RADIATION MODIFIED CHITOSAN/POLYVINYL ALCOHOL FILM WITH POLYVINYL PYRROLIDONE COATING FOR HEAVY METAL ION REMOVAL

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RADIATION MODIFIED CHITOSAN/POLYVINYL ALCOHOL FILM WITH POLYVINYL PYRROLIDONE COATING FOR HEAVY METAL ION REMOVAL

ABSTRACT

Chitosan (CS) / Polyvinyl Alcohol (PVA) films were obtained by solution casting method. To be used in the water treatment application, these film need to be improved in mechanical strength. In this study, 2% (w/v) chitosan and 5% (w/v) PVA were blend at different CS: PVA weight ratios (50:50, 70:30 and 90:10). These mixtures were then transformed into films by solution casting method. Mechanical properties of the films were evaluated using tensile strength test where, at 70:30 of CS: PVA ratio gave the best tensile strength. Therefore, this composition was selected to proceed with the radiation modification with Polyvinyl Pyrrolidone (PVP) coating. CS/PVA films were modified with layer of PVP and exposure to irradiation to improve its mechanical strength. The films were dipped into different concentrations of PVP solutions at 1%, 3% and 5% (w/v). They were then exposed to gamma radiation at 5,10,20 and 30 kGy. The tensile strength of CS/PVA films coated with 1% PVP was found to increase up to 31%. Elongation at break was improved by 1% PVP coating. Chemical structures of the films were obtained by Fourier transform infrared spectroscopy (FTIR). It showed that gamma irradiation might form crosslinking between the polymers chain. Morphology characteristic was done using scanning electron microscope (SEM) and Atomic force microscope (AFM). Surface morphology proved that by PVP coating and gamma irradiation increases the roughness of the films. Results obtained from SEM and X-ray diffraction (XRD) showed the compatibility between all the polymers used in this film. Adsorption capability of modified CS/PVA films towards copper (Cu) and lead (Pb) ions showed no significant different when compared with the original CS/PVA film.

While for adsorption of zinc (Zn) ion, modified CS/PVA showed the amount of Zn ion adsorbed was increased at 1% PVP coating compared with unmodified CS/PVA films. Can be concluded that modification of CS/PVA film with gamma irradiation and PVP coating improved the mechanical strength of CS/PVA film and sustained the adsorption capability of the film towards heavy metals ion such as Cu, Pb and Zn ions. Therefore, this modification is suitable to be used in water treatment application towards heavy metals ion adsorption.

Keywords: Chitosan, heavy metal, polyvinyl alcohol, polyvinyl pyrrolidone, radiation

RADIASI MODIFIKASI FILEM KITOSAN / POLIVINIL ALKOHOL DENGAN SALUTAN POLIVINIL PIROLIDON UNTUK PENYINGKIRAN ION LOGAM BERAT

ABSTRAK

Filem Kitosan (CS) / Polivinil Alkohol (PVA) diperoleh melalui teknik pembetukan larutan. Untuk digunakan dalam aplikasi rawatan sisa air, kekuatan mekanikal filem-filem tersebut perlu ditingkatkan. Dalam kajian ini, 2% (w/v) kitosan dan 5% (w/v) PVA dicampurkan pada nisbah berat CS: PVA yang berbeza (50:50, 70:30 dan 90:10). Campuran ini kemudiannya dijadikan filem melalui teknik pembentukan larutan. Sifat mekanikal filem tersebut diukur melalui ujian kekuatan tensil yang mana, pada nisbah CS: PVA 70:30 telah memberikan keputusan kekuatan tensil yang terbaik. Oleh itu, komposisi ini telah dipilih untuk lanjutan dengan modifikasi sinaran bersama salutan Polivinil pirolidon (PVP). Filem CS/PVA dimodifikasi dengan lapisan PVP dan didedahkan kepada sianaran untuk meningkatkan kekuatan mekanikal. Filem-filem ini direndam dalam larutan PVP pada kepekatan 1%, 3% dan 5% (w/v). Kemudiannya filem tersebut didedahkan kepada sinaran gama pada dos 5,10,20 dan 30kGy. Kekuatan tensil filem CS/PVA yang disaluti dengan 1% PVP didapati meningkat sehingga 31%. Penarikan pada takat putus juga meningkat pada salutan 1% PVP. Struktur kimia filem tersebut diperoleh melalui analisis menggunakan Spektroskopi Fourier Transform infra merah (FTIR). Ia menunjukkan bahawa sinaran gama mungkin menyebabkan taut-silang antara rantaian polimer-polimer tersebut. Pencirian morfologi dijalankan menggunakan mikroskop imbasan elektron (SEM) dan mikroskop daya atom (AFM). Morfologi permukaan filem menunjukkan bahawa salutan PVP dan sinaran gama meningkatkan kekasaran permukaan filem. Keputusan yang diperoleh daripada SEM dan analisis pembelauan sinar-X (XRD) menunjukkan keserasian semua polimer yang digunakan dalam menghasilkan filem ini. Keupayaan penjerapan filem CS/PVA termodifikasi terhadap ion tembaga (Cu) dan plumbum (Pb) menunjukkan tiada perubahan yang signifikan apabila dibandingkan dengan CS/PVA yang asal. Manakala CS/PVA termodifikasi menunjukkan peningkatan terhadap jumlah penjerapan ion zink (Zn) pada salutan PVP 1%. Boleh disimpulkan bahawa modifikasi filem CS/PVA dengan sinaran gama dan salutan PVP meningkatkan kekuatan tensil filem CS/PVA dan mengekalkan keupayaan penjerapan filem terhadap ion logam berat seperti Cu, Pb dan Zn. Oleh itu, modifikasi ini adalah bersesuaian untuk digunakan dalam aplikasi rawatan sisa air terhadap penjerapan ion logam berat.

Kata kunci: Kitosan, logam berat, polivinil alkohol, polivinil pirolidon, radiasi

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LIST OF SYMBOLS AND ABBREVIATIONS

CS : Chitosan

PVA : Polyvinyl Alcohol

PVP : Polyvinyl Pyrrolidone

NaOH : Sodium hydroxide

FTIR : Fourier transform infrared spectroscopy

SEM : Scanning Electron Microscope

AFM : Atomic Force Microscope

XRD : X-ray diffraction

Cu : Copper

Pb : Lead

Zn : Zinc

Cd : Cadmium

Hg : Mercury

Ni : Nickel

kGy : kiloGray

DD : Deacetylation

CHAPTER 1: INTRODUCTION

1.1 Background of study

Rapid development in various industries may help to improve economic factor for a country, but it also can lead to environmental pollution problems. Industrial wastewater streams contain heavy metals, which are hazardous to the community. Sources of the wastewater containing heavy metals can be produced from various types of industries. It may be produced from electroplating and metal surface treatment processes, which contain heavy metals in the wastewater such as copper, chromium, zinc, lead and others. Another examples of industries that generated significant quantities of heavy metals in their wastewater stream are printed circuit board (PCB) manufacture and wood processing industries (Barakat, 2011).

Heavy metals such as copper (Cu), cadmium (Cd), zinc (Zn), lead (Pb), iron (Fe) are toxic and can be harmful to the environment and indirectly affect organism and human being because of their high solubility in the aquatic environments. Serious health problem can occur from heavy metals such as cancer, organ damage, nervous system damage, reduced growth and development and to extreme cases, death (Barakat, 2011). Therefore, it is very important to have clean water sources by removing heavy metals from the source.

There are many techniques for removing heavy metal ions from the contaminated water such as chemical precipitation, ion exchange, adsorption columns and adsorptive membranes. However, membrane adsorption shows great properties to remove heavy metals and is a powerful technique compared with other techniques (Salehi et al., 2012).

The researchers have extensively used adsorption method to remove heavy metals from the contaminated water when compared with other method, as it is simple to prepare, the rate of removal is higher, cost of production is lower and it produced less secondary pollution (A. Li et al., 2016). Various materials especially from inorganic materials have been used in the other researches to produce absorbents and applied in water treatment such as clays, (Bhattacharyya & Gupta, 2011), exfoliated graphite (Z. H. Huang et al., 2011), carbon nanotubes (Inyang et al., 2014) and zeolites (S. Wang & Peng, 2010). However, most of these materials could not commercialize due to the very expensive production cost, low adsorption capacity and poor reusability. Synthetic organic materials or polymers have been also used in the research as absorbents including polyurethane, polypropylene and polystyrene (B. Li et al., 2015), (S. Li & Wei, 2012), (Sun, Xu, & Gao, 2013). Similarly, to inorganic materials, synthetic organic materials have drawbacks such as they are non- biodegradable and non-renewable and these need to be resolved.

Since inorganic materials, synthetic organic materials/polymers have some disadvantage as absorbents; many researchers extensively used natural polymers as the materials to produce absorbents. Natural polymers such as polysaccharides are commonly used in the studies. Chitosan is one of the polysaccharides that are abundantly available, cheap and most importantly has great properties such as biocompatible, biodegradable and non-toxic.

Chitosan (Cs) is derived from deacetylation of chitin and the second most abundant natural polymer after cellulose. Chitosan composed of β-(1-4)-2-amino, 2-deoxy-D-glucopyranose (glucosamine unit) as shown in Figure 1.1. Chemical structures of chitin and chitosan are similar to cellulose. The difference between these three polysaccharides is the position of acetamido group and amine group at the C-2 position for chitin and chitosan respectively instead of hydroxyl group in cellulose (Kurita, 1998, Nawrotek et al., 2010).

Chitosan is the only polysaccharide that has the property of natural alkaline and cationic. The chemical structures of polysaccharides; chitosan, chitin and cellulose can be seen in Figure 1.1. Chitosan which consists of amine and hydroxyl groups, act as active sites to bind heavy metal. This makes chitosan a great potential as wastewater treatment material (A. Li et al., 2016).

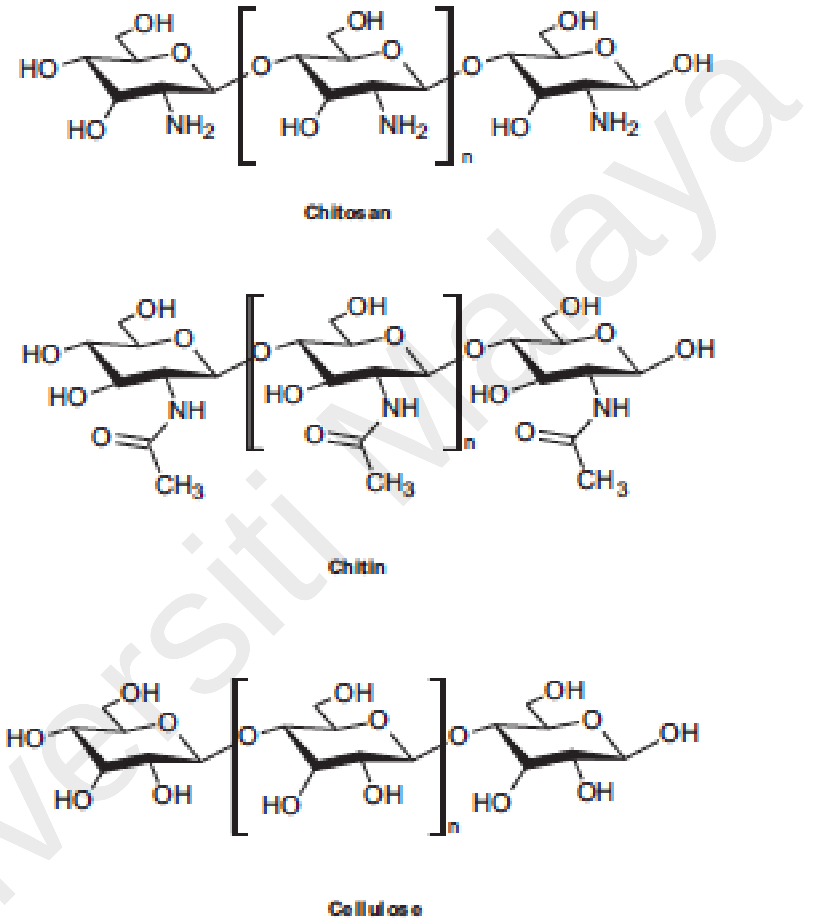


Figure 1.1: Structures of chitosan, chitin and cellulose (Shukla et. al., 2013)

Chitosan has been used to prepare composite adsorbents in many forms such as beads, flakes, powders and membranes or films. Adsorbents in beads, flakes and powder form that are usually used as dispersed adsorbents have difficulties to separate from the final product after treatment process despite of their large surface area. Film based chitosan is usually preferred compared to other forms due to no post-treatment filtration is required and stress free in the separation after process. High capacity of adsorption, fast kinetics, better reusability and easy to stack up and scale up are the other advantages of film type adsorbents which can improve the performance of filtration process (Salehi et al., 2016).

Although many advantages of film type adsorbents have been mentioned, mechanical property of the film is still a drawback that needs to be improved to produce best quality film for water treatment application. Many works/studies have been done related to chitosan-based films, which chitosan blended with other polymer to improve chitosan film properties.

1.2 Problem statement

Chitosan, which was obtained by deacetylation of chitin is available in many useful form and due to its unique chemical and biological properties, it has been a very attractive biomaterial (David, 1996). Some of the unique properties possess by chitosan are ability to form films, chelate metal ions and optical structural properties (M. N. V. R. Kumar, 2000). However, since chitosan have the strong intra- and inter-molecular hydrogen bonding, thus make chitosan partly crystalline and therefore, films made from chitosan based are too brittle and have a weak strain at break (D. Huang et al., 2012).

To overcome the mechanical strength of chitosan based films, blending with other polymer are commonly done. Biodegradable synthetic polymer such as Poly(vinyl alcohol) (PVA) has been widely used in the blending with chitosan. PVA is a water soluble synthetic polymer, which has good chemical and physical properties, film-forming capability and also is a non toxic polymer (Bahrami et al., 2002).

Although addition of synthetic polymer such as PVA can overcome the mechanical strength of chitosan-based films, however according to Dajian Huang et al., (2012) the mechanical properties of chitosan/pva composite should be further improved to meet the demand of practical applications. Currently there is a limitation of using chitosan in adsorption of heavy metal ions in large scale due to low mechanical strength (Zia, Q. et. al., 2019)

As for the use as chelate metal ions or metal ion adsorbent, excellent tensile and mechanical properties are necessary. Therefore, the modification of the chitosan/PVA film by coating with polyvinyl pyrrolidone (PVP) and expose to gamma irradiation is the aim of this study to improve the tensile and mechanical strength without interfering with the adsorption efficiency of the films.

