SYNTHESIS OF CHITOSAN-MULTIWALLED CARBON NANOTUBES NANOCOMPOSITE FOR THE REMOVAL OF REMAZOL BLACK B DYE

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KARTHIGESAN VELAUTHAM

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LIST OF ABBREVATIONS

AC	Activated carbon
BOD	Biological oxygen demand
CNTs	Carbon Nanotubes
COD	Chemical oxygen demand
CS	Chitosan
CS-MWCNTs	Chitosan Multiwalled Carbon Nanotube Nanocomposites
CVD	Chemical vapor deposition
Mw	Molecular weight
MWCNTs	Multiwall Carbon Nanotubes
PVA	Polyvinyl Alcohol
RBB	Remazol Black B
SWCNTs	Single-wall Carbon Nanotubes

LIST OF SYMBOLS

Symbols		Unit
B	Heat of sorption constant	J/mol
C_e	Concentration at equilibrium	mg/L
C_o	Initial concentration	mg/L
C_t	Concentration at specific time	mg/L
k_1	First order rate constant	min-1
k_2	Second order rate constant	g/mg.min
K_F	Freundlich constant	-
K_L	Langmuir constant	L/mg
K_T	Equilibrium binding constant	L/g
m	Mass of adsorbent	g
n	Adsorption intensity	-
Q_e	Adsorption capacity at equilibrium	mg/g
Q_m	Maximum adsorption capacity	mg/g
Q_t	Adsorption capacity at specific time	mg/g
R	Dye removal efficiency	%
R^2	Correlation coefficient	-
R_L	Separation factor	-
t	Time	min
V	Volume of dye	L

SINTESIS CHITOSAN-MULTIWALLED CARBON NANOTUBES NANOCOMPOSITE UNTUK PENJERAPAN PEWARNA REMAZOL BLACK B

ABSTRAK

Pembangunan industri tekstil secara tidak langsung diusahakan oleh penggunaan berlebihan pewarna reaktif yang menarik seperti remazol hitam B (RBB). Kehadiran pewarna tersebut dalam air sisa membawa kepada pencemaran air yang merupakan isu alam sekitar yang kritikal untuk dikendalikan. Tujuan projek ini adalah untuk mensintesis filem nanocomposite yang diperbuat daripada komposit chitosan (CS) dan/atau polyvinyl alcohol (PVA) yang digabungkan dengan tiub nano karbon dinding berlapis (MWCNTs) untuk penjerapan pewarna RBB. Parameter seperti kandungan berat CS dan PVA dalam komposit, dos penyerap dan kepekatan pewarna awal telah disiasat sepanjang kajian penjerapan kelompok. Masa keseimbangan penjerapan ialah 2880 minit (48 jam). Kapasiti penjerapan filem CS tulen dan kecekapan penyingkiran pewarna masing-masing mencapai 10.96 mg/g dan 91.796%, lebih tinggi daripada komposit CS-PVA lain dan PVA tulen. Penambahan MWCNT kepada CS tulen menghasilkan peningkatan kapasiti penjerapan penjerap. Kenaikan dos penjerap secara cekap meningkatkan peratusan penyingkiran pewarna RBB namun mengurangkan kapasiti penjerapan. Peningkatan kapasiti penjerapan boleh diperhatikan apabila kepekatan pewarna awal meningkat. Walau bagaimanapun, kepekatan pewarna awal tidak menjejaskan kecekapan penyingkiran pada keseimbangan tetapi masih menyumbang dalam kadar penjerapan. Isoterma penjerapan untuk kedua-dua CS dan CS-MWCNTs paling sesuai dengan model isoterma Temkin (R^2 = 0.9903 dan R^2 = 0.949) berbanding model isoterma Langmuir dan Freundlich. Model kinetik tertib pseudo-pertama paling sesuai untuk penjerapan CS dan CS-MWCNTs, maka ia dapat memberikan butiran yang lebih tepat tentang kinetik penjerapan berbanding model kinetik tertib pseudo-kedua. Filem CS dan CS-MWCNT berpotensi digunakan sebagai penjerap yang cekap untuk menjerap molekul pewarna RBB dalam air sisa.

SYNTHESIS OF CHITOSAN-MULTIWALLED CARBON NANOTUBES NANOCOMPOSITE FOR THE REMOVAL OF REMAZOL BLACK B DYE

ABSTRACT

Development of textile industries indirectly strived by the excessive application of attractive reactive dyes such as remazol black B (RBB). The presence of such dye in wastewater lead to water pollution which is a critical environmental issue to be handled. The purpose of this project is to synthesis a nanocomposite films made from composite of chitosan (CS) and/or polyvinyl alcohol (PVA) incorporated with multiwalled carbon nanotubes (MWCNTs) for the adsorption of RBB dye. Parameters such as CS and PVA weight content in the composite, adsorbent dosage and initial dye concentration were investigated throughout the batch adsorption study. The adsorption equilibrium time was 2880 minutes (48 hr). Pure CS film adsorption capacity and dye removal efficiency reached 10.96 mg/g and 91.796% respectively, higher than other CS-PVA blends and pure PVA. The addition of MWCNTs to the pure chitosan resulted in increased adsorption capacity of adsorbent. Increment in adsorbent dosage efficiently increases the RBB dye removal percentage however reduced the adsorption capacity of adsorbent. Increase in adsorption capacity can be observed when the initial dye concentration is increased. However, the initial dye concentration doesn't affect the removal efficiency at the equilibrium but still contributes in the adsorption rate. Adsorption isotherm for both CS and CS-MWCNTs adsorption of RBB dye experimental data best fits the Temkin isotherm model (R^2 = 0.9903 and R^2 = 0.949) compared to Langmuir and Freundlich isotherm models. Pseudo-first order kinetic model fits best for CS and CS-MWCNTs adsorption of RBB dye experimental data, therefore provides a much accurate details on the adsorption kinetics than pseudo-second order kinetic model. The CS and CS-MWCNT films can be potentially used as an efficient adsorbent to adsorb RBB dye molecules in wastewater.

CHAPTER 1

INTRODUCTION

1.1. Research Background

The textile industries (TIs) are the major sources of the global economy in many countries like China, India, Pakistan, Brazil, Bangladesh and Malaysia (Kishor et al., 2021). It is one of the world's largest and oldest industries, creates jobs that do not require any special skills, and as a result, it plays a significant role in creating employment possibilities, particularly in developing countries. As a result, it is critical to the growth of these countries' Gross Domestic Product (Ananthashankar, 2013) and also for world's multicultural exposure.

