et al., 2013) and even hazardous antibiotics (Tian et al., 2016).

2.2 Halloysite Nanotubes (HNT)

HNT is a naturally occurring nanosized aluminosilicate which has a hollow tubular shape (Liu et al., 2012a) due to the aluminosilicate sheets which roll up like a scroll (Bekiari et al., 2017). The aluminosilicate sheets are made up of two layers of aluminum, silicon, oxygen and hydrogen (Kamble et al., 2012), which consist of an alumina octahedron sheet and a silica tetrahedron sheet (Luo et al., 2011). HNT is very similar to kaolinite. Both of them are a 1:1 layer clay mineral (Hussin et al., 2011) and have the same structure as well as chemical composition (Luo et al., 2011). However, a monolayer of water molecules (H_2O) is present between the layers of HNT and separate them. Hence, the chemical formula of HNT is $Al_2Si_2O_5(OH)_4 \cdot nH_2O$. When $n = 2$, HNT is hydrated where a layer of water exists in the interlayer space. The interlayer spacing is 10 \AA hence it is called HNT- 10 \AA (Liu et al., 2014; Zhang et al., 2016). The interlayer water molecules are weakly held so that the transformation of HNT into different forms can happen readily (Luo et al., 2011). Thus when the HNT- 10 \AA is heated to $110 \text{ }^\circ\text{C}$, the water molecules between the interlayers of HNT disappear and cause the hydrated HNT- 10 \AA to be transformed into anhydrous form (when $n = 0$) with interlayer spacing of 7 \AA . This anhydrous form of HNT is named HNT- 7 \AA (Liu et al., 2014; Zhang et al., 2016). HNT are ultra-fine nanotubes with diameters less than 100 nanometres (nm), where

the external diameter is generally 30 – 190 nm while the internal diameter is approximately 10 – 100 nm. The lengths of the nanotubes lie in the range of 0.02 to more than 30 μm (Joussein et al., 2005; Zahidah et al., 2017). The structures of a typical HNT–7 Å and HNT–10 Å are illustrated by Abdullayev and Lvov (2010) and Yuan and coworkers (2008) respectively. The schematic diagrams are demonstrated in Figure 2.2 and 2.3.

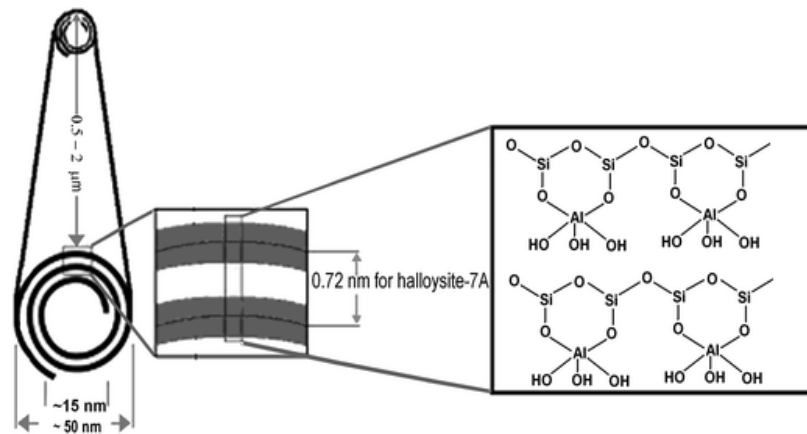


Figure 2.2: Schematic diagram of a typical HNT–7 Å (Abdullayev & Lvov, 2010).