1.3 Objectives of the study

i. To determine the mechanical strength of chitosan/PVA blend films by varying the chitosan/PVA mixture ratio and NaOH treatment.

ii. To modify chitosan/PVA film with PVP coating and gamma irradiation

iii. To observe the adsorption properties of PVP coated chitosan/PVA films on different types of metals.

CHAPTER 2: LITERATURE REVIEW

2.1 Wastewater

Definition of wastewater is water-carrying waste, which have been eliminated residences, institutions and industrial that mixed together with ground water, surface water and storm water. This water may contain inorganic chemicals, minerals and sediments, organic materials, nutrient that can help in plant growth or agents causing disease. It can also carry chemical toxicants from the waste discharged especially from the industrial site (Sonune, A. & Ghate, R., 2004).

2.2 Types of wastewater

There are many types of wastewater, and among those there are two major types. The two major types of wastewater are stated below:

2.2.1 Domestic

Domestic wastewater can be defined as wastewater that has been removed from residences, commercial institutions and related facilities (A.Sonune & R.Ghate, 2004). Domestic, which is more like related to household with several family members will eventually produce waste that generate from the toilet such as laundry waste and urine, kitchen sink, garbage disposal and also from washing machine as shown in Figure 2.1. In domestic wastewater, which contains generally very little quantities of contaminants yet, even modest quantity of contaminations can have a major effect on environment. Therefore, it is important to treat the domestic wastewater before release to the environment.

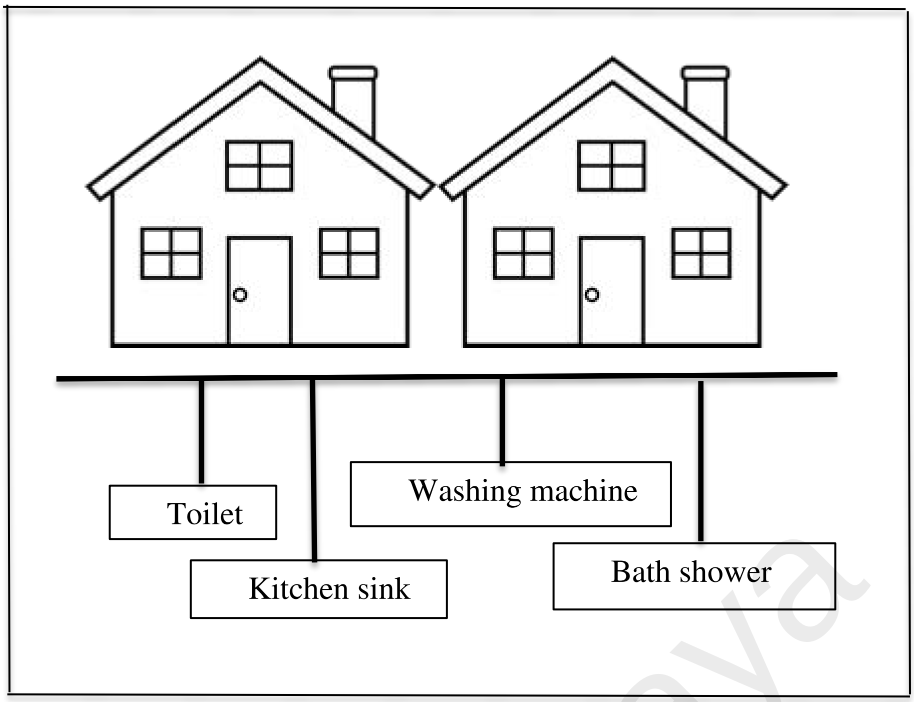


Figure 2.1: Sources of domestic wastewater

2.2.2 Industrial

In general, industrial wastewater is the unwanted water produced by the industrial production processes. The wastewater from industrial sources can be grouped into five categories; oxygen demanding materials, suspended solids, materials impart acidity or alkalinity, heat and toxic compound (Lacy, 1992). Report by UN WWAP in 2003, two millions of sewage, industrial and agricultural waste were discharged into the world's water. The waste's weight was equivalent to the entire human population of 6.8 billion people. Another report by Alam Sekitar Malaysia (ASMA) in 2007 revealed that 55% of rivers were slightly or significantly polluted by sewage, toxic chemicals from industrial, construction sites and poultry husbandries. As can be seen in Figure 2.2 the most sources of water pollution are from the industry and sewage treatment plant. Industrial waste is one of the sources of heavy metals pollution which needs more attention to be solved th as heavy metals are not easy to degrade by chemical or biological process and their toxic affects the ecosystem (Tam & Wong, 2000), (MacFarlane & Burchett, 2000).

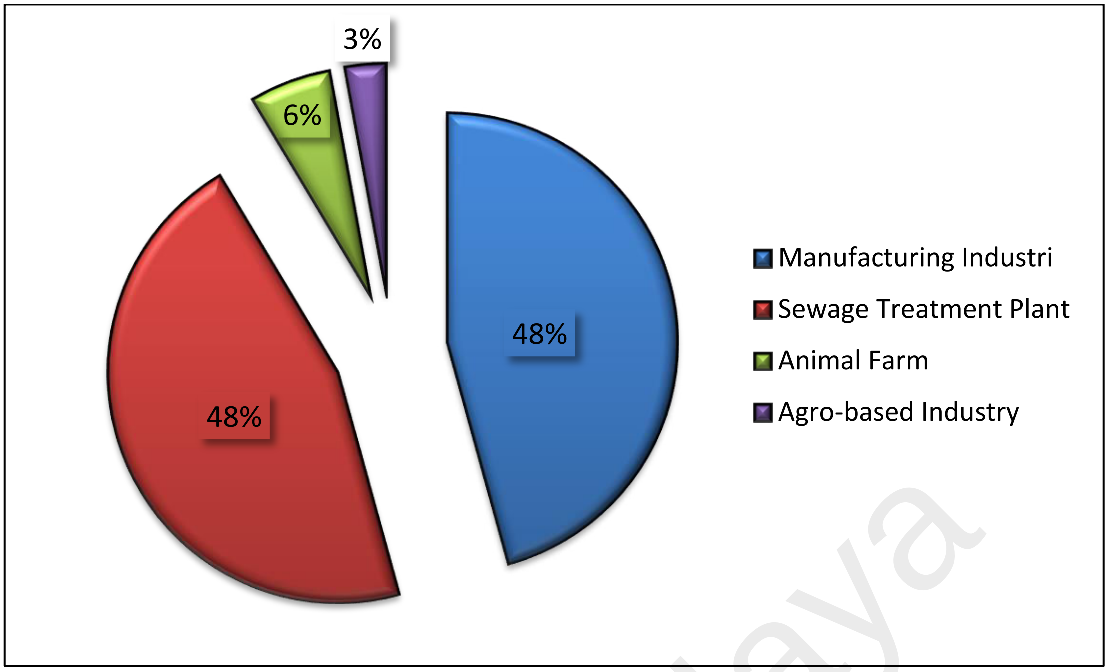


Figure 2.2: Sources of Water Pollution ((ASMA), 2007)

2.3 Heavy metals

Heavy metals such as copper, zinc, lead, cadmium, arsenic nickel and mercury are some of the examples of metals that have been discharged from the factory into the water system. Mining, batteries, welding, metal and alloys manufacturer are the most common contribution to the heavy metals pollution (Basso et. al., 2002). Figure 2.3 illustrates the sources of heavy metals pollutants. These heavy metals has been widely known as hazardous and the toxicity from the heavy metals can contribute to major health problem such as low energy levels, damage to blood composition, lungs, kidney, liver and other vital organs (Ahmaruzzaman, 2011). These health problems to human and animal can occur as metal ions can be transmitted into food chain because of leaching from waste dumps or water sources. The presence of metal ion even at low concentration can give big impact to the human health.

Other definition of heavy metal is a group of metals which most of them carrying positive charges and possesses atomic density greater than 6 gcm^{-3} (Vinodh, R., et al., 2011). Examples of defined heavy metals are cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn).

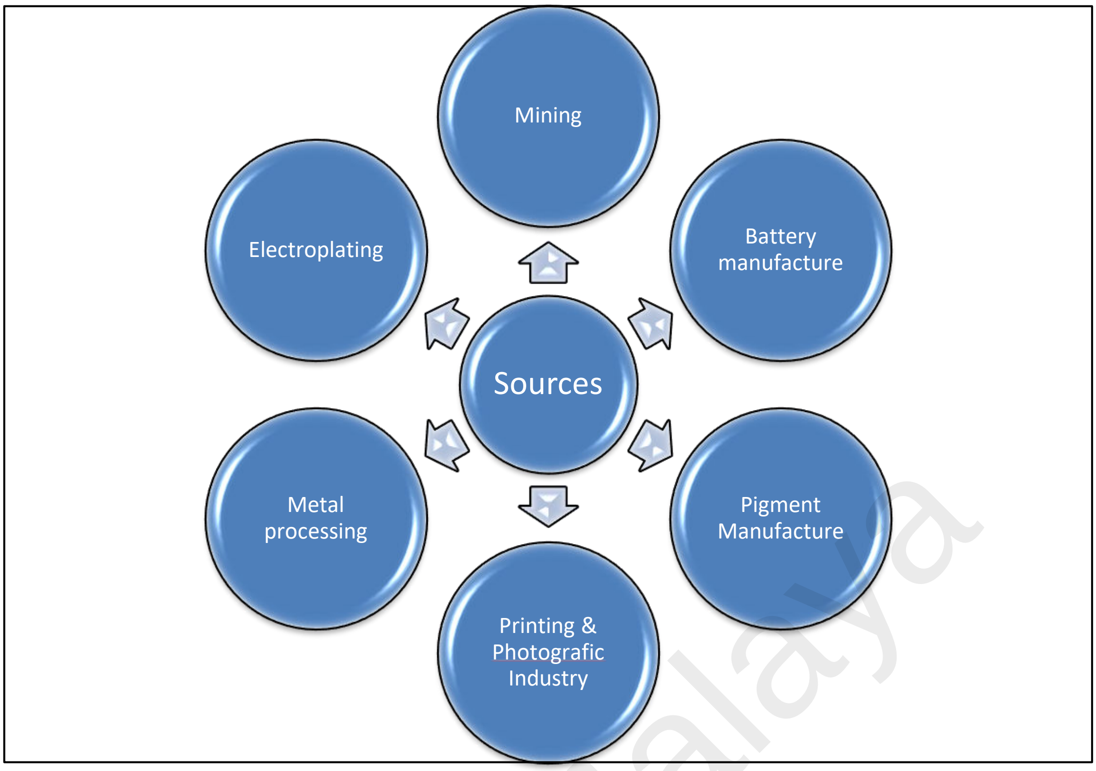


Figure 2.3: Sources of heavy metal pollutants

2.3.1 Copper (Cu)

There are several of industries that have widely using Cu (II) in their production such as printed board circuit production, fertilizer, paints and pigments as well as metal cleaning and plating baths (Aksu & Isoglu, 2005, Zhu et al., 2009). Senthilkumar et al., 2011 has mentioned that sources of copper ion leached out into the environment were from industrial waste.

Cu in low quantity or concentration however is an element that essential to human body, which is needed for the synthesis, functioning of the nervous system, energy production and forming connective tissue (Johari, 2012). However, if it taken in large doses or long term exposure, it may lead to serious health issues where liver and lung can be damaged (Alvarez-Ayuso et al., 2003). According to WHO (2004), when copper is taken even in a low dosage it can caused typical symptoms of food poisoning such as headache, nausea, vomiting and diarrhea.

2.3.2 Zinc (Zn)

Similar to copper, Zn at very low concentration is required for living microorganism where, this type of heavy metal is needed to maintain the metabolism of human body (Benavente, 2008). However, when exposed to long period of time or consume at higher concentration it will lead to health problem such as having poisoning symptoms and may cause impedance in growth development (Ahmaruzzaman, 2011) because they are not degraded and have a tendency to bio accumulate (Crini, 2005). Zinc has been widely used in dry cell batteries, to prevent rust where, zinc is coated on the surface and to produce alloys to look like brass and bronze, when is combined with other metals (Sohrabi, 2011).

2.3.3 Lead (Pb)

Lead is another common heavy metal, which is toxic and will cause various illnesses due to its; non –biodegradable properties and has the tendency to accumulate in living tissue (Shi et al., 2016). Some of the sources of wastewater carrying lead are usually from industries involved in producing or processing paint, lead-acid batteries, fertilizer, mining operations and fossil fuel (Wang et al., 2009).

Toxicity of lead can cause headache, anemia and diarrhea. Other affects caused by lead are malfunction of kidneys and teratogenic effects where it can cause problem on reproductive system. Beside that lead can affect liver, brain and nervous system as well (Liu et al., 2013).

2.4 Methods of Heavy Metal Removal

Due to extensive development in industrial sector, to improve the economic growth of the country, however may lead to environmental problem. The problem may rise due to failure of managing wastewater produced from the industries involved especially wastewater containing hazardous heavy metals. Health problem occurred from these heavy metals as briefly discussed before, is an eye opener to many researchers to proposed methods to remove heavy metals from water sources more efficiently. Some of the common methods of heavy metals removal will be discussed as each method has its own strength and limitation.

2.4.1 Chemical precipitation

This technique is a common method to remove heavy metals (dissolved) from the solutions. Chemical reaction between the soluble metal compounds and precipitation reagent will cause transformation of dissolved heavy metals into insoluble particles (Dahman, 2017). Then, to separate the particles from the solution, sedimentation or filtration processes are used. There are many process involved in this technique such as neutralization, precipitation and coagulation.

The most widely recognized precipitation technique is metal separation from solutions by formation of metal hydroxides using calcium hydroxide or sodium hydroxide as precipitant. This technique is most preferred due to the relative low expenses of hydroxide salts (Djedidi et al., 2009). Besides the low cost of hydroxide salts, sulphide precipitation is another chosen technique which performed better compared to other reagents due to its highly efficient and lower pH dependent (Tünay & Kabdasli, 1994), fast reaction rates and better settling properties (Lewis, 2010).

From both examples of chemical precipitation technique mentioned, the disadvantages may different depends on type of precipitation used. In general, the drawbacks of precipitation may leads to large amount of sludge contaminated with heavy metals and chemicals will be produced and further lead to disposal problem (Meunier et al., 2006). Performance of precipitation technique is also dependent on many factors such as type and concentration of ionic metals in the solution, precipitant used, reaction conditions and existence of other constituents which can be the constrain to the precipitation reaction (Dahman, 2017).