Reactive dyes are the most widely used in the textile industry (Tanyildizi, 2011)because they have great quality features on cellulose fibres including cotton, wool, rayon, and flax by forming a covalent link between the dye molecule and the substrate, resulting in excellent wash and light fastness properties (Phillips, 2020). Reactive dyes are also used in a variety of different applications, including exhaust dyeing, pad dyeing, and printing. According to MarketWatch.com, the global market for reactive dyes is estimated to reach 6918.5 million USD in 2021, increased from 4213.1 million USD in 2020 (Market Analysis and Insights, 2022). Remazol Black B (RBB) is a diazo dye which is one of the most commonly used reactive dyes in the textile industry (Huang et al., 2016).

Reactive dyes are just representing 20–30% of the total dye market (Tanyildizi, 2011). There are around 10,000 different dyes and pigments are manufactured each year around the world and are widely utilised in the dye and printing industries. Textile industries generates a large quantity of liquid waste that contains both organic and inorganic including synthetic dyes. Not all dyes applied to clothes are used up during the dyeing process, and a portion of these unused dyes is always rinsed out ending up in the wastewater a significant quantity. The textile sector, among other dye-using businesses, is claimed to use the most dyestuff, consuming around 10,000 tonnes per year worldwide (Rodríguez-Couto et al., 2009). Apart from that, this industry is noted for producing roughly 100 tonnes of dye effluent each year, the most dye wastewater produced by a single industry (Solís et al., 2012).

Water is required by animals and humans for daily activities such as bathing, cooking, drinking, and washing, hence the presence of dye effluents in water sources is unacceptable. The removal of dye molecules from water sources has become a serious environmental problem as well as a task in recent years. Following that, researchers looked at dyes, how they're used, and how to get rid of them in order to find remedies. To remove dye particles from water sources, dye makers, dye-using enterprises, and even the government employed these solutions. Textile effluent contains a high concentration of contaminants, including increased BOD, COD, colours, toxic compounds, and dissolved salts (TDS and TSS). Table 1.1 shows the international permissible standard dye effluent pollutant discharge. The properties of dye effluent emitted should all be below the maximum allowable quantity while toxic pollutants should be not released to water bodies at all (Katheresan et al., 2018).

Table 1.1: International standard of dye effluent discharge into the environment (Adapted from the work of Katheresan et al., 2018)

Factor	**Standard Allowed**
Biological oxygen demand (BOD)	Below 30 mg/L
Chemical oxygen demand (COD)	Below 50 mg/L
Colour	Below 1 ppm
pH	Between 6 – 9
Suspended solids	Below 20 mg/L
Temperature	Below 42^{o}C
Toxic pollutants	Not allowed to be released

The textile industry, particularly textile wet processing, is ranked second among freshwater consumers and polluters due to its reputation as one of the most environmentally damaging business sectors (Chakraborty & Ahmad, 2022). Reactive dyes such as RBB are harmful organic pollutants, which can cause several health problems, may end up in the water bodies if it is not treated well. Lai, (2021) stated that the dyes produced from textile industries had a huge impact which triggers damaging the water bodies on the river, also preventing the sunlight from penetrating the river. Thus, aquatics living beings will be endangered due to the reduction in the rate of photosynthesis. Industries that produce dye wastewater should begin to restore the damage and destruction they do to the environment, as well as to humans and animals. Dye-using industries should make an effort to avoid or reduce releasing dye wastewater into the environment, in cooperation with researchers who are striving to eliminate dye wastewater from the environment. Instead of polluting the environment, dye-using enterprises should start developing an effective dye effluent treatment system in their manufacturing factories.

1.2. Problem Statement

As a step towards treating the dye-polluted wastewater, an efficient and economic approach will be always the top priority for researches. Various studies and methods have been previously proposed and engineered for an efficient dye removal from wastewater. In contrast to biological and chemical methods, physical methods are the simplest yet efficient method in dye removal which is usually achieved by mass transfer mechanism with least amount of chemical usage which indeed proves as a greener solution (Fu & Wang, 2011; Shon et al., 2013). Recent studies have also verified that adsorption is the one of the physical methods mostly used in wastewater treatment due to its performance and cost effectiveness (Asif Tahir et al., 2016; Mu & Wang, 2016).

Research have proved that activated carbon (AC) as an effective adsorbent to remove a wide range of organic and inorganic contaminants from gaseous environments or dissolved in aqueous systems (Yin et al., 2007). Oxidizing agents are equipped to modify AC in order to enhance their unique physical and chemical characteristics and increase their affinity its target substances found in water. However, this procedure generally decreases the AC surface area (Rivera-Utrilla et al., 2011). Ghosh & Reddy, (2014) insisted that the high surface area, great absorption capacity, easy accessibility, high selectivity, and superior recyclability are all the characteristics of an ideal adsorbent for dye adsorption. In their work they have also quoted that, "activated carbon (AC) is an undoubtedly effective adsorbent, but its high-cost limits its large-scale usage, particularly in developing countries". In that case, for the treatment of wastewater and water, nanoparticles have been synthesized and employed as adsorbent materials as it offers a crucial chance to create practical solutions for scaling the adsorption process which is appropriate for commercial use (Abdulkhaleq Alalwan et al., 2022).

Carbon nanotubes (CNTs), a type of nanomaterial, have attracted the attention of many researchers in recent years due to their unique properties as a new type of adsorbent for the removal of environmental pollutants, such as high chemical and thermal stability, high porosity, large surface area, hollow and layered structures. Multiwalled carbon nanotubes (MWCNTs) have several advantages over single-walled carbon nanotubes (SWCNTs), including cheaper unit cost, greater thermal and chemical stability, and easier preparation due to improved growth control (Rostami et al., 2022a). However, CNTs have a highly hydrophobic adsorptive surface by nature. To address this issue in raw CNTs, various surface modification approaches have been investigated, including CNTs functionalization (Zare et al., 2015a) such as the development of polymer nanocomposites. The formation polymer nanocomposite using polyvinyl alcohol (PVA) and MWCNTs studied by Jagadish et al. (2016) claimed to be highly stable, easily storable, compact and could open up a new route for dye removal as it creates hydrogen bonds and weak van der Waals interactions, are used to adsorb dyes. Other than PVA, chitosan (CS) a natural polymer has also proved to have outstanding removal capacities for reactive dyes (He et al., 2016) such as RBB with low-cost and high effectiveness compared with other adsorbents used in the adsorption of dyes (Abbasi & Habibi, 2016). However, CS highly swollen in water, therefore losses its physical structure, resulting in low mechanical strength and poor acid resistant (He et al., 2016). Therefore, both PVA and CS can be incorporated into MWCNTs to achieve high dye removal efficiency at the same time it can be an effective way to overcome the limitations when the adsorbents are utilized alone.