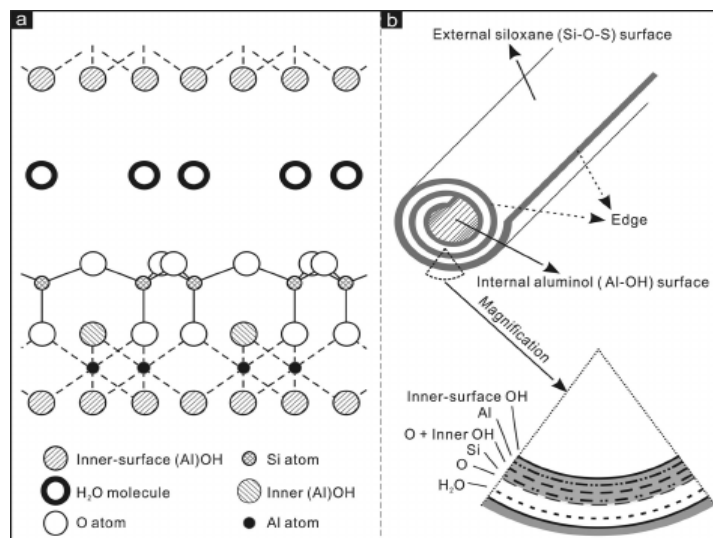


Figure 2.3: Schematic diagram of a typical HNT–10 Å (Yuan et al., 2008).

2.3 Applications of HNT

HNT is a highly versatile material and can be acquired abundantly. Thus, it is extensively used in different aspects of applications such as being used as an adsorbent, catalyst, support, carrier and even fire retardant.

2.3.1 Adsorbent

As mentioned previously clay minerals are most commonly used as an adsorbent, so as HNT. HNT is an excellent adsorbent for a wide variety of materials. Raw HNT without chemical pretreatment exhibits excellent removal for cationic dyes such as methylene blue (Zhao & Liu, 2008), malachite green (Kiani et al., 2011), methyl violet (Liu et al., 2011) and neutral red (Luo et al., 2010) due to the negatively charged surface of HNT. HNT has a unique hollow tubular structure where the outermost silica surface is negatively charged while the inner alumina lumen surface is positively charged. Thus, it can be used to adsorb both cationic and anionic dyes. This is proven in Zhao and coworkers' work where HNT was used to adsorb the cationic rhodamine 6G and anionic chrome azurol S (Zhao et al., 2013). Other than dyes, unmodified HNT is also an excellent adsorbent for metal ions such as silver ion (Kiani, 2014) and ammonium (Jing et al., 2017) and even synthetic antibacterial agent such as pefloxacin (Zhang et al., 2015). Even though HNT has shown great performance as an adsorbent, several modifications were employed nonetheless to further extend its versatility. For instance, unmodified HNT has shown efficient removal for anionic dye methyl orange (Chen et al., 2015) but modification of HNT with the surfactant hexadecyltrimethylammonium bromide (HDTMA) in order to graft ammonium cations on the surface of HNT resulted in a

more positively charged surface. This clearly increased its adsorption performance for this dye (Liu et al., 2012a). Hence, modified HNT is used as a better adsorbent for even more purposes such as the removal of more types of dyes (Riahi-Madvaar et al., 2017; Zeng et al., 2017) and metal ions (Zeng et al., 2016), ammonia gas (Liu et al., 2016), herbicide prometryn (Grabka et al., 2015) and even chemical intermediates such as chloroanilines (Szczepanik et al., 2014). The different modifications of HNT with different chemicals are summarized in Table 2.1.

Table 2.1: HNT modified in different ways for water remediation.

Adsorbent	Type of Modification	Modified with	Adsorbate	Reference
HNT	Surface modification	H ₂ SO ₄ , HNO ₃ , NaOH	Herbicide prometryn	(Grabka et al., 2015)
HNT	Surface modification	Hexadecyltrimethylammonium bromide (HDTMA)	Methyl orange	(Liu et al., 2012a)
HNT-Fe ₃ O ₄	Incorporation of magnetic nanoparticles	Magnetic Fe ₃ O ₄ nanoparticles	Naphthol green B	(Riahi-Madvaar et al., 2017)
HNT	Acid activation	Sulfuric acid	Chloroanilines	(Szczepanik et al., 2014)
APTES-HNT@PVDF membrane	Functionalization, membrane fabrication	3-aminopropyltriethoxysilane (APTES), polyvinylidene fluoride (PVDF)	Direct Red 28, Cu ²⁺ , Cd ²⁺ , Cr ⁶⁺	(Zeng et al., 2016)
D-A-HNT@PVDF membrane	Functionalization, membrane fabrication	Dopamine (DA), PVDF	Direct Red 28, Direct Yellow 4, Direct Blue 14	(Zeng et al., 2017)