2.4.2 Ion exchange

Generally, definition of ion exchange is movement of ions from one liquid phase to another (Dyer, 2000). Other researcher define ion exchange as reversible chemical reaction wherein an ion (an atom or a molecule that has lost or gained an electron and thus acquired an electrical charge) from a wastewater solution is exchanged for a similarly charged ion attached to an immobile solid particle (Dahman, 2017). Dardel, F.D. and Thomas V., 2006, have been called solid particle in this technique as ion exchanger where insoluble resins involved in this process. Resins play important role in this technique as the removal of ions increased as the amount of resin increased (Al-Asheh & Aidan, 2020). There are two types of resin used in ion exchange technique, which are cationic resins and anionic resin (Kansara N. et al., 2016). Examples of anion resins; DOWEX TAN-1, Purolite 502P and 860 and Amberlite PWA 9 have been used by K. Brezinski et. al., 2018 to investigate the total organic carbon (TOC) removal in the wastewater treatment. While, example of cation resin; sulfonated polystyrene divinyl benzene has been incorporate into thermoplastic polyurethane to develop a novel heterogeneous cation exchange membrane (Ahmad, et. al., 2020) and similar trend has been achieved where, higher removal of ions obtained when resin content was increased.

Even though this process does not involve in production of large mass of sludge containing heavy metals that may lead to disposal issue, this technique also possess disadvantage. Limitation of this technique is suspended solid produced from this technique is required to be treated by another process (Islam, 2016). Examples of processes involved in the removal of suspended solid in water treatment are sedimentation process (Nemerov, 2007), gravitational settling (Jover-Smet, et. al., 2017), coagulation and foam separation using surface-active protein (Suzuki & Maruyama, 2002) and by using electrocoagulation tank (Ni'am, et. al., 2006).

2.4.3 Membrane separation

This technique is generally to separate contaminants (solute) such as suspended and inorganic contaminants, organic pollutants and heavy metals from a liquid phase (solvent; typically water) (Muralikrishna & Manickam, 2017). Immobilized liquids, dry solids and solvent swollen gels are used as membrane in this process (Seader et al., 1997). Materials used for membrane usually in solid from and can be from organic polymeric materials or inorganic materials (Matsura, 1993). There are several separation processes such as reverse osmosis (RO), ultrafiltration (UF), hyperfiltration (HF) and nanofiltration (NF). These separation processes are differ depending on their pore size (Eykamp, 1995).

2.4.3.1 Ultrafiltration (UF)

UF method uses penetrable membrane to isolate heavy metals, macromolecules and suspended solids from solution based on size. Materials commonly used for UF such as polyethersulfone (Chu et al., 2016), polysulfone, polyacrylonitrile (Adamczak et. al., 2020). Compounds will be separated by molecular weights in the range of 1000 to 100,000 Da (1 to 100nm in size) (Vigneswaran, S. et al., 2005). These remarkable specialties will retain the macromolecules which, have bigger size than the pore size of the membrane while permit water and low molecular weights solutes to pass through the membrane (Salbani et al., 2001). As for in recirculating aquaculture system, 100 kDa membrane is the most suggested membrane to be applied (Widiasa et.al., 2018). UF dual-layer hollow membrane from poly(vinylediene fluoride) and poly(ether sulfone) with molecular weights cut-offs of 33 – 292 kDa has been promising membrane for the effective treatment of municipal wastewater (Liu et al. 2014). Common applications that have been used UF as their separation technique such as safe, clean economical and potent separation technique for wide range of contaminants in water and wastewater are some of the advantages of UF (Al Aani et. al., 2020). However, fouling of the membranes gives major disadvantage of ultrafiltration technique due to the accumulation of tiny droplets of oil, microorganism on the surface and caused the blockage of membrane pores (Ahmad et. al., 2020, Richards, H.L. et. al., 2012).

2.4.3.2 Nanofiltration (NF)

Properties of NF fall between the properties of UF and RO membrane, which makes NF itself unique (Kurniawan et al., 2006). The specialties of NF membrane are due to small pore size (2-5 nm) and membrane surface charge. These properties allow charged solutes with smaller size than the membrane's pore size and lower molecular weight to pass through the membrane (Vigneswaran et al., 2005). Beside that, NF can be operated at lower pressures (Hu & Dickson, 2006). NF has been widely used such as removing pesticide as it is categorized as organic contaminants (Yang et. al., 2010), removing heavy metal ions such as chromium from acid solutions (Gomes et. al., 2010), lead (Gherasim & Mikulášek, 2014) and also separate dyes (Zeng et. al., 2016). However, according to Cheng et. al., 2014, frequently industrial applications of NF membranes are limited to aqueous solutions.

2.4.3.3 Reverse osmosis (RO)

RO is predominantly being used to isolate or separate water from feed stream carrying inorganic ions and the purity of water recovered from this method is reasonably high (Muralikrishna & Manickam, 2017). Removal of heavy metals by reverse osmosis can be done by pressure involved where, water is driven to pass through the membrane while retaining the heavy metals (Kurniawan et al., 2006). Up to

2011, it has been reported that the most polymers used for commercialized RO are polyamides and cellulose acetate (D. Li & Wang, 2010, Lee et. al., 2011). As in 2019, reported by Yang et. al., 2019, the most dominant polymers that have been used to produce RO are cellulose diacetate, cellulose triacetate, piperazine and continuously being used are polyamides and cellulose acetate. Advantages of this process are it is a simple process and both of the recovered solvent which is called permeate and concentrated solute left by the membrane which is called concentrated can be recycled in some cases (Muralikrishna & Manickam, 2017). Membrane separation by RO membrane is a promising technique for removal of perfluoroctane sulfonate from semiconductor wastewater (Tang C.Y. et. al., 2006). Major drawback of RO technique is membrane fouling (Kang & Cao, 2012). Research done by Kim & Lee, 2005, by coating RO membrane with PVA has reduced fouling significantly. Although reverse osmosis is a simple process, yet it is quite costly even for procurement and as for operating as well where the high cost is due to the used of elevated pressures (Akpor & Muchie, 2010).

2.4.4 Adsorption

Adsorption is a process where adsorbate either molecule or ion existing in gas or liquid attach to the surface of an absorbent, which usually is in solid form (Artioli, 2008). In the case of removal of heavy metal ions from wastewater, process of adsorption involves adsorbent in a solid form that attached to metal ion in liquid state by physical attractive force, ion exchange and chemical binding (Demirbas, 2008). This technique has been reported to be the simplest, easiest, easy to handle, profoundly to be effective, available for different sorbents and can be obtained at low cost (Popuri, et al., 2009). The effectiveness of adsorption process have been shown where, heavy metal ions in effluent can be removed even at low concentration which is concentration below

100 mg/L (Kamari & Ngah, 2009). According to Artioli (2008), there are two types of adsorption which are physical adsorption and chemical adsorption.

2.4.4.1 Physical adsorption

In other word, physical adsorption is known by physisorption where the attachment of the adsorbates to the surface of adsorbents is due to physical forces (Artioli, 2008). The attachment could happen due to Van Der Waals forces where these forces occurred due to frail electrostatic interaction between the molecules (Muralikrishna & Manickam, 2017).

2.4.4.2 Chemical adsorption

The definition of chemical adsorption or chemisorption is attachment of the adsorbate to the surface of the adsorbents by chemically bound (Artioli, 2008). Natural materials such as Zeolites and clays are the two materials that carry properties of chemical adsorbents naturally (Grutzeck & Marks, 1999). Besides that, activated carbon has been widely used as chemical adsorbent (Aksu, Z. & Kabasakal, E. 2004, Al-Asheh, S., Banat, F. & Masad, A., 2004). Those are the examples of materials used as chemical adsorbents. In usual case, this process can only occur when adsorptive is in contact or exact contact with the surface. By means it is a single layer process compared to physical adsorption, which can adsorb molecules in multiple layers (Webb, 2003).

In general, performance of the adsorption process is depending on the pH and temperature of the environment. As for example, removal of malachite green (dye) from aqueous solution by adsorption on oil palm trunk fibre showed that the adsorption decreased as the pH decreased. Where, the adsorption was insufficient at pH below 4 (Hameed & El-Khaiary, 2008). Other research that has been carried out showed that adsorption of copper ions from aqueous solution by rubber leaf powder can only be occurred at around pH 4-5. At this pH value, there was more exposure of adsorbent surface carrying negative charge (Ngah & Fatinathan, 2008). As for temperature affect the sorption properties, for example for lead and cadmium ion metals adsorption, the range of temperatures which favor to adsorption was at the range of 10 – 45°C with the optimum temperature at 40°C (J.Horsfall & Spiff, 2005). The most important factor in the adsorption process is the surface. Therefore, the more of surface available, the better the capability of the adsorbent to adsorb substances (Artioli, 2008).

2.5 Natural materials as adsorbent

There are various materials have been used to produce adsorbent in a form of thin film to remove heavy metals and the most widely material used as adsorbent is activated carbon due to its efficiency in trace elements removal from water (Aksu & Isoglu, 2005). However, the cost of activated carbon may be an issue as it is highly in cost and therefore, not suitable to be used in big scale industries (Kurniawan, et al., 2006a).

Alternative to high cost activated carbon, low cost materials especially derived from natural sources have been used as adsorbent. These natural sources are abundantly available, cheaper, and most importantly have the capability of heavy metal removal. Natural sources commonly used to produce thin film adsorbent are clay, coconut shell and chitosan.

2.5.1 Clay

Clay is naturally consists of colloid fraction (< 2μm) soils, sediments, rocks and water. Dimensions of the particles of clay may be varied from crystalline, amorphous, platy or fibrous (Bhattacharyya & Gupta, 2006). By adjusting the content of water, clay can show characteristic of plasticity and may also harden when the water dries up (Uddin, 2017). Clay is able to remove at about 70% of the waste in water (removal system) due to its properties such as high surface area, possess range of structural and surface properties as well as mechanical and chemical stable (Adeyemo, et al., 2015, (Bhattacharyya & Gupta, 2006).

Clay has colloidal property that makes it efficient to adsorb dyes. Nano-clays has been studied to be effectively removal for crystal violet and methylene blue from wastewater (Chen, Y-M. et al., 2011). Even un-modified clay such as Turnisian raw clay had showed efficiency for removal of anionic dye Reactive Red 120 from aqueous solutions (Errais, E. et. al., 2012).

2.5.2 Coconut shell

Coconut shell is one of agricultural waste, where India is producing 3.18 million tones annually (Gunasekaran, et al., 2012). However this kind of waste when it going through certain process it may be useful to the society as such it can be used as a filler to produce freezing resistance material and capable as adsorption when it burnt into charcoal form (Aswathy et al., 2016). Amuda, et al., 2007 also reported that coconut shells as it abundantly available and can be obtained at low cost, it has been used as adsorbent to remove heavy metal and organics from municipal and industrial wastewater. Coconut (*Cocos nucifera L.*) shell in powder form has been reported that, it is successful used as adsorbents for the removal of lead, copper, cadmium and arsenic from aqueous solutions (P.C. Okafor et al., 2012).

2.5.3 Chitosan

Chitosan, a polysaccharide where it can be derived from chitin, which can mostly be found in exoskeleton of crustaceans shells such as shrimp, crab and lobster. Chitosan is abundantly available and has been extensively used in wide scope of applications as it has great properties such as biocompatibility, biodegradability, antibacterial properties (Zetty Azalea et al., 2018) and non-toxic (Karlsen & Skaugrud, 1991). Medical, pharmaceutical, chemical, agricultural and environmental fields are some of the applications involving chitosan as their main material to produce their products (Esam Abdulkader El-Hefian et al.,2014).

On the polymeric backbone of chitosan consist of –NH_2 and –OH groups which acts as active sites and responsible for the excellent performance as natural adsorbent for metal ions (Ngah & Fatinathan, 2008). Figure 2.4 shows the chemical structure of chitosan (H. Chen et al., 2010).

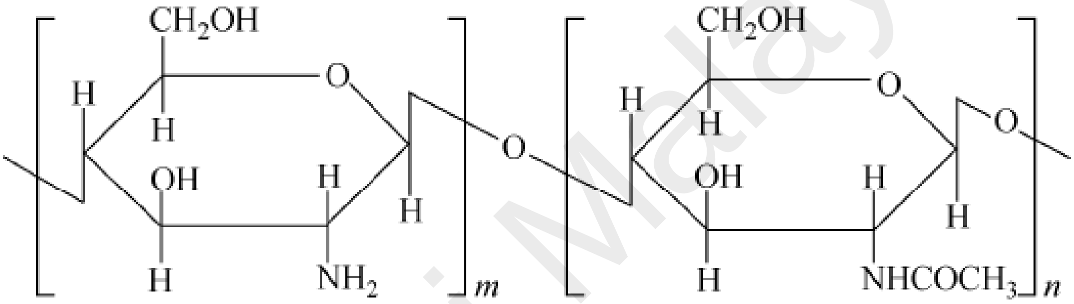


Figure 2.4: Chemical structure of chitosan (M. N. V. R. Kumar, 2000)

2.6 Properties of chitosan

Chitosan has been a popular subject of interest because of its unique properties and it is convenient to modify to meet certain criteria. Properties of chitosan can be divided into three groups; physical properties, chemical properties and biological properties. These properties are depending on the degree of deacetylation (DD) and molecular weight distribution (Rabea et al., 2003).

2.6.1 Physical properties

Degree of deacetylation will influence the molecular weight of chitosan where, at lower value of DD, the higher the molecular weight and it will deliver better mechanical strength and higher chemical stability (Nagasawa, K. et al., 1971). Chitosan is amorphous and can be dissolved at a pH below than 6 in aqueous organic acid solutions for example formic acid and acetic acid (Esam Abdulkader et al., 2014). In solubility, DD also play important main roles where DD should be at least 85% complete for the solubility to be achieved. Other factors that contribute to the solubility of the chitosan are concentration of acid to be used and distribution of acetyl groups and type, (Kubota & Eguchi, 1997).

2.6.2 Chemical properties

Existence of amino groups in chitosan, make it differ from other polysaccharides and contributes to strong positive charge. Convenience of modification of chitosan is because of cationic properties and can be modified thru many techniques such as grafting, crosslinking and blending (Zetty Azalea et al., 2018). Presence of hydrogen bonding in its molecular structure makes chitosan a rigid polymer. Therefore, it is easy to form chitosan into film with high mechanical strength (Esam Abdulkader et al., 2014).

2.6.3 Biological properties

The uniqueness of chitosan including non-toxic property makes it favorable to be used in food industry. Besides that, chitosan is also biodegradable, biocompatible, have anti-bacterial and wound healing properties that, make it useful in medical field (Chatelet et al., 2001).

2.7 Chitosan films

There are several methods to prepare chitosan film, which are thermal gelation, solidification of melt and solution casting (Cagri et al., 2003). Solution casting is one of the popular methods to prepare film because it is easy and simple method.

In general, to produce chitosan film, solution was poured and spread evenly on a petri dish and let dried. The film was then immersed in sodium hydroxide solution for neutralization to take place (Vieira & Beppu, 2005, Nogueira Campos et.al., 2005, Noriega & Subramaniam, 2011, Takara et. al., 2015). Some of the researchers neutralized chitosan film with the combination of NaOH and ethanol solution (He, et al., 2011).