In this study, CS-PVA polymer composite will be synthesized through solution casting method for the removal of RBB dye to investigate the polymer composite's adsorbing efficiency. The PVA and CS amount ratio used in nanocomposite will be the main parameter to be considered where the best ratio will be then used to further investigate other parameters such as the adsorbent dosage, dye concentration and effect of MWCNTs incorporation into the polymer composite will be evaluated to analyse its effects on RBB dye removal performance. Also, the removal of RBB dye using CS-PVA-MWCNTs is yet to be reported.

1.3. Objectives

The objectives of this research are:

i. To investigate the effect of PVA and chitosan ratio in nanocomposite towards the adsorption capacity and dye removal efficiency

ii. To investigate the effect adsorbent dosage, dye concentration and addition of nanoparticle MWCNTs to polymer composite towards the adsorption capacity and dye removal efficiency

iii. To investigate the adsorption isotherm and kinetic of the RBB dye adsorption using PVA-CS-MWCNTs nanocomposite

1.4. Scope of Study

For this study, polymer composites made of PVA and CS will be reinforced with MWCNTs nanoparticles to form a nanocomposite for the removal of RBB dye. The composite film for adsorption is synthesized through solution casting method.

Batch studies for the study were carried out using PVA-CS blend polymer composite, pure PVA polymer, pure CS polymer and CS-MWCNTs nanocomposite. Batch study on the effect of weight ratio of PVA and CS in the polymer composite is carried out initially. The best adsorbent is chosen, and further studies such as the effect of MWCNTs addition to polymer composite, the effect of adsorbent dosage and effect of initial dye concentration were carried out. The equilibrium time of the adsorption is at 48 hr.

1.5. Sustainability

Figure 1.1: The 17 Sustainability Development Goals

The 17 Sustainability Development Goals (SDG) is there for us to ensure that sustainable development is taking place in all countries regardless of its development level in order to ease the all the jobs of responsible parties and strengthen the capacity of the state to achieve the desired outcomes. Figure 1.1 shows all the 17 SDGs that currently projected by United Nations (UN) organizations. These goals stand as a guideline to all developments and innovation in line with our Earth's sustainability, taking in count of the importance of all living organisms.

As a small part of contribution to these goals, in this study there are 2 Goals that will be adapted and applied to ensure the study has a positive and sustainable impact to our Mother Earth. The 2 Goals are: GOAL 6: "Ensure access to water and sanitation for all" and GOAL 14: "Conserve and sustainably use the oceans, seas and marine resources for sustainable development". The study covers the removal of RBB dye using sustainable and low-cost adsorbents which have potential to treat the wastewater in real world scenario.

CHAPTER 2

LITERATURE REVIEW

2.1. Synthetic Dyes

Mauveine, the first human-made organic aniline dye, was discovered by William Henry Perkin in 1856 after a failed attempt at complete quinine synthesis. Thousands of synthetic dyes have been created since then. Chemicals, petroleum by-products, and earth minerals are the main resources used to make synthetic dyes (Ziarani et al., 2018).

Synthetic dyes are used in a variety of sectors, including leather, paper, and textiles, because of their colour-giving capabilities. Each year, it is estimated that 700,000 tonnes of diverse colourants are produced from approximately 100,000 commercially available dyes. When dyes have served their purpose, they are frequently thrown into environmental water bodies without further consideration. The presence of dye effluents in the environment is known to be caused by five major enterprises, as shown in Figure 2.1 (Katheresan et al., 2018).

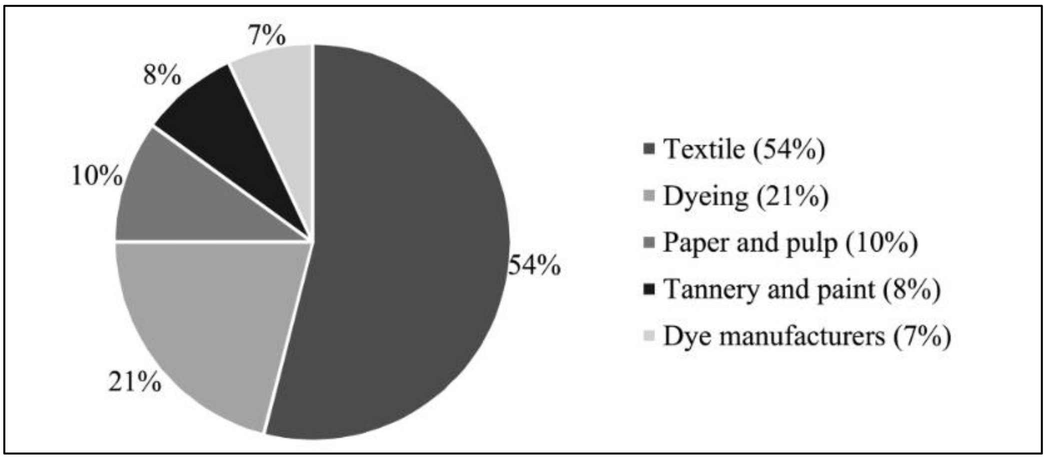


Figure 2.1: Industries responsible for the presences of dye effluent in the environment (Katheresan et al., 2018)

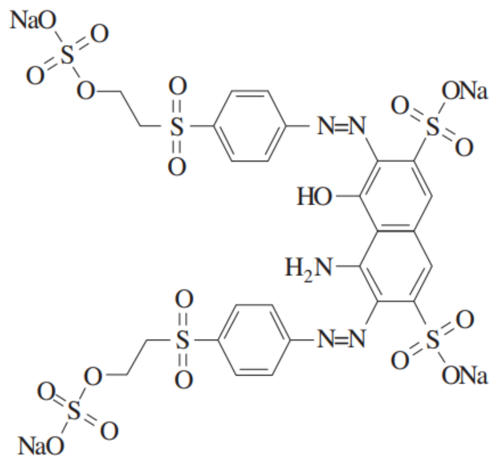
2.2. Remazol Black B

Reactive dyes are commonly used in textile industries because of simple dyeing procedure and covalent binding with cellulose fibres (El-Zawahry et al., 2016a). Remazol Black B (RBB) dye is a diazo dye and is one of the most commonly used reactive dyes in the textile industry (Huang et al., 2016b). The presence of one or more –N≡N– (azo) bonds defines the azo reactive dyes. They are brightly coloured, have good colour fastness, easy to apply, and use little energy. As a result of their extensive use for colouring cellulose, reactive dyes account for over 45 percent of all textile dyes manufactured annually (Tunç et al., 2009). Additionally, remazol dyes feature a masking group that prevents them from interacting with water, allowing them to last longer in water. Increasing the pH or the temperature of the dye solution may eliminate this condition (Ananthashankar, 2013).