2.3.2 Catalysis

A number of works have reported the use of HNT in the field of catalysis. It has to be noted that HNT is less commonly used as a catalyst itself compared to a support for active phases in catalysis. However, several findings on the usage of HNT as a catalyst were discovered. The usage of raw HNT as a catalyst in hydrogen (H_2) generation from methanolysis of sodium borohydride ($NaBH_4$) was reported and good catalytic performance was shown (Sahiner & Sengel, 2017a). However a much better performance was achieved by modifying HNT with 3-aminopropyltriethoxysilane (APTES) (Sahiner & Sengel, 2017a) and with various amine groups (Sahiner & Sengel, 2017b). In order to make HNT a better catalyst, several modifications were done to HNT using different agents. Popular pretreatments for HNT including intercalation (Cheng et al., 2011; Mellouk et al., 2009) and chemical treatments such as bleaching (Szczepanik et al., 2015) as well as acid and alkali treatments (White et al., 2012). For instance, HNT was modified via ion exchange treatment using aqueous solution of NH_4NO_3 and was employed as an acid solid catalyst for the production of α -arylstyrenes through direct alkenylation (Zhao et al., 2016).

2.3.2(a) HNT as Supports in Catalysis

In the field of catalysis, HNT has been widely used as a support. Multiple researches have reported this in literature. For example, HNT was used as a support for metal nanoparticles like gold in the catalytic oxidation of benzyl alcohol (Philip et al., 2017) and cyclohexene (Cai et al., 2011), as well as silver nanoparticles in the polymerization of alkylsilanes (Li et al., 2014). Besides, HNT was also used as a

support for metal oxide catalysts like copper and cobalt oxides for the oxidation of toluene to CO₂ (Carrillo & Carriazo, 2015), and biomimetic catalyst like hematin in the biomimetic polymerization of aniline (Tierrablanca et al., 2010). Although HNT can serve well as a support due to its high surface area available, its lack of surface functional group can at times cause leaching of the active phase. Hence, researches have strived to modify its surface as a mean to anchor the active phase to HNT. The modification of HNT has been extensively reported across the years using different approaches. Organosilane modification is one of the most frequently used treatment for HNT to increase the affinity between HNT and the loading molecules and at the same time retain the biocompatibility. This is achieved by grafting the specific functional groups of organosilane, such as the ethoxyl groups of APTES, onto the surface of HNT, which resulted in occurrence of a stronger interaction that provides a stronger electrostatic attraction between the modified HNT and loading materials (Pandey et al., 2017). This modification was applied for the deposition of palladium (Pd) nanoparticles onto the APTES-modified HNT for the hydrogenation of styrene to ethylbenzene, where coupling reaction occurred between the ethoxyl groups of APTES and hydroxyl groups of HNT during the surface modification of HNT before deposited with Pd nanoparticles (Zhang et al., 2013). Furthermore, the surface of HNT was modified with aminosilanes in the Atom Transfer Radical Polymerization (ATRP) of methyl methacrylate (MMA) into poly(methylmethacrylate) (PMMA) (Barrientos-Ramírez et al., 2011). Even though the usage of natural HNT as a solid support for this polymerization was reported (Barrientos-Ramírez et al., 2009), however they showed that the aminosilanes grafted HNT can be served as a support and as a ligand simultaneously for the copper catalyst used in the ATRP of MMA. Moreover, HNT was treated with hydrochloric acid to remove contaminants from