2.8 Mechanical strength of chitosan film

Chitosan has a good film-forming property, which makes it a potential material for many applications such as food packaging (Suyatama, N.E. et. al., 2005), edible films and coating (Tual, C. et al., 2000), water treatment, biosensor, artificial skin and controlled drug delivery (Tiwari, A. & Singh, V., 2007, Zhang J. et. al., 2007 & Wang, S.-F. et. al., 2005). Despite the film-forming ability of chitosan, there is a limitation of using chitosan alone to form film which, it is brittle and has low mechanical property (Zhang, Z.-H. et al., 2015, Zhang, J.P. & Wang, A.Q., 2009, Suyatma, N.E. et. al., 2004, Cheung, M.K. et. al., 2002).

Therefore, to increase the mechanical property of chitosan film some cross-linking agents such as formaldehyde, glutaraldehyde and glyoxcal has to be included in the process of preparation of the film (Rokhade, A.P. et. al., 2007 & Liu, C.-G. et. al., 2005). Besides cross-link agents, chitosan also can be blended with other polymer like PVA, PVP and PEO to overcome the brittle issue (Cheung, et. al., 2002).

Mechanical strength of chitosan base film in wastewater treatment application is one of the important parameters for absorbents where, mixing of sorbents and pollutants always being carried out by using stirring reactors (Wang, F. et. al., 2014). Major secondary pollution might be happened if during the procedure, the film or adsorbents carrying toxic heavy metals break up (Wang, B. et. al., 2017). Therefore, chitosan base films need to have improved mechanical strength to meet the practical industrial wastewater treatment process.

2.9 Blend of chitosan

Blend of chitosan often involve blending chitosan with synthetic polymer to produce better performance of complex film. There are widely studies have been carried out of this combination to find out the potential for better performance of the blend effects on the physical, mechanical and biological characteristic of the film (J. Li, 2008; Lim et. al., 2014; J. Li, et. al., 2010). For example, Abdel-Mohsen, A. M., et. al., 2011, has blended chitosan with PVA for biomedical applications. While, other study has been carried out by blending chitosan with PVA for removal and recovery of Pb (II) (Fajardo et. al., 2012). Other reason of why chitosan needed to be blended with other polymer is to further improve the properties of original chitosan such as hydrophobicity, melt temperature and glass transition temperature (Rathke and Hudson, 1994).

Common synthetic polymers that have been used to blend with chitosan to form a film is PVA which can improve the flexibility of chitosan film (Bahrami et al., 2002). Some of hydrophilic synthetic polymers such as PVP and PEO could reduce the water moisture barrier of blend film (Srivanasa et al., 2003). However, by blending chitosan with polymers with hydrophobic properties such as poly (lactic acid) (PLA), poly (vinyl acetate) (PVAc) and poly (caprolactone) (PCL) can improve the moisture barrier properties, reduce the hydrophilic natura of chitosan-based films and able to reduce overall of water /matrix interaction (J. Li, 2008).

2.10 Polyvinyl alcohol (PVA)

PVA is a synthetic polymer which is biodegradable, non-toxic and has excellent properties to form film due to hydroxyl groups that are abundantly available hence, helping in the formation of intermolecular hydrogen bonding (Choo et. al., 2016). PVA is a semi-crystalline polymer, cheap and has good mechanical properties. PVA is a thermoplastic and biocompatible polymer and has been widely used to blend with various biopolymer to improve mechanical strength of the film (Zheng, H. et. al., 2001; Tripathi et al., 2009; Casimiro et. al., 2016; Choo et. al., 2016; Teodorescu, M. et. al., 2017). Schematic diagram of chemical structure of PVA is shown in Figure 2.5

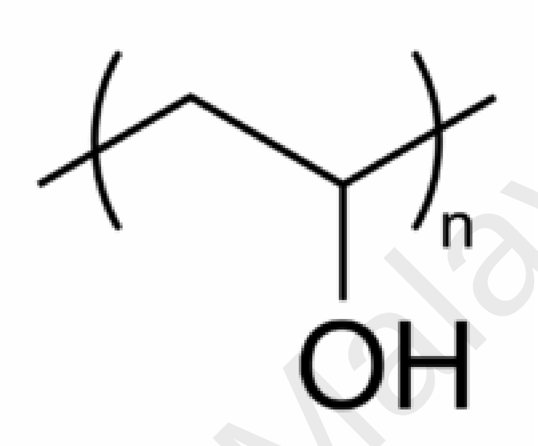


Figure 2.5: Chemical structure of PVA (Kadir, 2010)

2.11 Polyvinyl pyrrolidone (PVP)

PVP is a synthetic water soluble polymer that possesses tremendous characteristics especially in wastewater treatment. As it has the excellent capability of reversibly coordinating to various metal ions, low cytotoxicity and biocompatible (Lu et al., 2011). Several researchers have been reported that PVP hydrogel has been used as adsorbent to remove heavy metal ions form wastewater such as Pb(II), Cu(II) and Cd(II) (El-Hag Ali et al., 2003, Yildiz et al., 2010, (Tuncer Caykara & Inam, 2002). Chemical structure of PVP is shown in Figure 2.6.

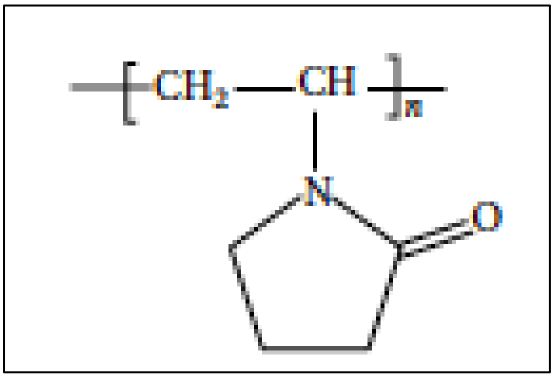


Figure 2.6: Chemical structure of PVP (Elkady et al., 2015)

2.12 Radiation

Radiation or ionizing radiation is a one a tool or processing to modify polymers. This process is effective, versatile and clean where the processing can be done in convenient temperature (commonly at room temperature), in any physical form and no initiator needed in this process (Saphwan et al., 2016).

2.12.1 Radiation sources

There are two main sources of radiation that have been used in radiation chemistry which are electron beams (EB) and gamma radiation. EB is basically generated from electron accelerators while gamma radiation from radiation sources; commonly used is Cobalt-60. Wide range of applications have been applied using these two types of radiation such as curing of coatings, crosslinking of polymeric materials (Conqueret et al., 2016). The difference between gamma and electron irradiators is shown in Table 2.1.

Table 2.1: Characteristics of gamma and EB

Characteristic	Gamma	EB
Energy	1.17 and 1.33 MeV	0.2 – 10 MeV
Dose rate	Low	High
Penetration	High	Low
Maintenance	Co-60 source need to be replaced, decay 1%/month	Electronic part to be replaced

(Darwis et al., 2015).

2.12.2 Radiation modification

Interactions between polymer materials and radiation from sources like gamma ray, EB or X-ray will produce free radicals. This process is due to the energy of irradiation has been absorbed by the backbone of the polymer materials. This reaction can occur without the presence of catalyst, initiator, monomers, crosslinkers or any other additives (Bhattacharya, 2000, Idris, 2008). Generally there are three types of reactions or modification involve in radiation processing: (1) crosslinking where network is form by the connection of polymer chains, (2) grafting, where the polymerization of new monomer and grafted to the base polymer chain and (3) chain scission or degradation, where the reducing of molecular weight of polymers due to chain scission to the polymer chain (Idris, 2008).

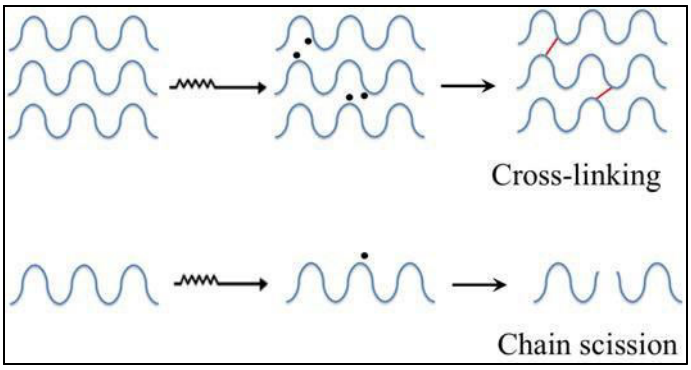


Figure 2.7: Schematic of radiation crosslinking and chain scission (Coqueret, X. et al., 2016)

During radiation process, both crosslinking and chain scission reactions can take place but only one of the reactions can be dominant for certain polymers (Gull, N. et. al, 2018). As for example, polymers possess more hydrogen atom on the side such as polyethylene will crosslink under radiation. While, polypropylene is one of the example of polymer that will undergo chain scission when expose to radiation (Makuuchi & Cheng, 2012).

2.12.2.1 Radiation effect on natural polymers

Polysaccharides such as cellulose, starch, alginate, chitin and chitosan are known as natural polymers. Polysaccharide in particular like chitosan has attracts so many attentions due to its unique properties such as the ability to adsorb materials like heavy metal ions, fats, proteins and cholesterol (Q. Li et al., 1992). However, exposure of chitosan in solid form to irradiation will lead to chain scission or degradation where molecular weight of chitosan will be reduced resulting to reducing in viscosity as well (Sabharwal et al., 2004). According to Czechowska-Biskup et al., (2005) degradation of chitosan can be occurred in any form, not only in solid form but also in suspension, paste, solutions and other physical forms. This make radiation is the simplest way to degrade polysaccharides. Several applications of modified chitosan by radiation are shown in Table 2.2.

Table 2.2: Applications of chitosan by irradiation modification

Potential Application	Product
Medical and health care	- Controlled drug release - Diet supplement - Artificial models of organs - Wound dressing
Environment	- Adsorbent
Agriculture	- Plant elicitor - Plant growth promoter

(Chmielewski, 2010)

2.12.2.2 Radiation effects of polymers in solution

Diluted polymer solutions when expose to ionizing radiation, water will absorb most of the energy released by the radiation. This will lead to intermolecular crosslink (Conqueret et al., 2016). The formation of hydroxyl radicals (•OH) by water radiolysis is the main process involved in the radiation synthesis. Polymer in aqueous solution will reacts with the hydroxyl radical to generate polymer radical, which then link with each other. This is the mechanism of polymer crosslinking (Janusz M. Rosiak, 1991). Nevertheless, crosslinking not always happened by the radicals generate by radiation. This is may happen when some radicals were gone by oxidation, or could not find counter-radical nearby. Another reason is when the combination between polymer chains could not be happened due to lack mobility of the polymer chains (Makuuchi & Cheng, 2012). This is the reason why crosslinking and chain scission always co-exist under radiation and cause competing process.

Polysaccharides might as well be able to go through crosslinking reactions over chain scission, when irradiated under certain conditions such as dose rate and concentration of the polysaccharides itself (Wach et al., 2001). Table 2.3 shows few characteristics to compare between radiation processing and conventional methods. Chemical crosslinking, silane crosslinking and peroxide crosslinking are some of the example off conventional method of crosslinking (Manas, D. et. al., 2018).

Table 2.3: Comparison between radiation processing and conventional methods.

Characteristic	**Radiation Processing**	**Chemicals**
Temperature	Occurs at room temperature	Up to 200 °C used
Chemical residues	No chemical additives / catalyst required	Chemicals additives needed for crosslink to take place
Handling	Easy – controlled and organized from the beginning until end of production	Difficult – can lead to human error
Reaction	Can be controlled by the dose rate	Limited – depends on concentration & purity of initiators
Sterilization	Can be done together with the modification	Separation sterilization needed after end of production

(Chmielewski et al., 2005, Bhattacharya, 2000).

2.13 Summary

There are two major types of wastewater: domestic and industrial. Industrial wastewater is one of the sources the carry heavy metals. This type of pollutions that mainly derived from industry need to be paid more attention as heavy metals are toxic and harmful to the ecosystem. Examples of heavy metals that have been discharged from the factory are copper, zinc, lead, cadmium and mercury. These heavy metals are hazardous and can cause major health problem such as damage to blood composition, lungs, kidney and other vital organs.

Several methods have been developed to remove heavy metals from water sources like chemical precipitation, ion exchange and membrane separation. Adsorption process is on of membrane separation techniques has been widely used and effective to remove heavy metal ions. Activated carbon has been widely used to produce adsorbent however, due to its high cost natural sources have been used as alternative to activated carbon. Some of natural sources that have been used are clay, coconut shell and chitosan as they are abundantly available, cheap and most importantly have the capability of heavy metal ions removal.

Chitosan is the most promising material to be used as adsorbent due to its property to adsorb metal ions. As adsorbent, chitosan will be prepared into film form. However, it has a limitation of brittleness. Chitosan has been blended with some other synthetic polymer such as PVA and PEO but the mechanical strength of the film need to be improved to meet the demand of practical application.

Therefore, CS/PVA film need to be modified. PVP also has the capability to remove heavy metals and radiation processing is another tool to modify polymers. Radiation is safe and green processing where it does not involve chemical to crosslink the polymer so that it will not produce chemical waste in order to produce membrane, which can help to solve pollutions issue.

In chapter 3, the methodology to produce CS/PVA film and its modification is described. The properties of un-modify and modify CS/PVA by several technique such as mechanical test, gel content, swelling and adsorption properties are also explained.