Reactive dyes have been identified as problematic compounds in textile wastewaters because they are water-soluble, exist in higher concentrations in wastewater than other dye classes, and are primarily found in hydrolyzed form, which is difficult to remove using conventional treatment systems (Tunç et al., 2009). As a consequence, reactive dyes become highly toxic to aquatic ecosystems and the environment. Sivaraj et al., (2001) in research stated that the presence of such dyes (such as azo dyes) in water bodies are potentially mutagenic and carcinogenic, causing serious damage to the liver, digestive system, and central nervous system, as well as affecting agricultural production and underground water quality. In that case, it is environmentally important that the RBB is totally removed from the wastewater before being released to our water bodies.

The chemical structure and characteristics of RBB compound is shown in Table 2.1. Information was extracted from “Reactive Black 5” compound summary published in the webpage of National Center for Biotechnology Information, 2022 and from the work of Farrokhi et al., (2014).

Table 2.1: The Characteristics of RBB (Farrokhi et al., 2014)

Remazol Black B (CAS No. 12225-25-1)	
Molecular Structure	
Molecular Formula	$C_{26}H_{21}N_5Na_4O_{19}S_6$
Synonyms	Reactive Black 5
Molecular Weight	991.8
Chemical Class	Anionic, Diazo
Reactive Group	Sulfatoethylsulfone
Maximum Absorbance Wavelength (nm)	597

2.3. Dye Removal Methods

Dye concentrations in textile and household wastewater are reported over a wide range of values in literatures as the composition of textile industry wastewater differs from factory to factory and place to place, depending on the manufacturing process, factory equipment, kind of fabric produced, chemicals utilised, fabric weight, and season or fashion sense (Yaseen & Scholz, 2019). The textile wastewater has a high colour intensity, high biological and chemical oxygen demand and high total dissolved solid. The textile wastewater produced from cotton dyeing industry is extremely polluted due to presence of reactive dyes (Holkar et al., 2016).

Presence of colour in water may cause scarcity which is very important for aquatic life thus leading to a bad effect for our environment. Removing the toxics and colours that produced by the dyes from the industrial effluent can reduce the treatment cost of river water which will be used for drinking purpose. Therefore, prior to discharge of textile wastewater into river, various physical, chemical and biological methods to decolour or remove the dye is developed in an economic and efficient way such as shown in Figure 2.2. (Saratale et al., 2011).

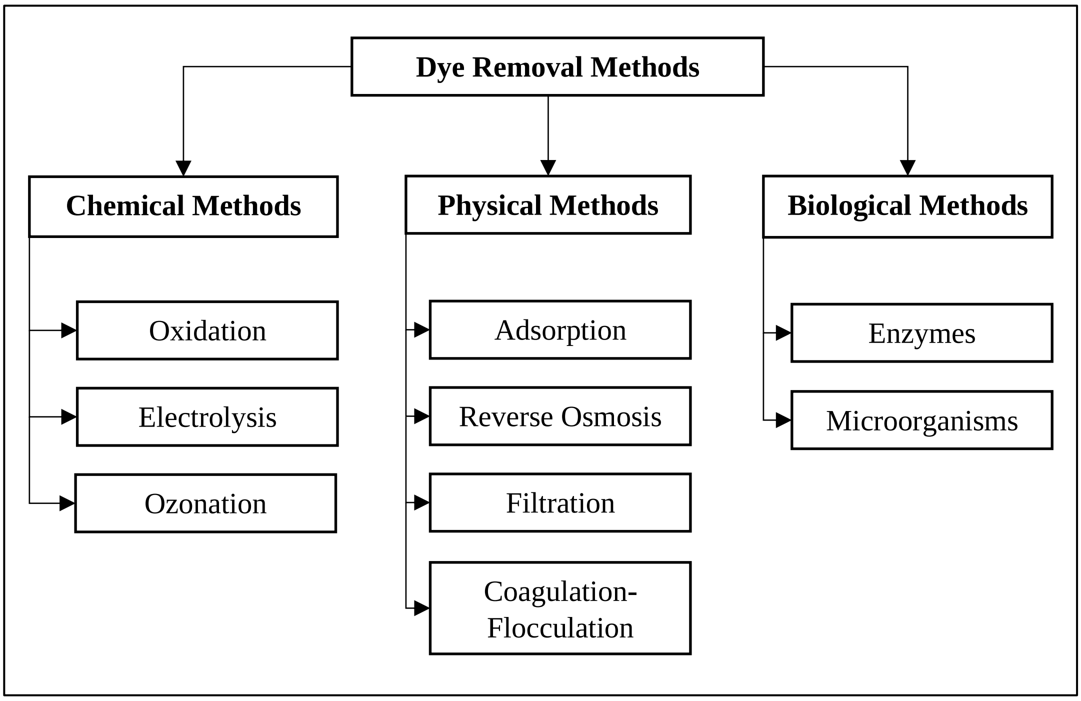


Figure 2.2: Dye Removal Methods (Saratale et al., 2011)

2.4. Adsorption

Adsorption is a physical separation method in which fluid, liquid, or gas molecules bond to the outer and interior surfaces of a solid object which is termed as the adsorbent. The separation is based on the selective adsorption such as thermodynamic or kinetic selectivity of the contaminants by an adsorbent having a specific interaction between its surface as well as the adsorbates surface (Crini et al., 2018).

Adsorption is often considered as a simple, low-cost, efficient, reusable, environmentally friendly, and quick approach for treating industrial effluents containing dyes, and it produces non-toxic secondary pollutants (Senguttuvan et al., 2022). Adsorption method is opted substantially in wastewater dye removal treatment due to its great decolorization efficiency for wastewater comprising many types of dyes. The major features that need to be considered when choosing an adsorbent for colour removal are high affinity, compound capability, and adsorbent regeneration ability (Jadhav & Srivastava, 2013).