HNT surface and inner pores and was applied as a support for the NiO and CoO catalysts for the catalytic hydrocracking of heavy crude oil (Abbasov et al., 2016). Also, HNT was modified with chlorosilane and reacted with 2-mercaptobenzimidazole to create a novel supported antioxidant to enhance the interaction between HNT and natural rubber, as well as preventing the volatility and migration of 2-mercaptobenzimidazole (Zhong et al., 2015). Other than this, HNT was also functionalized with amino before loading with noble metals (rhodium, platinum and palladium) to prepare a model composite catalyst for catalytic reduction of 4-nitrophenol (Zou et al., 2015). Besides, an N-doped ZnO/HNTs catalyst was synthesized by assembling the N-doped zinc oxide nanoparticles into HNT for the degradation of methyl orange dye (Cheng & Sun, 2015). Additionally, immobilization was performed on HNT with metalloporphyrins to create a novel heterogeneous catalyst for the oxidation of cyclo-octene, cyclohexane and n-heptane (Machado et al., 2008).

2.3.3 Carrier

In addition, HNT has been extensively applied as a carrier for many different compounds especially drugs and chemicals. This is due to HNT having a lumen size greater than 10 nm which is considerably sufficient to host diverse guests (Tan et al., 2013). As such, natural HNT has been proven as a carrier for the uptake of antibiotics and antihistamine medicines (Jiang et al., 2016) and as an excellent pharmaceutical excipient with outstanding compression properties for making tablets, as well as stable controlled and sustained release ability (Yendluri et al., 2017). Likewise, modifications were done to boost the potential of HNT. Organosilane modification was performed on HNT with APTES and the results showed improved

loading of ibuprofen onto HNT due to the electrostatic attraction between APTES and ibuprofen (Tan et al., 2013). Similar modification was applied for the loading of aspirin (Lun et al., 2014b) and the immobilization of α -amylase enzyme onto HNT as an efficient support for the studies of enzyme loading and release (Pandey et al., 2017). In a separate study, the internal aluminum oxide within the inner tube of HNT was selectively etched via acid treatment to enlarge the lumen size and results showed that the loading of benzotriazole was increased up to 4 times (Abdullayev et al., 2012). Acid treatment can be applied in conjunction with heat treatment, where acid treatment can disaggregate HNT particles, remove impurities and urge dissolution of inner HNT layers. Heat activation on the other hand can eliminate the physically attached water molecules and cause the structural rearrangement of HNT which leads to changes in surface and pores properties, and at the same time aid the release of adsorbed drugs. Application of these treatments resulted in better adsorption and in vitro release of cationic drugs (Wang et al., 2014). Besides acid treatment, alkali treatment was found to have similar effect on the adsorption and release of the same drug (ofloxacin) and can lengthen the release of the adsorbed drug (Wang et al., 2013). Apart from this, HNT was further encapsulated with benzotriazole–copper film after loading with brilliant green to extend the sustained release of this antiseptic agent up to 200 hours (Wei et al., 2014). Lastly, HNT has even been applied as a multifunctional nanovehicle for targeted drug delivery system in cancer diagnosis and therapy. In this case, folic acid and magnetic nanoparticles were grafted onto HNT after minor organosilane modification on HNT to synthesize an anticancer drug delivery vehicle (Guo et al., 2012).