CHAPTER 3: MATERIALS AND METHOD

3.1 Flow Chart of the Experimental

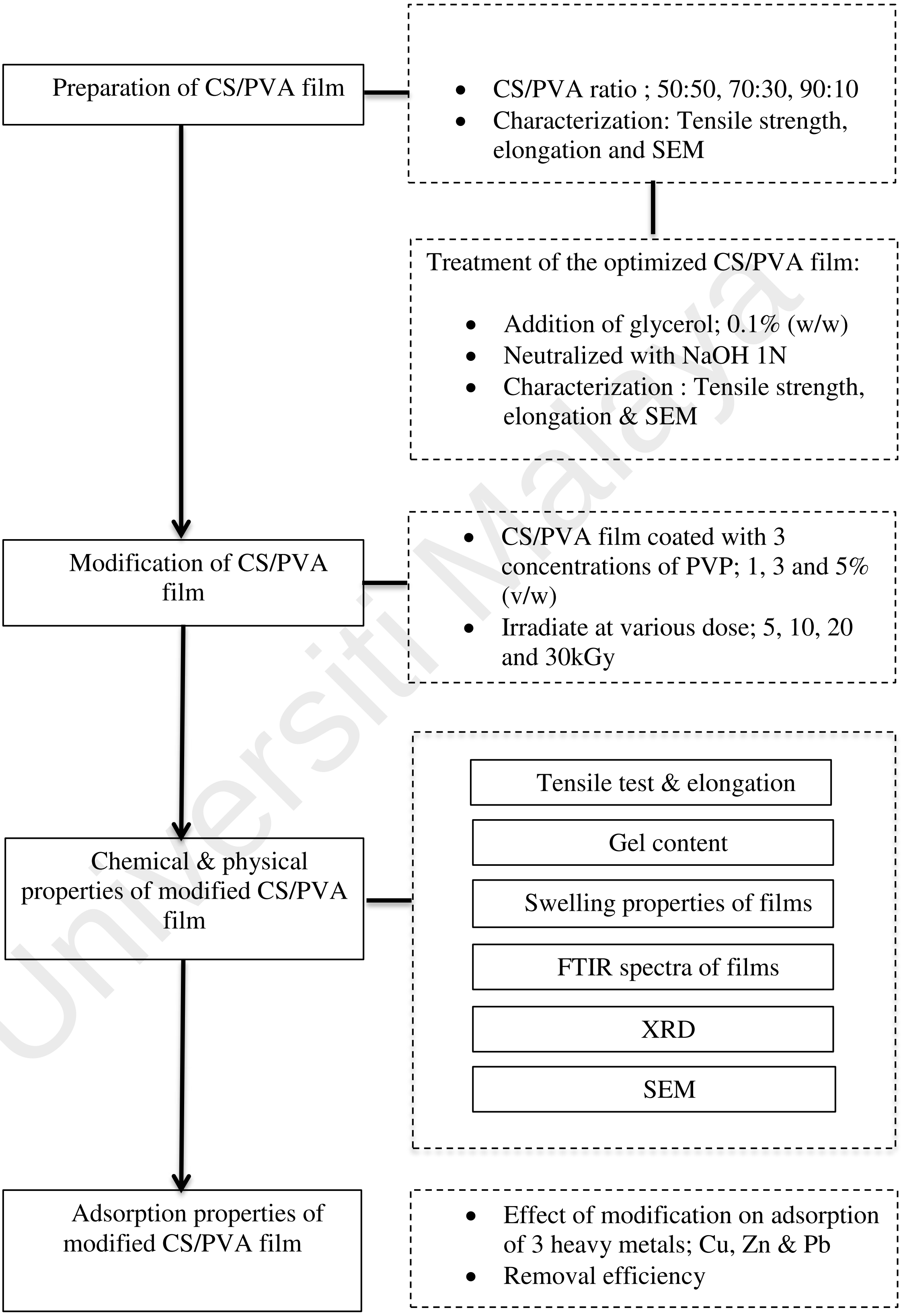


Figure 3.1: Flow chart of the experimental

3.2 Materials

Chitosan (CS), medium molecular weight (190,000 – 310,000 Da) and deacetylation percentage (DD) of 75 – 85 % was purchased from Sigma Aldrich, Iceland. This chitosan was acid soluble, brownish in colour and in powder form. PVA 96% hydrolyzed with approximation of molecular weight 146,000 – 186,000 Da and PVP with molecular weight of 58,000 Da were purchased from Acros Organics, U.S.A. Glacial acetic acid from HmbG Chemicals was used as the solvent to dissolve chitosan. Sodium hydroxide, analytical grade was purchased from Fisher Scientific, UK was used to neutralize chitosan/PVA film. Analytical reagent grade of glycerol was purchased from Fisher Chemical. Copper (Cu), Zinc (Zn) and Lead (Pb) standard solutions were used as sources of heavy metals, supplied by Scharlau, Spain. Nitric acid for analysis 95% and Ammonia solution 35% analytical grade were used to adjust the pH of heavy metal solutions were purchased from MERCK, Germany and Fisher Scientific, UK, respectively. Ultra-pure water (Heal Force ultra pure water system) with a resistivity greater than 18MΩ/cm was used to prepare all solutions. All chemicals were used without further purification and freshly prepared solutions were used in all experiments.

3.3 Film preparation

3.3.1 Preparation of CS/PVA film

Chitosan and PVA solutions were mixed at different chitosan: PVA weight ratios (50:50, 70:30 and 90:10). Chitosan has the heavy metal ions adsorption property, therefore chitosan/PVA mix ratio starts from 50:50 for having higher chitosan content (Mucha et al., 2005). Chitosan solution was prepared by dissolving 2% chitosan powder in 1% acetic acid solution. The chosen concentration of chitosan because it was the highest concentration could be obtained due to its high molecular weight. The chitosan solution was then filtered to remove dust and other impurities before mixing with PVA solution as shown in Figure 3.2. PVA solution was prepared by dissolving the PVA powder 12.5 gram in 250 ml ultra-pure water. Films were obtained by casting method, which 7 ml of the CS/PVA mixed solutions were poured onto polystyrene petri dishes followed by drying at room temperature for 48 h as shown in Figure 3.3 (Wan et al., 2003). Some of the mixture was added with 0.1% (w/w) of glycerol before poured onto the petri dish (Kanatt et al., 2012). Dried films were then soaked in 1N of NaOH for 1 h. This step was for neutralization (Vieira & Beppu, 2005). Then, washed four times with 250 ml of RO water to remove the excess of NaOH (Vojdani & Torres, 1989). The films were let dry at room temperature for 24h. Dried films were kept under evacuated desiccator over fresh silica gel until use. All films obtained were transparent, uniform and free of air bubbles.

Figure 3.2: Chitosan solution was filtered to remove dust and impurities

Figure 3.3: CS/PVA polymer blend were casted in the petri dish

3.3.2 Preparation of modified CS/PVA films with PVP coating and gamma irradiation

Chitosan/PVA films were then soaked in different concentration of PVP solutions (1, 3 and 5%) for 15 – 20 minutes. The films were then immediately kept in the plastic bag and sent to gamma facility (Sinagamma) for irradiation process to take place. Gamma dose were varied from 5 – 30kGy. When the irradiation process was completed, the films were dried again at room temperature for 24h. Dried films were kept under evacuated desiccator over fresh silica gel until use. All films obtained were transparent, uniform and free of air bubbles.

3.4 Characterization

3.4.1 Characterization of CS/PVA film

CS/PVA films were analyzed by using Universal Testing Machine for mechanical strength study and Scanning electron microscope (SEM) for morphology of the film.

3.4.1.1 Mechanical strength of CS/PVA Films

Mechanical strength of films was evaluated by tensile strength and elongation at break. This was performed using Shimadzu AG-X plus Universal Testing Machine. The test were carried out according to ASTM Standard Method D 882 (ASTM, 2012). Testing specimens were cut into strips with 40 mm length and 10 mm width (Figure 3.4). Gauge length and crosshead speed was 20 mm and 5 mm/min, respectively. A minimum of five specimens was tested for each sample and average were calculated. Tensile strength results were used to choose the optimum blending and modification condition.

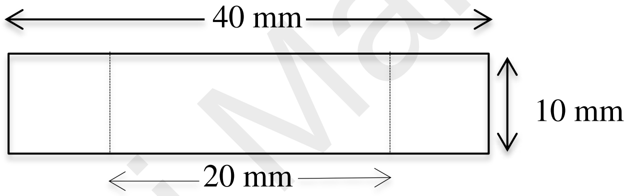


Figure 3.4 : A schematic diagram of a specimen for tensile test

3.4.1.2 Morphology of CS/PVA film

Scanning electron microscope (SEM) (Model FEI Quanta 400, USA) was used to perform morphology analysis in this study. To explore cross section of the film, specimens were fractured and mounted on stubs and coated with a thin layer of gold using a sputter-coater and allowed dry before the analysis.

3.4.2 Characterization of modified CS/PVA film

3.4.2.1 Mechanical Strength of modified CS/PVA Films

Mechanical testing plays an important role in characterize the films as the main objective of the study is to improve mechanical strength of the modified CS/PVA film. This was performed using Shimadzu AG-X plus Universal Testing Machine. The test were carried out according to ASTM Standard Method D 882 (ASTM, 2012). Testing specimens were cut into strips with 40 mm length and 10 mm width (Figure 3.4). Gauge length and crosshead speed was 20 mm and 5 mm/min, respectively. A minimum of five specimens was tested for each sample and average were calculated. Tensile strength results were used to choose the optimum modification condition.

3.4.2.2 FTIR Analysis of modified CS/PVA films

The FTIR measurements of blended film and modified film were performed using Bruker TENSOR FTIR. The spectra were obtained at a frequency range of 3600 cm^{-1} to 500 cm^{-1} with a resolution of 4 cm^{-1} and 16 times scanning. FTIR was performed to examine the chemical structures of the film before and after modification.

3.4.2.3 Determination of gel content of modified CS/PVA films

Gel content is a technique to determine the formation of radiation induced cross linking to the film. Films were cut into small pieces and placed in the tea bag as shown in Figure 3.7. The tea bags were then soaked in distilled water and autoclave for 15 minutes at 121°C. The samples were then dried in oven at 60°C until reached constant weight (Idris, 2008). The estimation of gel content was measured by the insoluble part after immersion in water. A minimum of five specimens was tested for each sample and average were calculated. Gel content was calculated using equation:

$$\% \, Gel\ content = \frac{W_2}{W_1} \times 100 \qquad \text{-------------} \qquad (3.1)$$

where W_1 is the initial weight of film and W_2 is the weight of insoluble part after immersion.

Figure 3.5: Samples in the tea bags after immersion in the water

3.4.2.4 Degree of swelling

Swelling performance of modified and un-modified chitosan/PVA film was done by immersing known weight of the film in distilled water at room temperature for 24 h. Excessive water remain on the film was removed by dapping with tissue paper and immediately weighed (Chowdhury et al., 2015). A minimum of five specimens was tested for each sample and average were calculated. Swelling degree of films were calculated by following equation.

$$Swelling\ (\%) = (\frac{W_S - W_D}{W_D}) \times\ 100 \qquad \text{-------------} \qquad (3.2)$$

where W_S and W_D represent the weight of swollen and dried film, respectively.

3.4.2.5 X-ray Diffraction (XRD)

Modified and un-modified CS/PVA film X- ray diffraction patterns were recorded using PANAlytical Model PW 3040/60 X'Pert Pro. The samples were scanned at 2θ angles between 5° and 60°. Since CS films were modified with PVP radiation, XRD was done to identify whether the crystalline or amorphous of the materials had changed after the irradiation.

3.4.2.6 Morphology Analysis

Atomic Force Microscope (AFM) with Nano Wizard II from JPK Instruments was used to perform surface roughness analysis of modified CS/PVA film. Specimens were cut into small size and located on glass slide and AFM measurement was done using the contact mode cantilever.

3.4.3 Adsorption Study of Modified CS/PVA films

Copper, zinc and lead standard solutions were used in this study as a batch mode. A minimum of three specimens was tested for each sample and average were calculated. This experiment was carried out by soaking 0.1 g of film in 50 ml of the specified metal ion solution with its initial concentration of 20 mg/L for 24 h at room temperature. This study was carried out at room temperature and was shook at 120 rpm. pH value of the copper, zinc and lead solution was adjusted to 5.5, 5.0 and 5.0 respectively by adding 1% of ammonium hydroxide or 1% of HCl. All tests were done in the room temperature (25°C). pH meter (Sartorius, PB-10) was used to determine pH value of the solution. Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer 800 Analyst) was employed for determination of copper ions. The amount of copper adsorbed onto the film was calculated by the following equation

$$q = \frac{(C_0 - C_t) \times V}{m} \qquad \text{-------------} \quad (3.3)$$

Where, C_0 and C_t are initial copper concentrations and at t time in (mg/L), V was the volume of adsorbate (L) and m was the weight of the film (g) (Liu et al., 2009).

Removal efficiency (RE) of metal ion in percentage was calculated by the following equation (Lee et al., 2015).

$$RE\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{--------------} \quad (3.4)$$

Where, C_0 and C_e represent the initial metal ion concentration and concentration at equilibrium respectively.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Mechanical strengthening of CS/PVA blend film

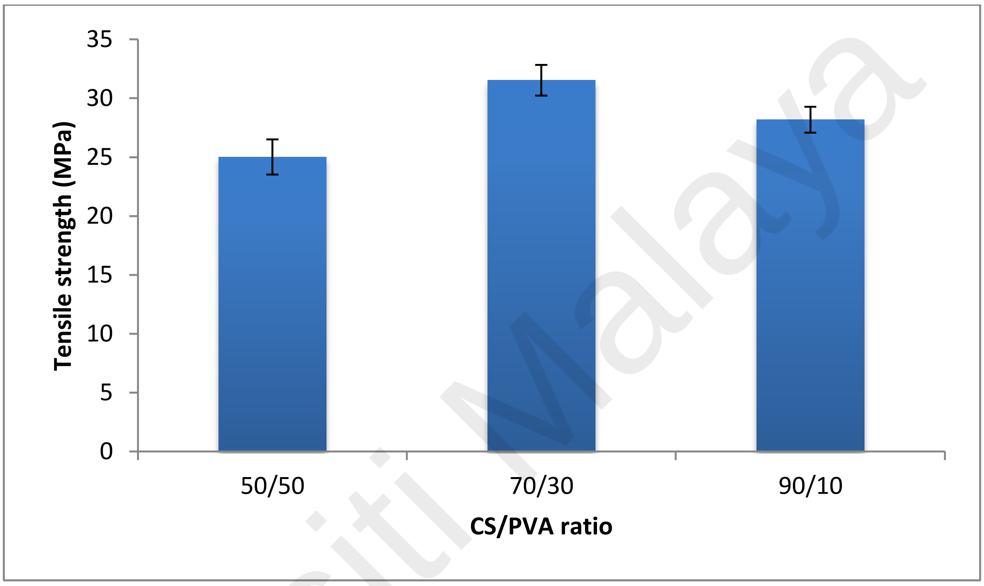
The main objective of this study was to increase the mechanical strength of the chitosan/PVA. It is known that chitosan has superior adsorption property for heavy metal ions. However, the mechanical properties of chitosan film are still low to make it a commercial product. Optimizing the chitosan/PVA ratios, followed by NaOH treatment and addition of plasticizer, was the first done in this study. The tensile strength and elongation at break of the film were considered for this purpose.