2.5. Multiwalled Carbon Nanotubes (MWCNTs)

Since last decade, the application of CNTs in wastewater treatment, specifically in dye and heavy metal removal were widely studied compared to any other carbon-based adsorbents. CNTs are basically rolled up graphene sheets that forms a cylindrical structure. There are two types of CNTs, which are single-walled carbon nanotubes (SWCNTs) and MWCNTs as shown in Figure 2.3 (a) and (b) respectively (Zare et al., 2015b). CNTs length can be scaled from nanometers to millimeters while diameter up to 100 nanometers along with large specific surface area, high porosity, hollow and layered structure. These properties allow the CNTs to have very strong interactions with other molecules through through π–π electronic and hydrophobic interactions (Gupta et al., 2013). Multiple strategies such as CNTs functionalization are being studied in recent years to improve CNTs performance and better dispersion and interaction across matrix surfaces. Such example is the adhesion of polymer matrix to CNTs, which displays significant tensile strength and other mechanical properties improvement (Rostami et al., 2022b). As per reported by Mallakpour & Khadem, (2016), the addition of CNTs is not only capable of changing the physiochemical properties of the nanocomposite, but it also provides the efficacy to remove hazardous substances in the wastewater. MWCNTs will always have an upper hand over SWCNTs with the benefits such as lower unit cost, high thermal and chemical stability as well as easier preparation process (Rostami et al., 2022b) which makes MWCNTs the appropriate choice for dye adsorption.

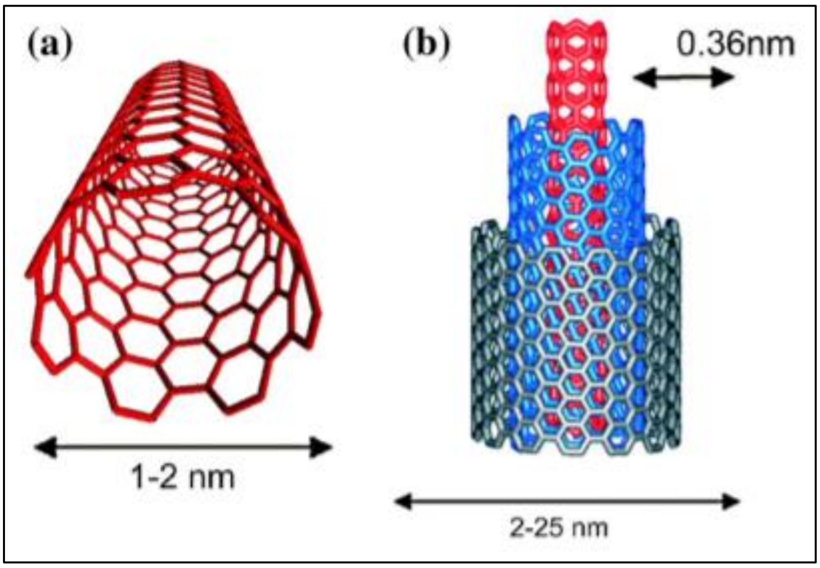


Figure 2.3: The schematics of (a) SWCNTs and (b) MWCNTs
(Zare et al., 2015b)

2.6. Chitosan

Chitosan is a linear biopolymer that is one of the most effective and environmentally friendly adsorbents being used for dye adsorption techniques. High hydrophilicity, ease of modification, biodegradability, nontoxicity, and super absorbency are the amazing qualities of chitosan. It has a lot of amino and hydroxyl groups, which makes it a good adsorbent for removing contaminants like dyes and heavy metals. However, because to its high swelling index, low chemical stability in acidic environments, weak mechanical strength, and low surface area, chitosan use in adsorption technology is quite limited (Reghioua et al., 2021). In order to avoid these limitations, chitosan is often modified by cross-linking reaction, in which a cross-linking agent links chitosan chains using covalent bonding that aldehydic function react with the amino groups in chitosan (He et al., 2016). Carbon nanotubes (CNTs) can be also used for the modification of chitosan due to the properties such as unique structures and mechanical properties and high electrical conductivity (Abbasi, 2017). Figure 2.4 shows the molecular structure of chitosan.

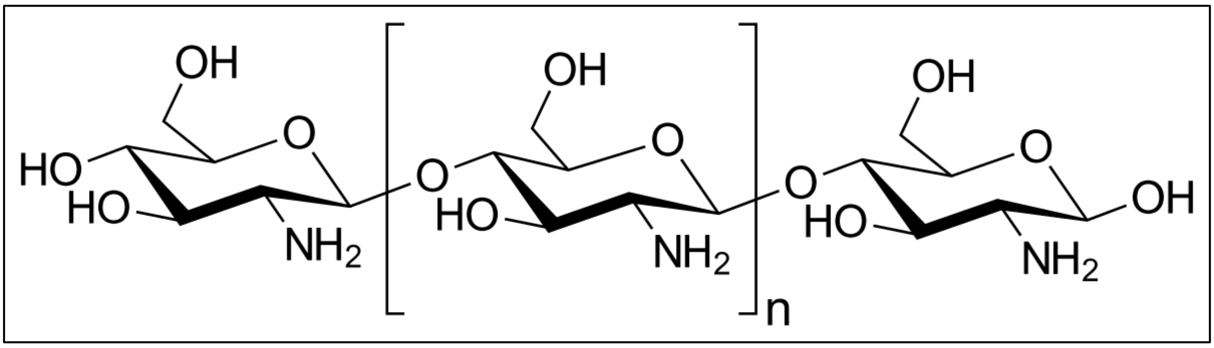


Figure 2.4: Chemical structure of Chitosan

2.7. Polyvinyl Alcohol

Polyvinyl alcohol (PVA) is a highly hydrophilic, nontoxic, and biocompatible polymer with good mechanical strength, thermal stability, and pH stability. It can be utilised to make hydrophilic surfaces that are beneficial to biological demands. This is due to PVA's highly polar character, which helps to prevent fouling in certain applications. Non-polar surfaces, on the other hand, increase water contaminant adsorption through hydrophobic interactions, which include natural organic compounds like humic and fulvic acids (Wan Ngah et al., 2011). In recent studies, adhesion of PVA to host matrix verifies the improvements in film-forming ability, wide temperature window, and making it fillers dependent electrical and optical properties (Bhavsar et al., 2022). Figure 2.5 shows the molecular structure of PVA.