2.3.4 Fire Retardant

Last but not least, HNT is commonly applied as an additive especially in polymers due to its fire retardant properties. The addition of HNT into polymers was reported to have improved the thermal properties of polymers like polyamide (Marney et al., 2008), polypropylene (PP) (Du et al., 2006), butadiene-acrylonitrile rubber (NBR) (Rybiński & Janowska, 2013), polyvinyl alcohol (PVA) (Liu et al., 2007) and linear low density polyethylene (LLDPE) (Jia et al., 2009). However, the incorporation of HNT into polymer is a challenge especially in terms of ensuring a smooth dispersion in the polymer matrix. To overcome this issue, several approaches were implemented. Some of the most common methods used to mix filler into polymer to form composite materials include in situ mixing (Zilg et al., 1999), mechanical mixing (Ismail et al., 2013), melt mixing (Teh et al., 2004) and solution mixing (Rajasekar et al., 2009) methods. Aside from these, the easiest way of dispersing HNT into polymer was with the aid of surfactant as a dispersing agent (Lin et al., 2011). Previous researches have proven that the incorporation of appropriate amount of HNT into polymers resulted in higher thermal stability and flame retardancy (Lecouvet et al., 2013), enhanced elastic properties, hardness, increased tensile strength and better swelling barrier of the composite materials (Ismail et al., 2013; Pal et al., 2009).

2.4 Polymers as Adsorbents

Other than clays, polymers are also commonly used as adsorbents. Over the decades, polymeric adsorbents have started gaining attention and appearing as a potential substitute for nanoparticles like activated carbon as an efficient adsorbent

(Pan et al., 2009). The reason behind this is polymeric adsorbents exhibit large surface area, flexible surface chemistry as well as facile regeneration (Pan et al., 2009). Furthermore, polymeric adsorbents display many advantages over traditional adsorbents such as having better mechanical resistance and strength. Besides, polymer adsorbents are much easier to be reused and desorbed for many adsorption cycles as well as the potential of selectively choosing functional groups to compose the polymer (Galicía-Aguilar et al., 2017). Polymeric adsorbents are generally used in the removal of potentially poisonous organic pollutants that are found all over the world like phenolic compounds (Ipek et al., 2017; Păcurariu et al., 2013), aromatics (Liu et al., 2009; Nojavan & Yazdanpanah, 2017) and polyaromatic hydrocarbons (Long et al., 2008; Ncube et al., 2017). Besides organic pollutants, polymer adsorbents are also used to remove pharmaceuticals and drugs (Domínguez et al., 2011; Zheng et al., 2017) and even to adsorb drug for oral sustained release formulations (Wang & Yan, 2017). In recent years, a new polymer adsorbent, conductive polymer has drawn ample attention for the removal of heavy metals as well as organic compounds in wastewater. Conductive polymers like polypyrrole, polyaniline and polythiophene (Balint et al., 2014) and its composites are employed to remove different heavy metal ions like uranium(VI) (Abdi et al., 2017), manganese(II) (Hallajiqomi & Eisazadeh, 2017), chromium(VI) and nickel(II) (Shi et al., 2018), cadmium(II) (Mohamadi & Abdolmaleki, 2017), palladium(II) (Pang et al., 2018), mercury, lead and silver (Choi & Jang, 2008) ions. Conductive polymers combine the beneficial properties of both metals and polymers, enabling it to possess metallic and electrical conductivity, excellent thermal stability, and at the same time retain flexibility in processing and synthesis (Balint et al., 2014; Hallajiqomi & Eisazadeh, 2017). These properties have made it a better adsorbent compared to

conventional polymers, especially in removing heavy metals. Moreover, magneto-responsive polymers can be synthesized by inserting magnetite nanoparticles, namely iron(II) and iron(III), into monomers followed by polymerization to remove radioactive metal ions like uranium(VI) (Akl et al., 2016) and thorium(IV) (Ozay et al., 2011) in aqueous media.