4.1.1 Effect of polymer ratios on the mechanical strength of CS/PVA film

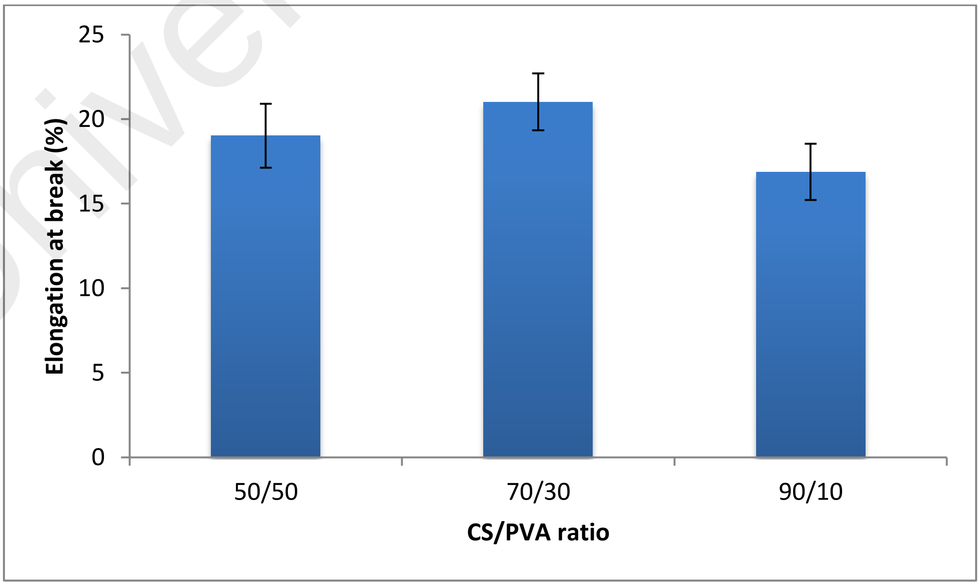
Figure 4.1(a) and (b) shows the effect of different chitosan/PVA ratios on the tensile strength and elongation at break respectively. The highest value for tensile strength obtained was 65.14 MPa from (CS70: PVA30), this was a 57% increase compared to chitosan film as shown in Table 4.1. This result is similar to what was reported by Hyder & Chen (2009) and Park et al. (2011). The increase in tensile strength is attributable to the formation of physical bonds between the two polymers on their inter-polymeric networks, which in turn enhances the mechanical quality of the film (Bonilla et al. 2014). The observation on formation of physical bonds were also reported by Bahrami et al. (2002), where they noted that –OH functional group in the PVA interacted physically with $-NH_2$ functional group from the chitosan, which contributed to the enhancement of tensile strength of the blended film.

Table 4.1: Mechanical Properties of CS only and CS/PVA at different ratio

Samples	Tensile Strength (MPa)	Elongation at break (%)
CS100 (CS only)	20.08	16.28
CS50 : PVA50	25.01	19.02
CS70 : PVA30	31.53	21.02
CS90 : PVA10	28.18	16.86



(a)



(b)

Figure 4.1: The effect of different chitosan and PVA ratio on (a) tensile strength and (b) elongation at break

Figure 4.1 (b) shows the elongation at break of CS/PVA blend film at different ratio of the polymers. Basically, as the amount of PVA was increased in the blend, the flexibility of the film was also increased. The 70:30 provided the highest value of elongation at break at 21.02%. Similar observations were reported in other studies, namely Hyder & Chen, 2009, Esam at al. and Bahrami 2003. In this study, the 70/30 ratio provided the highest tensile strength and elongation at break for the film, therefore, the ratio was used throughout the study.

4.1.2 The effect of addition of plasticizer and NaOH neutralized on the mechanical strength of CS/PVA film

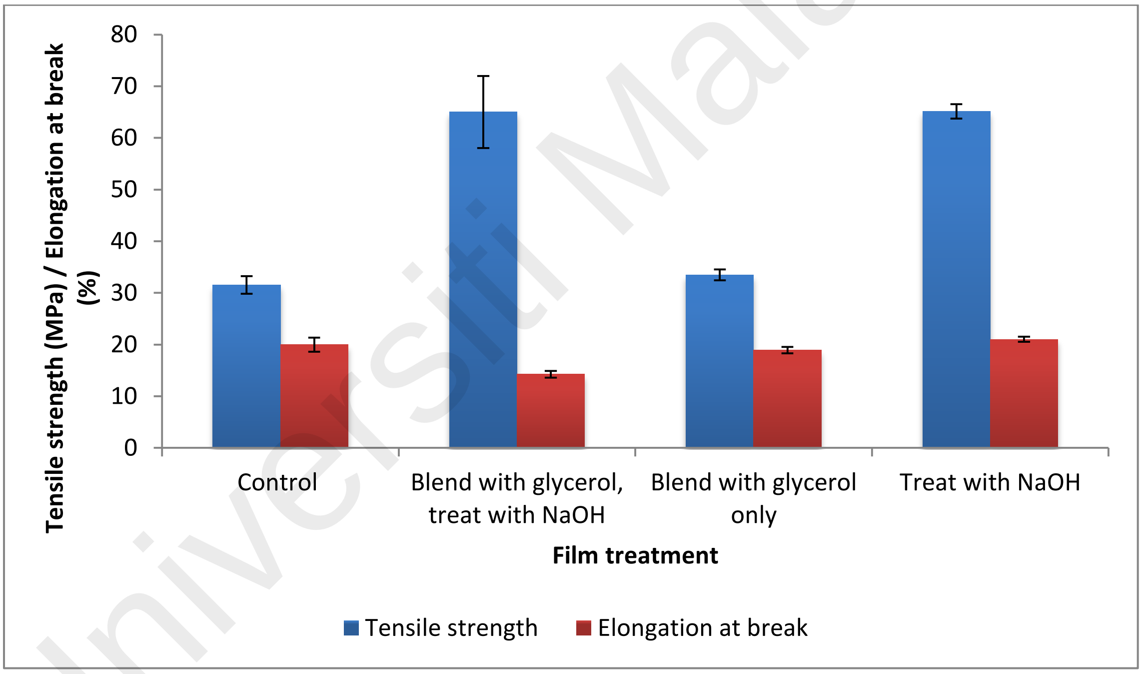
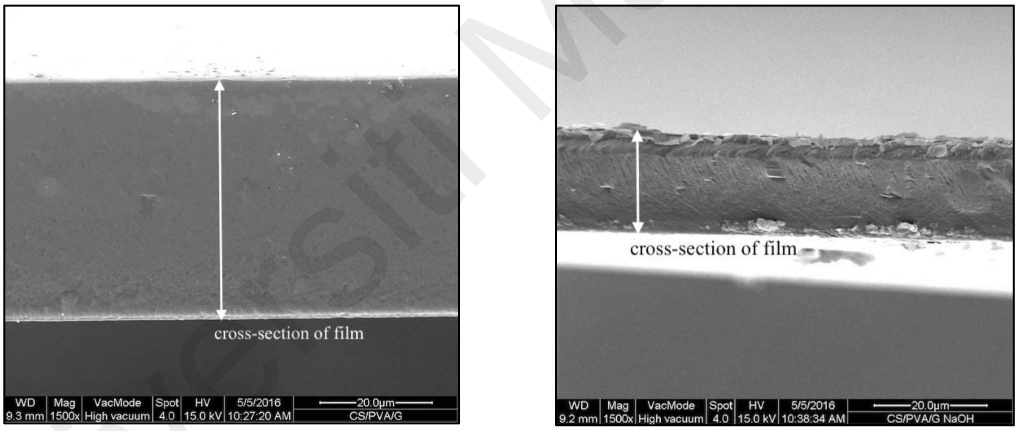


Figure 4.2 : Tensile strength and elongation at break of film with addition of plasticizer and NaOH neutralization at composition CS:PVA (70:30)

Tensile strength and elongation at break of the films with glycerol, neutralized with NaOH as well as control sample (without glycerol and NaOH) are shown in figure 4.2. CS/PVA film treated with NaOH showed highest value of tensile strength, this was twice of CS/PVA film's (control) tensile strength. This can be explained by the presence of acetic acid in the molecules causing a reduction in the tensile strength of the film as the remaining acid acted as a plasticizer (Campos et. al, 2005). In this study, the neutralization step during the preparation of the film not only removes the acid residue, but also generates NH_2 groups on the chitosan (Noriega & Subramanian, 2011).

Addition of glycerol did not yield any significant difference in the tensile strength as compared to the control sample. This may be due to the presence of glycerol, which act as a plasticizer that does not contribute in increasing the tensile strength. Elongation at breaks for all samples shown no significance difference, however the highest value was obtained through the neutralization step with NaOH only. Therefore, the step neutralization with NaOH in preparing CS/PVA films was used throughout the study.

4.1.3 Effect of neutralization with NaOH on the morphology of the film



(a) (b)

Figure 4.3: SEM image of cross-section film: (a) CS/PVA film, (b) CS/PVA film neutralized

Figure 4.3 shows the morphology of the cross section of control film, (a) and film neutralized with NaOH, (b). In figure 4.3(a), the film, which was not treated with NaOH (control) shows dense and compact, solid as well as uniform structure. It was a normal view for a standard film without any treatment applied. Changes can be seen on the morphology of the cross section of the film that was neutralize, in this case showing laminar formats. The SEM image shows changes in the microstructure that may improve in the overall mechanical properties as compared to the films that were not neutralized with NaOH (Nogueira Campos et al., 2005), (Llanos et al., 2015). According to Takara et al. (2015), the technique involved throughout the processing of the film is critically affected by its morphology. The irregular, dense and compact structure may be due to initial quick evaporation, and later the sublayers experienced slower rate of evaporation when the top layer became solidify.

4.2 Characterization of modified CS/PVA film by coating

Modified and un-modified CS/PVA films with PVP coating were analyzed by tensile test, FTIR, AFM and XRD.

4.2.1 Mechanical strength of modified CS/PVA film

Figure 4.4 shows the tensile strength of un-modified and modified CS/PVA film.

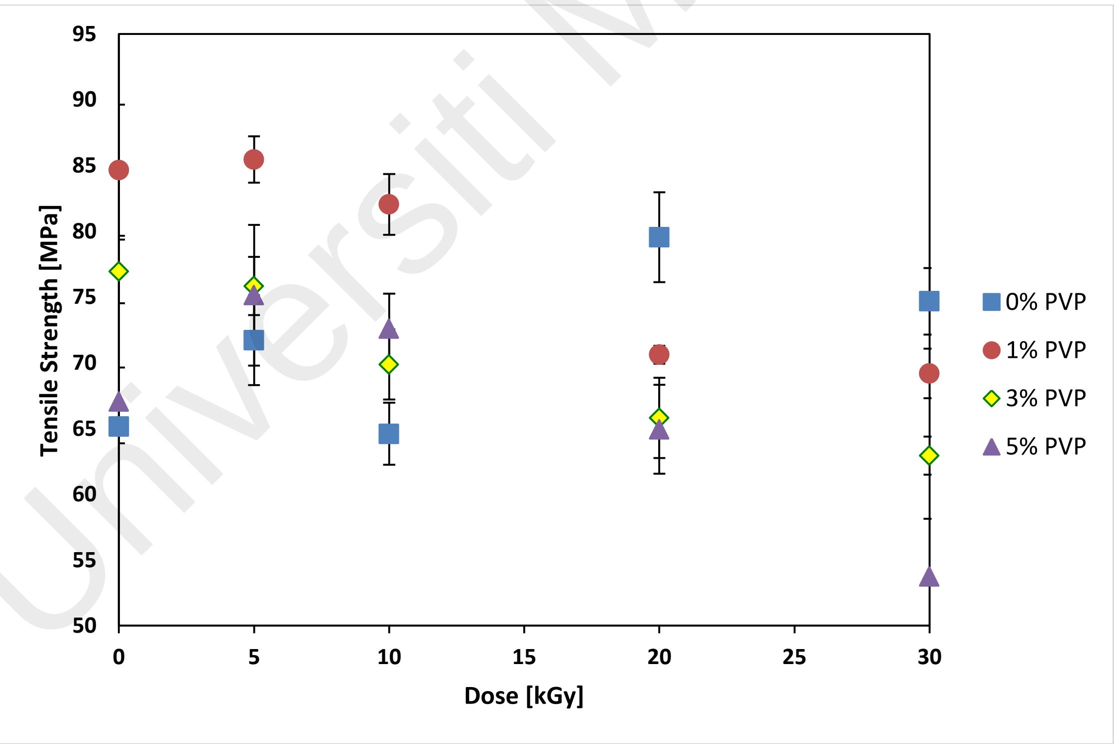


Figure 4.4 : The effect of PVP coatings concentrations on tensile strength of CS/PVA films as a function of dose

PVP coatings of up to 5% had no significant impact on the final thickness of the films where, un-modified CS/PVA film at 0.015 mm while coated with 5% at 0.018 mm. Figure 4.4 shows the tensile strength of bare CS/PVA films and its PVP coated form, irradiated with gamma irradiation at 5, 10, 20 and 30 kGy. Generally, for non-radiated samples, addition of PVP enhances the CS/PVA film tensile strength; this is expected as coating of PVP provides physical support on CS/PVA films (Kumar, R. et. al., 2019). This may due to the interaction of carbonyl groups in the pyrrolidone ring of PVP, with amino and hydroxyl groups of chitosan through the forming of hydrogen bonds (Li, J. et. al., 2010, Sizílio, R.H. et. al., 2018). Bare CS/PVA films generally improved upon irradiation. This however, is still lower than the tensile strength provided by 1% PVP coated samples especially below 10 kGy irradiation. A coating of 1% PVP at 5 kGy, showed higher tensile strength as much as 31% compared to the bare CS/PVA film. This can be attributed to PVP-PVP chain crosslinkings as discussed in FTIR study that provide support on the coated CS/PVA films. However, a slight decrease can be observed at 10 kGy, where the tensile strength was only 26% higher compared to the bare CS/PVA film, this improvement, albeit lower than that of 5 kGy, was caused by the competing nature between crosslinking and degradation when polymers are subjected to ionizing radiation (J.M. Rosiak, 1998). At this irradiation dose, the chains degradation effect is more predominant than that of crosslinking compared to the one at 5 kGy. Kiran, E. and Rodriguez, F., 1973 had achieved the similar pattern. The same trend was observed for CS/PVA films coated with 3% and 5% respectively at greater degradation rates. It can be seen that, the stronger decline in the tensile strength occurred at higher PVP concentration coatings. At higher solution concentration regime, the required dose to form gel phase is proportionate to the concentration of polymer (J.M. Rosiak & Ulanski, 1999), therefore, higher dose is required to produce enough radicals for polymers at higher concentration to produce gel compared to a more dilute system. In this case, from a covalent crosslinkings point of view, lower numbers of crosslinking networks are formed on CS/PVA film coated at higher concentration of PVP at the same irradiation dose. The lower amount of crosslinkages means lower strengthening effect from PVP, hence the lower tensile strength values.