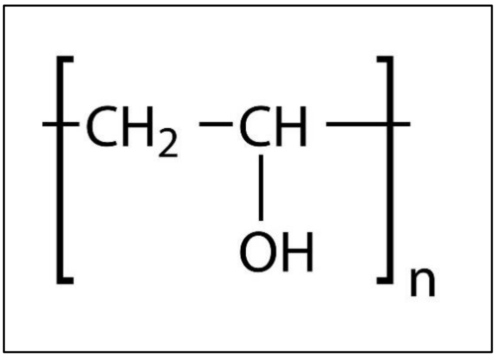


Figure 2.5: Chemical structure of PVA

2.8. Adsorption Isotherm

Adsorption isotherm can be defined as an empirical relationship to relate the connection between the adsorbent and adsorbate in an adsorption process. For instance, adsorption isotherm can predict how much adsorbate amount can be absorbed by the adsorbents at equilibrium by graphical representation (Desta, 2013). Three most used adsorption isotherms are Langmuir, Freundlich and Temkins relations (Mate & Mishra, 2020).

i. Langmuir Isotherm

This model applies when the adsorbed molecules do not interact and the adsorbate and adsorbent form a monolayer at equilibrium. The linearized formula that governs this model is:

$$\frac{1}{q_e} = \frac{1}{Q_m K_L}\left(\frac{1}{C_e}\right) + \frac{1}{Q_m} \quad \text{[Equation 2.1]}$$

The value of Q_m (maximum adsorption capacity) and K_L (Langmuir constant) were estimated from the plot of $1/q_e$ vs $1/C_e$.

ii. Freundlich Isotherm

The adsorption process is assumed to take place on a heterogeneous surface of the adsorbent in this model. For this model, the equation is as follows:

$$\log q_e = \log K_F + \frac{\log C_e}{n} \quad \text{[Equation 2.2]}$$

The value of K_F (Freundlich constant also known as adsorption capacity) and n parameter is estimated from the plot log q_e vs. $log\ C_e$. The n parameter indicates heterogeneity, hence for value between 0 and 10 the adsorption is favourable. The greater value of n suggests stronger adsorption intensity.

iii. Temkins Isotherm

Adsorption isotherms of water pollutants are increasingly being correlated using the Temkin isotherm equation (Chu, 2021). The linearized equation for this model is given as:

$$q_e = B \ln K_T + B_T \ln C_e \quad \text{[Equation 2.3]}$$

The value of B (constant related to heat of sorption) in J/mol and K_T (equilibrium binding constant) in L/g were computed from the linear plot of q_e vs. $ln\ C_e$

2.9. Adsorption Kinetics

The kinetics of adsorption processes can be used to determine the efficiency of adsorption and the suitability for scaling up events (El-Zawahry et al., 2016b). Adsorption kinetics is plot that defines the rate of retention or release of a solute from an aqueous-phase to solid-phase interface at a given adsorbent dosage, temperature, flow rate or pH (Kajjumba et al., 2018). Thus, to analyse the mechanism and efficiency of adsorption in this study, Lagergren and

Morris-Weber pseudo-first order and Ho and McKay pseudo-second order kinetic models have been applied to the experimental data.

i. Pseudo-first order (PFO) kinetic model

The Lagergren model, PFO describes the adsorption of solute onto adsorbent following the first order mechanism (Kajjumba et al., 2018). The equation is expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{[Equation 2.4]}$$

where q_t is adsorbate adsorbed onto adsorbent at time t (mg/g), q_e is equilibrium adsorption capacity (mg/g), and k_1 is first order rate constant (1/min). On integration of equation 2.4 the linear form can be written as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{[Equation 2.5]}$$

ii. Pseudo-second order kinetic model

The rate of the second-order model is determined by the amount of dye adsorbed on the adsorbent's surface and the amount adsorbed at equilibrium (El-Zawahry et al., 2016b). The model assumes that the rate of solute adsorption is dependent on the number of available sites on the adsorbent (Kajjumba et al., 2018). The equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \text{[Equation 2.6]}$$

where q_t is the amount of dye adsorbed (mg/g) at time t, q_e is the maximum adsorption capacity (mg/g) for second-order adsorption, and k_2 is the second-order rate constant (g/mg min). On integration of equation 2.6 the linear form can be written as:

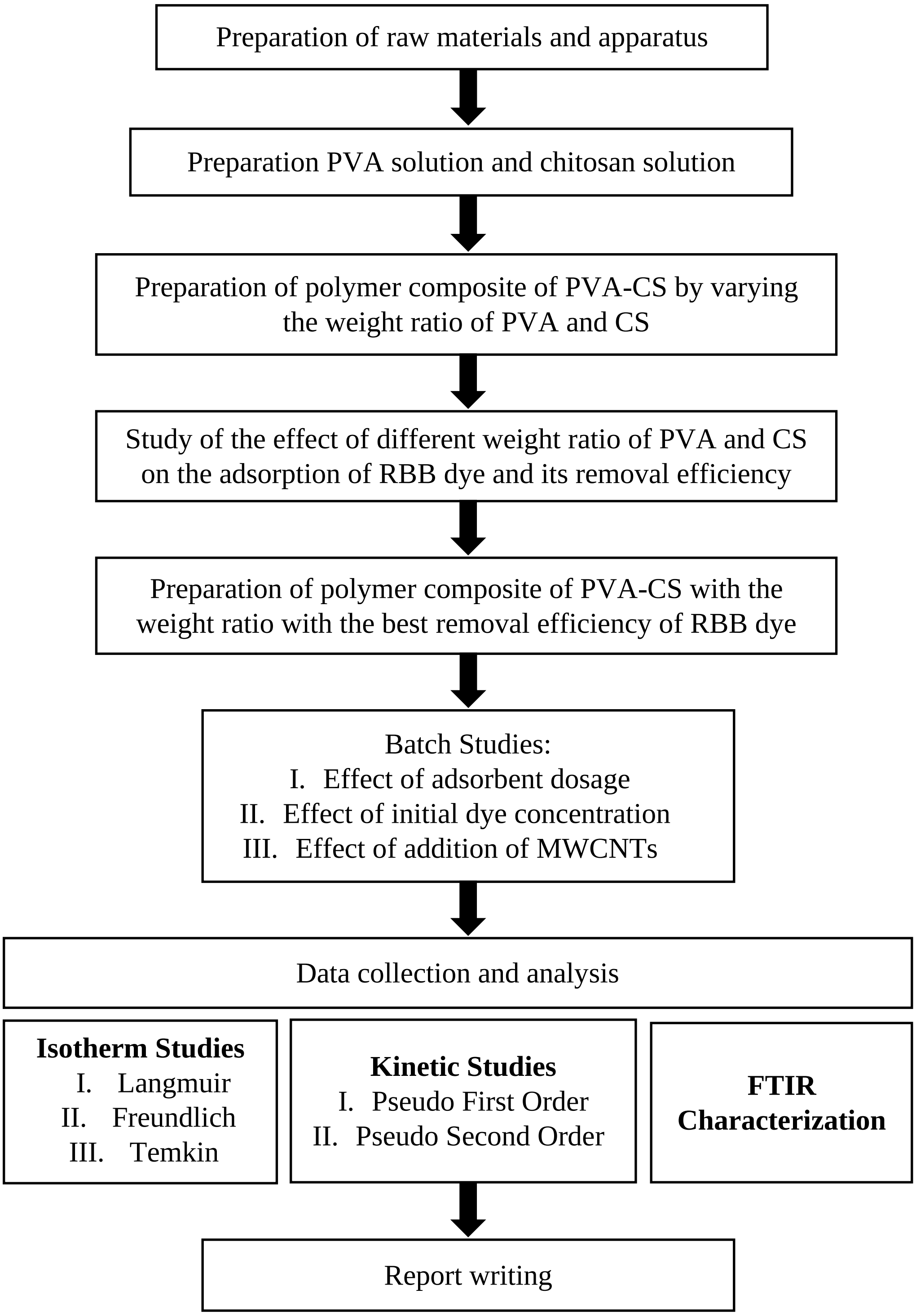
$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2}\right] + \frac{t}{q_e} \quad \text{[Equation 2.7]}$$