2.5 Polymer to Immobilize Adsorbents

Nanomaterials were proven as efficient adsorbents with promising adsorption ability due to their nanoscale size which provide large surface area and ample active sites for adsorption. However, the downside of these nanoparticles is magnified when it comes to mass transport and separation as well as regeneration (Zhao et al., 2011) due to the high dispersibility of the nanoparticles in aqueous solution (Akl et al., 2016). Hence, the fabrication of hybrid nanocomposite materials has been introduced to resolve these situations. Nanoparticles are impregnated or coated onto host materials like granular activated carbon (Siriwardane et al., 2017; Suresh Kumar et al., 2017), silica (Maučec et al., 2017), alumina (Tan et al., 2016b) and polymer (Alizadeh Fard et al., 2017). Comparing to other host materials, polymers are notably attractive for their adjustable pore size, flexible surface chemistry, excellent stability and splendid mechanical strength (Zhao et al., 2011). To date, polymers have been commonly applied as supports for a wide variety of substances to be used in different applications. The use of polymer-supported nanoparticles is especially popular for adsorption of contaminants like organic dye rhodamine 6G (Elfeky & Al-Sherbini, 2011), cationic dye MB (Li et al., 2015), anionic dye Amido Black 10B and heavy metal Cr (VI) (Hu et al., 2016). The application of polymers as supports to accommodate multiple adsorbents including

metal oxides (Ali et al., 2017), clay (Wang et al., 2015) and carbon nanotubes (Bankole et al., 2017) has also been reported extensively. For instance, polyaniline was used to support different metal oxides (SiO_2 , TiO_2 , Al_2O_3 , and Fe_3O_4) to remove organic dye congo red from aqueous solution (Ali et al., 2017), while sulfonated HNT was used as a novel filler to create polyethersulfone hybrid nanofiltration membrane for dye purification of Reactive Black 5 and Reactive Red 49 (Wang et al., 2015). Besides, PEG-6-arm amino polyethylene glycol (PEG-NH₂) and polyhydroxybutyrate (PHB) were functionalized with carbon nanotubes (CNT) respectively to give nano-adsorbents of PEG-CNT and PHB-CNT for the removal of chemical oxygen demand (COD) from electroplating wastewater. In addition to this, PEG-NH₂ with PHB functionalized CNT (PEG-PHB-CNT) was also prepared for comparison purposes (Bankole et al., 2017). Nanoparticles and adsorbents can be immobilized onto polymer through several methods, such as sol-gel (Ghanei-Motlagh & Taher, 2017), in-situ synthesis (Jia et al., 2017), electrospinning (Tański et al., 2017), chemical polymerization (Ali et al., 2017) and solution mixing (Rajasekar et al., 2009) methods. In-situ synthesis is generally adopted to prepare polymer based nanocomposites where many nanoparticles especially transition metal sulfide or halide can be preloaded into the polymer matrix (Zhao et al., 2011). Electrospinning was found to be a simple technique to produce polymeric samples with high porosity, small pore size with high surface area (Liu et al., 2014). However, it is difficult to get the optimum parameters for this method. Solution mixing on the other hand is an easy method that can give well dispersed nanoparticles in a polymer by dispersing the nanoparticles and polymer in a particular solvent before casting to get the nanocomposite film (Liu et al., 2014). Among these methods, solution mixing method is recommended for small sample sizes, making it the most common method

applied for the incorporation of HNT into polymer (Liu et al., 2014).

2.6 Natural Rubber (NR)

Polymers can be classified into two main categories, namely natural polymer and synthetic polymer. Natural rubber (NR) is the typical example of a natural polymer as well as elastomer. NR is composed of poly(cis-1,4-isoprene) chain and is acquired from *Hevea brasiliensis* plant (Siririttikrai et al., 2017). It is regarded as a sustainable polymer and has been extensively used for many applications centuries ago. Its high elasticity, economical and distinctive properties have made it one of the most important polymers nowadays (Martins et al., 2008). It is well known that NR has been extensively used to manufacture a wide variety of daily products, waterproof leather and fabrics, and to manufacture an abundance of industrial, household, office stationeries and even some electrical instruments (Turnip et al., 2017). Despite NR's remarkable properties, several techniques have been introduced to modify the properties of this polymer to increase its value as well as its versatility in terms of application. Among them is by the addition of sulfur to form vulcanized rubber. In this process, crosslinking between the polymer chains occur resulting in a decrease in flexibility, increase in hardness and melting point. As a result, vulcanized rubber is stronger and can last longer than natural rubber. Hence, this type of rubber has been applied as tires, shoe soles and a wider range of products. To date, a more recent technique or approach to further optimize the properties of NR is discovered, that is to form NR nanocomposites by incorporating different types of fillers. Common fillers that are generally used in NR include metals (Pazhooh et al., 2017), metal oxides (Niamlang et al., 2017), graphene (Yaragalla et al., 2015), carbon nanotubes (Jose et al., 2017) and clay (Rezende et al., 2010). The