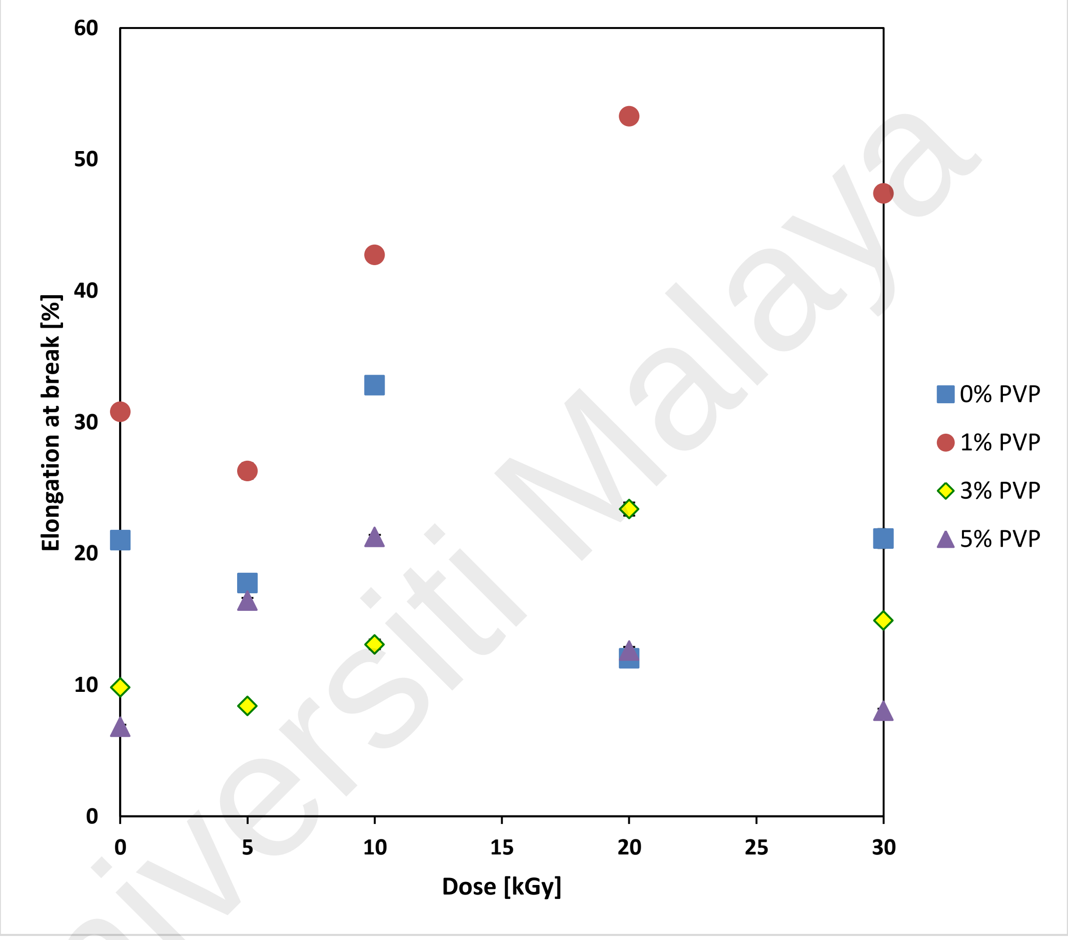


Figure 4.5 : The effect of PVP coated concentration and irradiation dose on elongation at break of CS/PVA film

Figure 4.5 shows the elongation at break data for bare CS/PVA films and its PVP coated form at different concentration, irradiated with gamma irradiation at 5, 10, 20 and 30 kGy. Unlike its improvement in tensile strength when subjected to gamma radiation, at around 20% elongation, bare CS/PVA film has lacks elasticity throughout the dose range. This is expected due to the partial crystallinity of CS. A coating of 1% PVP improves the elongation at break to 53% up to 20 kGy of irradiation dose. This suggests that PVP-PVP crosslinkings provide a useful flexible support to CS/PVA films. PVP coatings at higher concentration however, do not provide such support. This agrees with the higher gelation dose for higher samples concentration from tensile strength studies. A plateau as seen in uncoated CS/PVA films suggests that dose increase will not improve the elongation at break for samples with higher concentration PVP coatings. At this point, it was decided that 1% was the best PVP coating concentration. It gives the best tensile strength and elongation at break, thus further characterization and testing were directed on this particular concentration.

4.2.2 Infrared spectroscopy

FTIR measurements were done and illustrated in Figure 4.6 and 4.7 where spectrum of chitosan film will be discussed followed by spectra of modified and un-modified chitosan film.

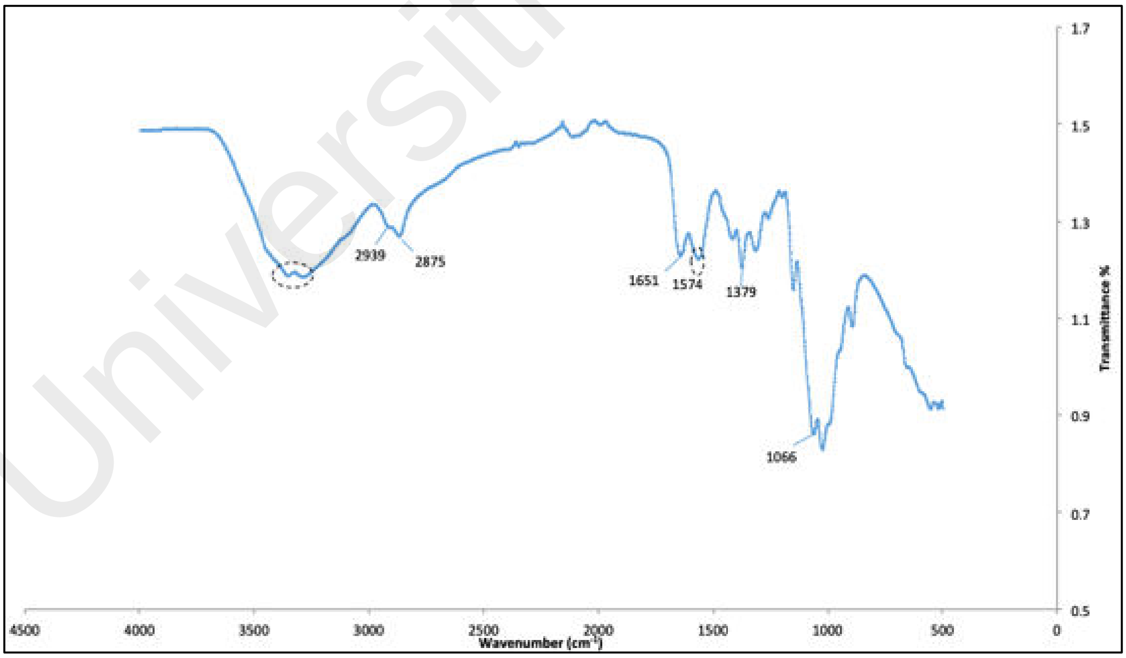


Figure 4.6: FTIR spectra of chitosan

Figure 4.6 shows FTIR spectra of CS. FTIR measurement for chitosan is also done to compare and confirm the absence of chitosan in the CS/PVA film later. The major peaks showed in the spectrum for chitosan will be explained further. Peak visible at 1574 cm^{-1} is attributed to the deformation and bending of $-NH_2$ and broad peak at the range of 3750 – 3000 is due to stretching vibrations of OH group. Peaks at 2939 and 2875 are related to C-H bond in $-CH_2$ and $-CH_3$ respectively. Spectra of 1379 and is attribute to methylene group from the bending vibrations and vibration of CO is shown at the peak of 1066 (Paluszkiewicz et al., 2011).

Figure 4.7 shows the FTIR spectra of (a) CS/PVA film, (b) PVP, 1% PVP coated CS/PVA and irradiated at (c) 0 kGy, (d) 5 kGy and (e) 30 kGy. The broad band of FTIR spectras for all CS/PVA films at around 3450 - 3200 cm^{-1} are attributable to hydroxyl –OH stretching vibration as well as –NH stretching vibration (Ghobadi et. al., 2017). Introduction of PVA into chitosan is made evident by a peak at 1446 cm^{-1} which was caused by –CH-OH bending vibration of PVA (Zhuang et. al., 2012). The shifts of absorption peaks to 3357 and 3283 cm^{-1} indicate introduction of –OH group from PVA. Increment in peak intensity at 1650 cm^{-1} indicates the interaction between amine are from CS and –C-OH from PVA. A reduction in peak intensity at 1576 cm^{-1} indicates a reduction in $-NH_2$ group. Figure 4.6(b) shows PVP spectra, strong band at 1645 cm^{-1}, 1421 cm^{-1}, 1281 cm^{-1} and weak band at 2917 cm^{-1} are attributed to C=O stretching, C-N stretching, O-H bending and C-H stretching vibrations, respectively (Kaplan Can, 2005), (Singh & Pal, 2011) and (C. Yang et al., 2010).

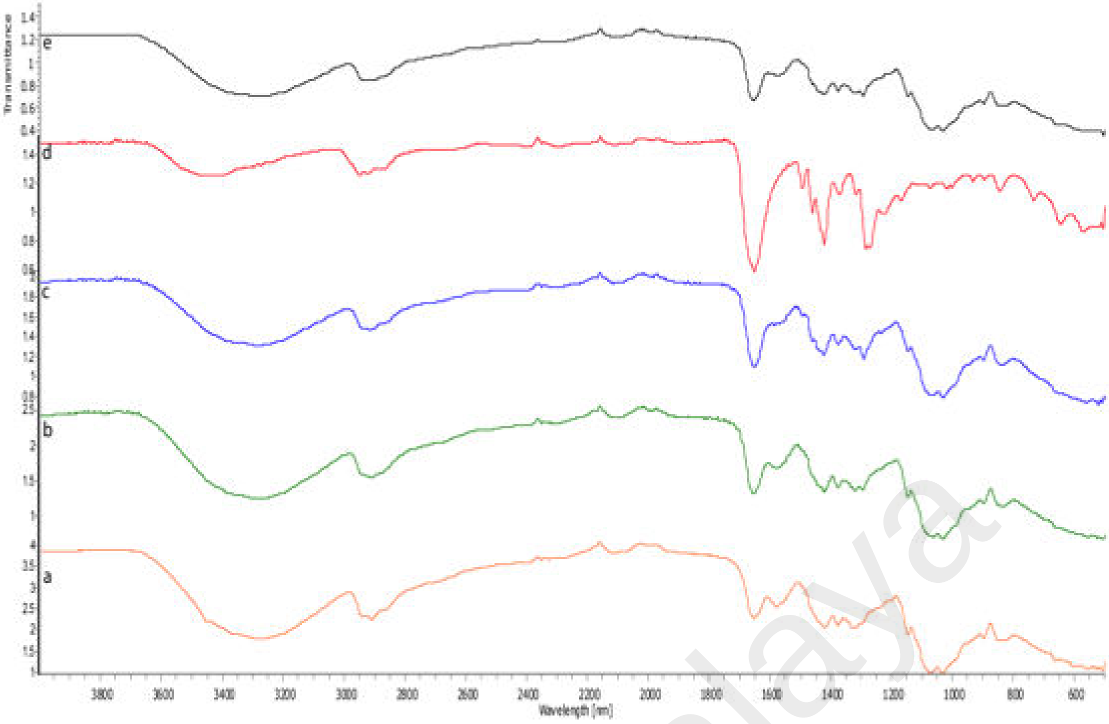


Figure 4.7 : FTIR spectra of (a) CS/PVA, (b) PVP, (c) CS/PVA + PVP 0kGy, (d) CS/PVA + PVP 5kGy and (e) CS/PVA + PVP 30kGy

As shown in Figure 4.7 (c), 4.7 (d) and 4.7 (e), amide group from PVP at peak 1645 cm^{-1} is very intense. This however, is reduces after the coated films were exposed to gamma ray at doses mentioned above. The reduction in the intensity suggests an interaction of C=O groups with H bending either from –OH groups from CS or PVA. This is further supported by the increase in the intensity of –OH peak in CS/PVA films upon introduction of PVP. When the films were exposed to gamma ray at doses mentioned above, the peaks at around 2938 cm^{-1}, 2909 cm^{-1} and 2875 cm^{-1} become more intense and shifted to lower wavenumbers. These indicate formation of C-C linkages that may be formed from chemical crosslinking by gamma irradiation.

4.2.3 Gel content and swelling ratio of modified CS/PVA film

To support the results obtain from the FTIR, gel content test was carried out. Gel content is part of the gel or film that does not dissolve when heated in a hot water up to 80°C (Mahmud, 2017). Gel content of CS/PVA film coated with 1% PVP (0 kGy) and irradiated at various gamma dose (5, 10, 20 & 30 kGy) is shown in Figure 4.8.

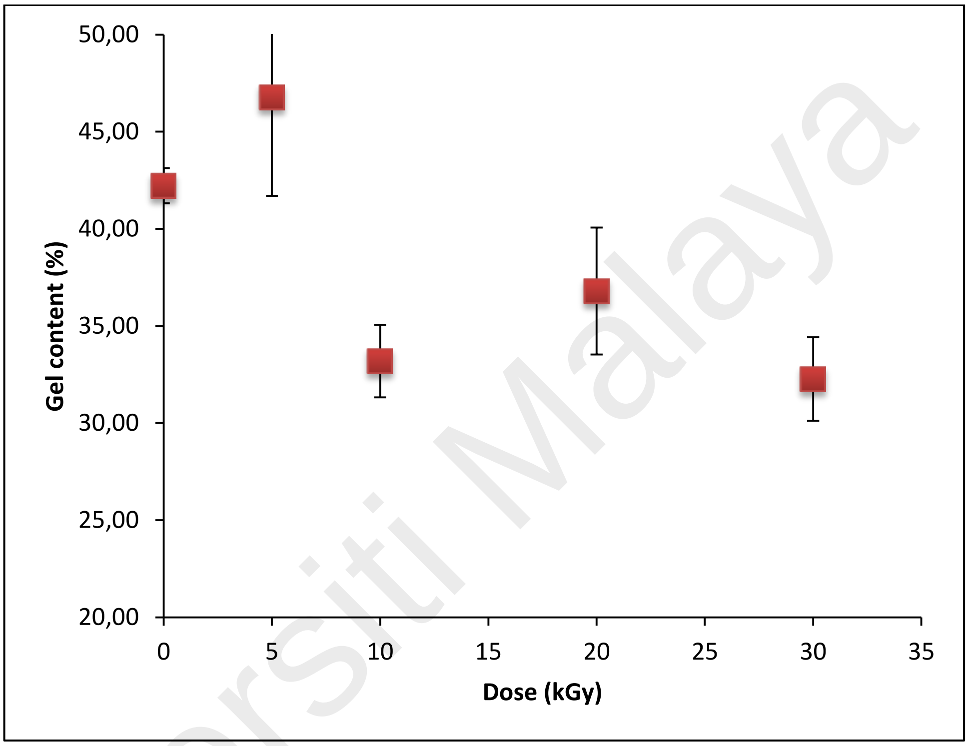


Figure 4.8: Gel content of CS/PVA film coated with 1% PVP and irradiated at various dose.