CHAPTER 3

MATERIAL AND METHODOLOGY

3.1. Research Methodology

Flowchart below represents the methodology flow for the research: -



3.2. Material

Polyvinyl alcohol (Avg. M_w = 85,000 to 124,000, 87 to 89% hydrolyzed, purchased from SIGMA), chitosan (85% deacetylated powder, purchased from Alfa Aesar), multiwalled carbon nanotube powder (Purity > 95%, prepared from CVD method), acetic acid (M_w = 60.05 g/mol, Density = 1.05 kg/l), sodium hydroxide pellets, ethanol and deionized water.

10 wt.% acetic acid is prepared by adding 23.8 mL of pure acetic acid into 225 mL of deionized water and left for stirring by the magnetic stirrer under the fume hood for an hour to obtain homogenous solution. Meanwhile, a mixture of NaOH-ethanol solution is prepared for treating the chitosan or chitosan-PVA films which contains acetic acid. The mixture of NaOH-ethanol solution is made up of 3 wt.% NaOH solution, 47 wt.% ethanol and 50 wt.% deionized water. PVA films will be treated with pure ethanol only.

3.3. Equipment

All the equipment that were used in this study for preparation and collecting data are listed on Table 3.1 below.

Table 3.1: List of equipment used

Equipment	Model	Purposes
Electronic Balance	SHIMADZU AY220	To measure the weight of PVA, CS and MWCNTs
Magnetic Stirrer	IKA C-MAG HS-7	To stir sample/solution
UV-Vis Spectrometer	Cary 60 UV-Vis	To measure absorbance of dye solution
Bath Sonicator	BRANSON 3800	For dispersion of MWCNTs in CS solution
Ultrasonic Tip Sonicator	Hielscher UP200S	For dispersion of MWCNTs in CS solution

3.4. Synthesis of adsorbent films

3.4.1. Preparation of PVA solution

8 wt.% PVA solution was prepared by dissolving 24g PVA powder into 276 mL of deionized water. The solution was heating at 70°C for 4 hr followed by overnight stirring at room temperature with the apparatus setup shown in Figure 3.1.

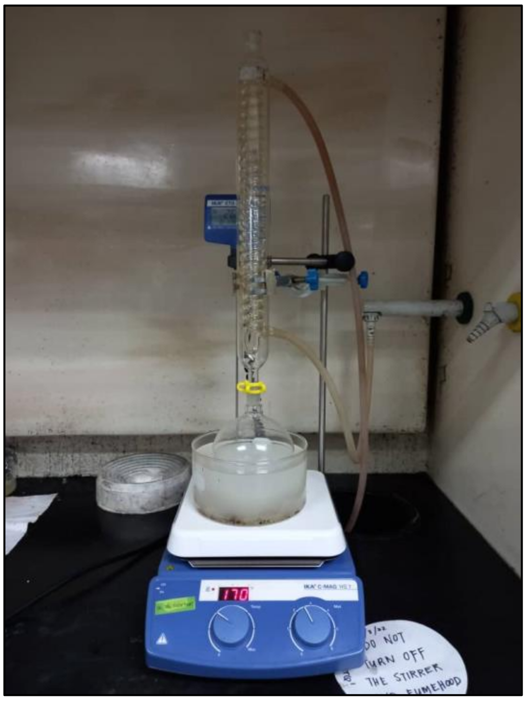


Figure 3.1: Apparatus setup for PVA solution preparation

3.4.2. Preparation of chitosan solution

2 wt.% Chitosan solution was prepared by dissolving 5g of chitosan powder into 245 mL of 10 wt.% acetic acid. The solution was stirred overnight at room temperature with the apparatus setup shown in Figure 3.2.

Figure 3.2: Apparatus setup for CS solution preparation

3.4.3. Preparation of PVA-chitosan polymer composite film

PVA-CS polymer composite was desired to be prepared with 5 different sets of weight ratio as per listed in Table 3.2. An illustration on Figure 3.3 may assist on how the preparation of 5 different weight ratio PVA-CS polymer composite is done. 375 mL of pure CS and PVA solution each is prepared prior to the composite preparation. The desired weight of PVA and CS is mixed and stirred using magnetic stirrer at room temperature overnight to obtain a homogenous solution. 150 g of pure PVA and CS each is also prepared as a part of desired weight ratio. Then, 25 mL the mixed solution is casted on a clean petri dish and dried for 48 hr at room temperature under the fume hood. Afterwards, the casted film will be treated with a mixture of NaOH-ethanol solution and let under the fume hood overnight. Dried films are then carefully peeled of the petri dish using forceps and washed with deionized water to remove the excessive NaOH. It is then dried at room temperature overnight. Figure 3.4 shows the pure CS polymer film prepared through solution casting method. Similarly, other films are prepared.