use of metals such as silver (Rathnayake et al., 2012) or metal oxides such as TiO₂ (Seentrakoon et al., 2013) in NR increases the value of NR in terms that they exhibit antibacterial and antifungal properties. This characteristic is important as it is well known that NR can cause severe allergies due to the natural occurring proteins in natural rubber latex. Graphene, carbon nanotubes and clay on the other hand can enhance the thermal and mechanical properties of NR, while graphene can also improve the gas barrier properties of NR. Meanwhile, all of these fillers can improve the adsorption ability of NR in removal of different pollutants. Previous works have reported that NR was adopted as an adsorbent for both organic (Krueyai et al., 2015) and inorganic (Hasanuddin et al., 2017) pollutants. Being an adsorbent, NR may have the ability to adsorb dyes such as MB in aqueous medium without the aids of fillers.

2.7 Methylene blue (MB)

Methylene blue (MB) is selected in this study because it is the most common soluble dye in water. The formula of MB is C₁₆H₁₈N₃SCl and its structure is given as below (Soni et al., 2012):

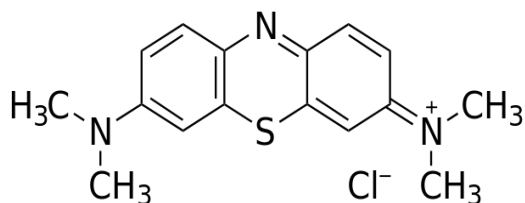


Figure 2.4: Structure of MB.

MB is extensively used for dyeing textile, cotton, silk, printing and some medical purposes (Conrad et al., 2015). Even though MB is not strongly hazardous to human

beings, it can cause eye irritation for both humans and animals, skin irritation and even systemic effects (Soni et al., 2012; Yagub et al., 2012). Upon inhalation, it can lead to short periods of rapid breathing or temporary breathing difficulty. Whereas upon ingestion, it may induce a burning sensation and trigger nausea, vomiting, diarrhea, gastritis, excessive sweating, mental confusion and methemoglobinemia (Soni et al., 2012). Critically, acute exposure to MB can provoke increased heart rate, cyanosis, jaundice, Heinz body formation, tetraplegia and necrosis (Soni et al., 2012). Therefore, removal of MB from wastewater has been one of the greatest environmental concerns and significant attention has been drawn worldwide. The most commonly used methods of removing MB from wastewater are the degradation and decolorization techniques. For degradation, metal catalysts such as TiO_2 (Singh et al., 2013), ZnO (Shen et al., 2008) and Fe_2O_3 (Lassoued et al., 2018) are regularly used. Decolorization on the other hand is mostly reported for employing different adsorbents such as activated carbon (Kumar, 2006), graphene (Liu et al., 2012b), biomass (Vilar et al., 2007), clays such as halloysite nanotubes (Zhao & Liu, 2008), bentonite and sepiolite (Bilgiç, 2005), natural (Hasanuddin et al., 2017) and synthetic polymers (Umoren et al., 2013; Yang et al., 2015). Nanoparticles and adsorbents in free powder form undoubtedly exhibit excellent performance in dye adsorption as compared to membrane or polymeric adsorbents due to their large surface area. However as mentioned previously, the powder form makes recollection and reusing after adsorption extra troublesome. Even though some adsorbents like HNT claim to have suspension with high stability and the dye adsorbed onto it can be deposited in a short period of time (Kiani et al., 2011), this process has clearly added more steps into the recollection procedures.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