Table 3.2: Weight ratio of PVA-CS composites

Set	Weight percentage of PVA	Weight percentage of CS
1	100%	0%
2	75%	25%
3	50%	50%
4	25%	75%
5	0%	100%

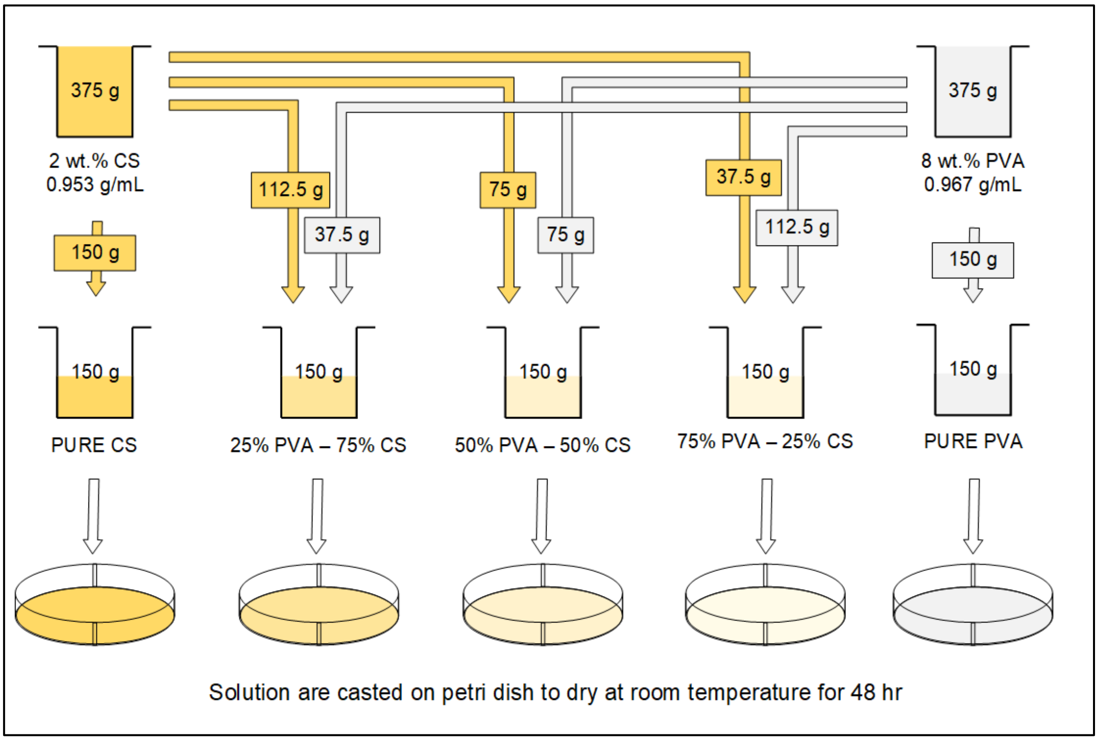


Figure 3.3: Illustration of PVA-CS polymer composite films preparation

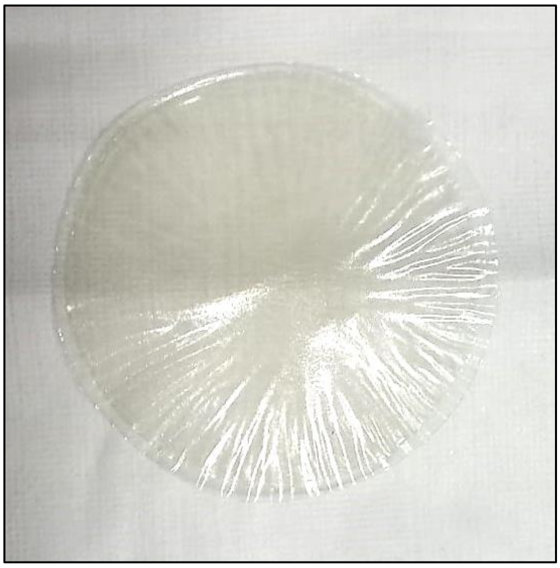


Figure 3.4: Pure CS polymer film

3.4.4. Preparation of CS-MWCNTs nanocomposite film

The polymer composite is prepared by mixing the prepared PVA and chitosan solution at desired weight ratio and stirring for overnight at room temperature. Then, 2.406 g of MWCNTs was added into the 250 ml of polymer solution in order to form 1 wt.% of MWCNTs fillers in the suspension. To get a stable and homogenous dispersion, the solution was sonicated using ultrasonic bath sonicator for 2 hr as shown in Figure 3.5, followed by sonication with ultrasonic tip sonicator with a high-powersonic tip operated at 50 Hz rate frequency and 90% amplitude for 1 hr in as shown in Figure 3.6. Then, 25 mL the mixed solution is casted on a clean petri dish and dried for 48 hr at room temperature under the fume hood. Afterwards, the casted film will be treated with a mixture of NaOH-ethanol solution and let under the fume hood overnight. Dried films are then carefully peeled of the petri dish using forceps and washed with deionized water to remove the excessive NaOH. It is then dried at room temperature overnight. Figure 3.7 shows the CS/MWCNTs polymer nanocomposite film prepared through solution casting method.

Figure 3.5: Sonication using bath sonicator

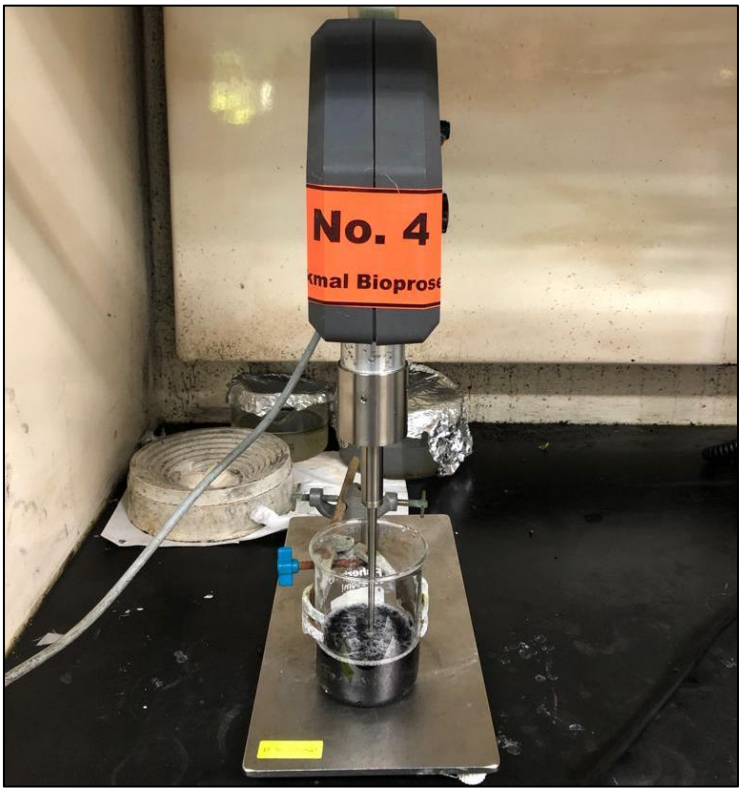


Figure 3.6: Sonication using ultrasonic tip sonicator