All materials were used as received. The natural rubber, NR (60% dry rubber content) was obtained from the Malaysian Rubber Board, Kuala Lumpur as a gift. Halloysite nanotubes, HNTs were acquired from Sigma-Aldrich, USA. Sodium dodecyl sulfate, SDS (99%) was supplied by Acros Organics, Belgium while methylene blue, MB was purchased from R & M Chemicals, U.K. Hydrochloric acid, HCl was obtained from QRëC™, Malaysia whereas sodium hydroxide, NaOH was acquired from J. T. Baker, U.K.

3.2 Methods

3.2.1 Preparation of NR-HNT Composites

A series of NR-HNT composite film samples with different weight percentages (wt%) of HNT (10, 30, 50 and 70 wt%), were prepared. The amount of HNT in each of the materials employed is presented in Table 3.1. Typically to prepare 10 wt% HNT in NR, approximately 1.6 g of NR was weighed and placed into a sample vial. As much as 0.1 g of HNT was dispersed in 2 mL of 0.1 M SDS. The dispersed HNT was then added drop by drop into the previously measured NR while stirring with a magnetic stirrer. The mixture was continuously stirred for 2 hours for homogenization. After that, the mixture was cast and dried in an oven at 45 °C. Similar procedures were repeated for the preparation of the NR-SDS sample without the addition of HNT, whereas NR sample was prepared with only the addition of 2 mL distilled water to ease casting.

Table 3.1: Amount of HNT used to prepare each NR-HNT film.

NR-HNT Sample	Average Weight of HNT (g)	Average Weight of NR (g)
10 wt%	0.0982	1.6368
30 wt%	0.2943	1.6350
50 wt%	0.4894	1.6313
70 wt%	0.6867	1.6349

3.3 Characterization Techniques

3.3.1 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) was conducted on all the NR-HNT, NR and HNT samples using a PerkinElmer Frontier FT-NIR Spectrometer (UK) to analyze the composition of the samples. Each sample was placed on the detector platform. The pressure tower was turned so the compression tip was pressing on the sample. After adjusting the pressure exerted on the sample, the sample was scanned in the range of 650 – 4000 cm^{-1} .

3.3.2 X-Ray Diffraction (XRD)

The XRD analysis was carried out on HNT, 10 wt% and 50 wt% NR-HNT samples using a Bruker D8 Advance X-ray powder diffractometer (Germany). The analysis was done using Cu – $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA) in the 2θ range of $10^\circ - 90^\circ$.

3.3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was performed on NR and the NR-HNT samples with various wt% of HNT. A strip-like shape was cut out from the NR-HNT sample and broken into half after freeze drying with liquid nitrogen. After placing one of the pieces onto an aluminum stub, the sample was coated with gold and inserted into a Zeiss Supra 50VP, SEM from Germany to view the distribution of HNT in NR.

3.3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out for NR and all of the NR-HNT samples as well as HNT to investigate the thermal stability of the composites. As much as 10 mg of each sample was measured and placed in a sample pan. After the heating rate and temperature were set, the sample pan was inserted into a Mettler Toledo TGASDTA 851e (Switzerland). Each of the sample was heated from 30 to 920 °C at a rate of 20 °C min⁻¹ under nitrogen flow. After reaching 920 °C, the temperature was held for 5 min at 920 °C then cooled back to 30 °C. The data was acquired in the range of 30 – 920 °C.

3.3.5 Point of Zero Charge (PZC)

The point of zero charge (pzc) of NR and 10 wt% NR-HNT were determined to compare the pzc of both samples. The pzc was determined by adapting the method used by Fernandes and Santana (Fernandes Machado & Santana, 2005) with a A3502 pH meter. As much as 30 mL of ultrapure water was placed into 5 different beakers. The pH of the solution was adjusted to pH 2 – 10 (initial pH) using