Gel content of un-modified CS/PVA film was 24.15%. When films were modified with PVP coating only and was not irradiated to gamma ray, there was increasing in gel content when compared with un-modified CS/PVA film. The increment in gel content is significant with the value of improvement 74.82%. This may due to the formation of hydrogen bonds between carbonyl groups of PVP with amino and hydroxyl groups of chitosan (Sizílio, R.H. et. al., 2018).

When CS/PVA film coated with 1% PVP were further exposed to gamma irradiation particularly at dose of 5kGy, there was slightly increased in gel content when compared to the film, which was not irradiated. However, when the irradiation dose increasing, there was a drastic decreased. For the creation of the film by using radiation technique to form crosslinking, this is a common situation. It was called critical absorbed dose or gelation dose where, there was a formation of three-dimensional (3D) network. This 3D formation of network is occurred due to the recombination of polymer chains either with the same polymer chains (intra molecules) or with different polymer chains (inter molecules) (C. Yang et al., 2010). Further exposure of the film at the higher irradiation dose, the degradation take place where, termination of network dominate over recombination of the inter or intra molecular radicals (Qiu et al., 2007; Zhao, Xu, Mitomo, & Yoshii, 2006).

Results obtained from the swelling test in water for the modified CS/PVA film coated with 1% of PVP are shown in Figure 4.9. Swelling result of un-modified CS/PVA film in water was 123.90 %. There was no significance difference when CS/PVA film was only coated with 1% PVP without exposure to gamma irradiation where, the swelling result obtained was 122.32%. As the dose of the irradiation increase up to 10 kGy, the swelling gradually increased. The highest swelling value of modified CS/PVA film was when the film was irradiated at 10 kGy with the value of 140.46%.

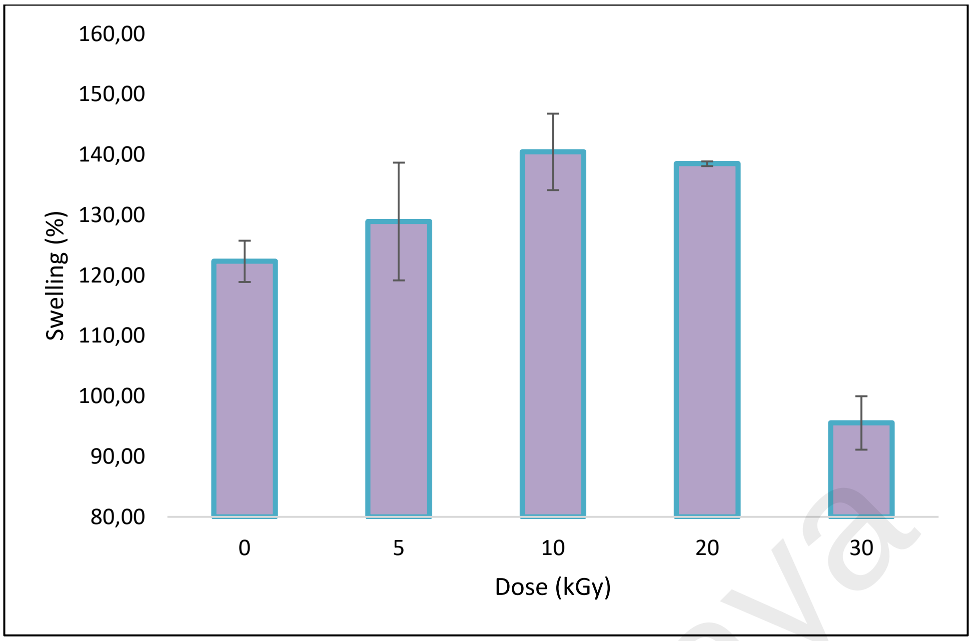


Figure 4.9: Effect of irradiation dose on swelling degree of CS/PVA film coated with 1% PVP in water

It can be seen that by increasing the irradiation dose, the swelling ratio also increase up to the dose of 10kGy. As the dose of irradiation was further increased, the swelling value started to decrease. This result obtain was similar with the result obtained by Nguyen & Liu, 2019. The swelling degree of the film decreased as the dose of irradiation increased generally due to the degradation of chitosan dominantly took place over crosslinking when expose to higher irradiation dose. Where, dismissing of hydrophilic chitosan occurred to produce low molecule of chitosan (Zhai et al., 2004) (Zhao et al., 2006). Other discussion has been reported and suggested that the decreasing of the swelling ratio at higher irradiation dose is because, not all of the chains have been crosslinked. Some of them that were not crosslinked will soluble in the solution (Ramnani et al., 2004). Other researcher also supported this result and reported that, commonly soon after gelation dose, the swelling will be recorded as the highest value and later decreased as the absorb energy increased (Felinto et al., 2007).

As swelling result shows at 10 kGy of irradiation dose give highest value of swelling ratio, this dose was selected and will be further discussed in this chapter.

4.2.4 X-Ray diffraction of chitosan, PVA and PVP

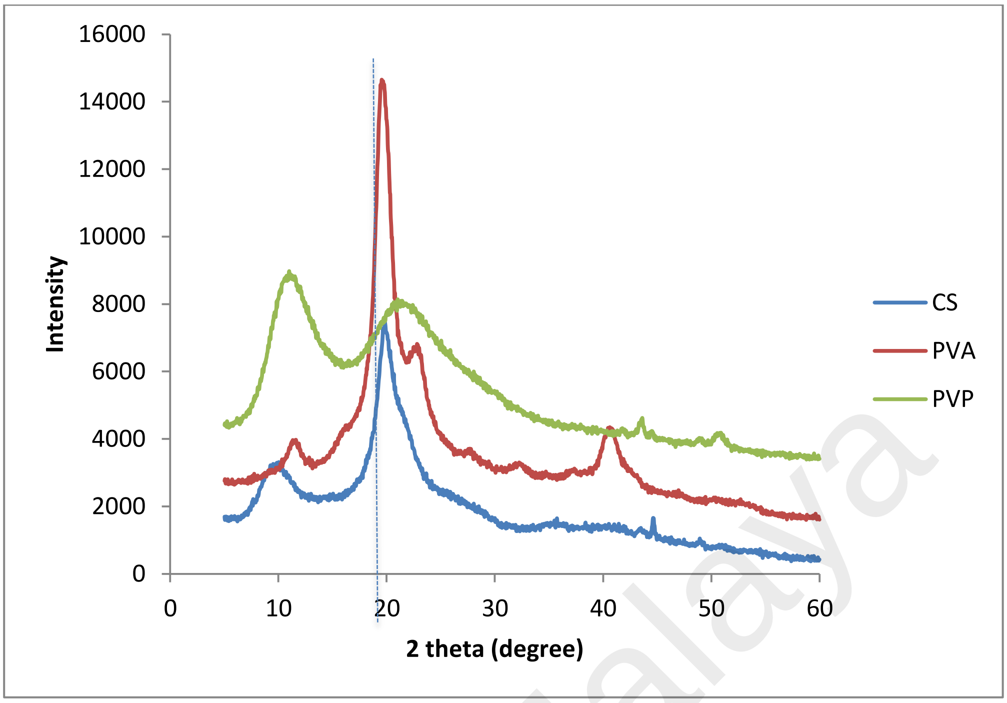


Figure 4.10: XRD spectra of raw materials - Chitosan, PVA and PVP

The X-ray diffraction obtained as shown in Figure 4.10. Chitosan has two broad peaks at around 2θ = 9.8° and 19.8° and these peaks indicate semi-crystalline properties of chitosan (Vaghani, Patel, & Satish, 2012). While, PVA has four peaks located approximately at 2θ = 11.1°, 19.4°, 22.4°, 40.4° indicated that PVA has the semi-crystalline properties as well. These characteristic peaks of chitosan and PVA similar to the x-ray diffraction pattern obtain by (Nguyen & Liu, 2013). For pure PVP, X-ray diffraction shows two broads peaks located at around 2θ = 10.7° & 20.8° indicated amorphous characteristic of PVP (Abdelrazek, Ragab, & Abdelaziz, 2013; Sivaiah, Kumar, Naresh, & Buddhudu, 2011).

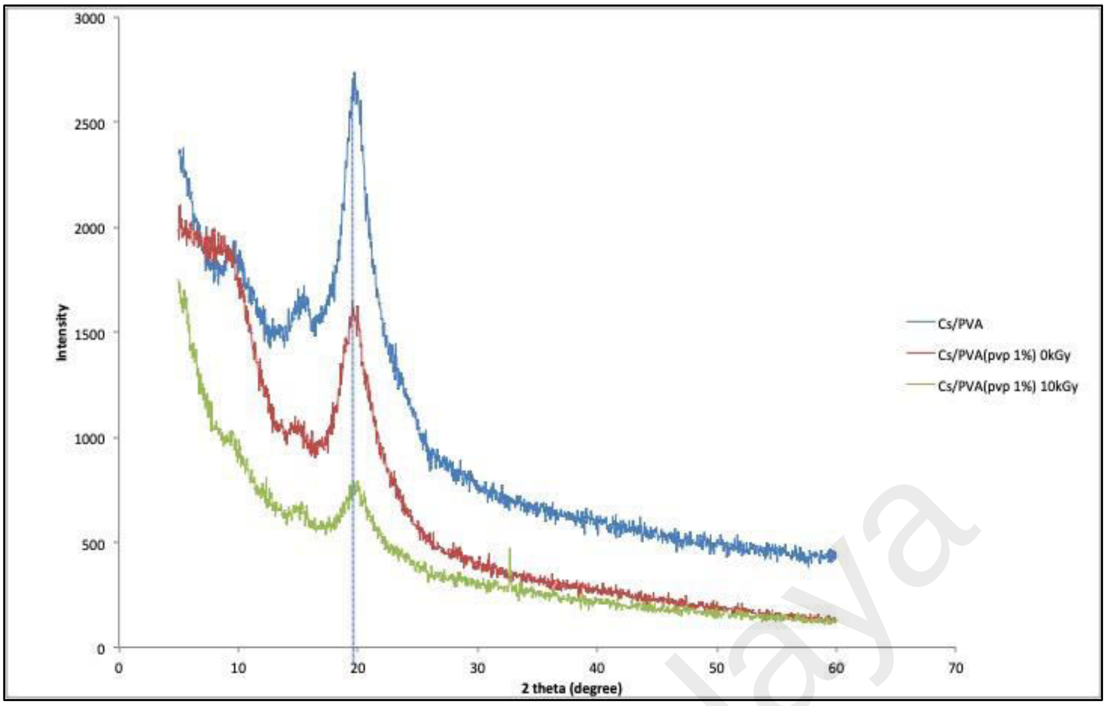
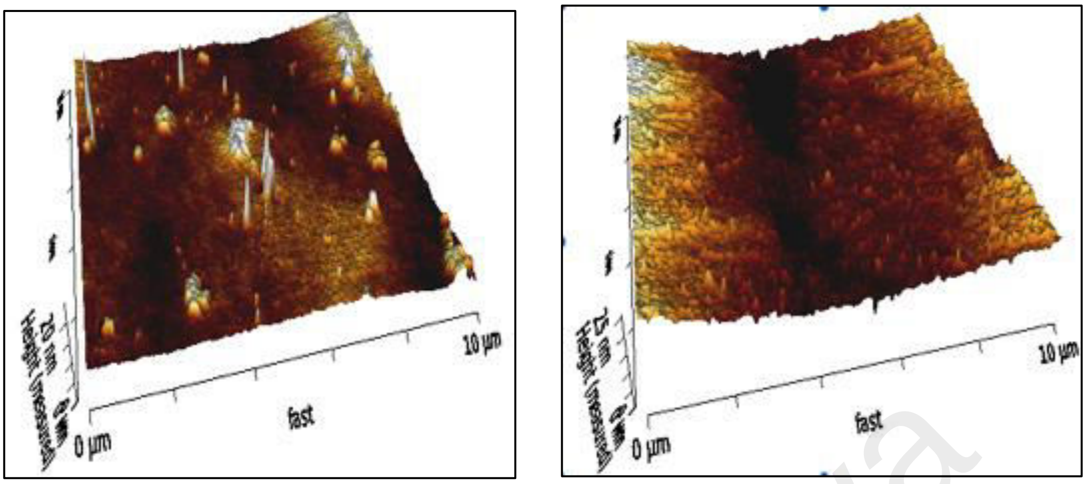


Figure 4.11: XRD spectra of CS/PVA, CS/PVA (PVP 1%) 0kGy and CS/PVA (PVP 1%) 10 kGy

For all CS/PVA films with or without coated with PVP showed the peaks were slightly shifted towards lower diffraction angle however, the main diffraction peak show approximately at 2θ = 19° in the XRD patterns. These patterns can confirmed a complex formation (Abdelrazek et al., 2013) and indicated that all polymers are highly compatible and there are good interactions between Chitosan-PVA and also between PVP and Chitosan/PVA film (Nagahama et al., 2009).

As the films exposed to gamma radiation, the XRD pattern shows the peak intensities decreased dramatically. This outcome is clearly shown that is attributed by the decreased in the crystallinity of the film (Nguyen & Liu, 2013).

4.2.5 Surface morphology of the film by AFM



(a) (b)

Figure 4.12: AFM images of a) un-modified CS/PVA film and b) CS/PVA coated with 1% PVP irradiated at 10 kGy

Figure 4.12 shows the surface condition of the bare and PVP coated films and the effect of irradiation on its surface roughness. Brightness area shown in the AFM images gives some information about the surface morphology. The brighter spot shows peaks available on the surface while when the brightness decrease indicated the valleys on the surface of the specimen. 1% of PVP coating and irradiation at 10 kGy did not affect the surface roughness of the films. As shown in Figure 4.11, CS/PVA film and CS/PVA film coated with 1% PVP and irradiated at 10 kGy, gives not much different in surface roughness. The average value surface roughness, R_a for CS/PVA film un-modified and CS/PVA film modified with 1% PVP at 10 kGy was 1.181 nm and 2.198 nm respectively. Although there is an increment in the value of average roughness of the modified film, but it is not significant enough. The adsorbents properties towards metal ion is related to the roughness of the surface of the films where, surface roughness enhances the reactivity for ions adsorption (Salehi et al., 2013). The adsorption properties will be discussed later in this chapter.

4.3 Adsorption study of modified CS/PVA film

Adsorption study was carried out for both modified and un-modified CS/PVA film. All three concentrations of PVP coated on the CS/PVA film were studied with the exposure to the gamma irradiation. Heavy metals used in the study were copper (Cu), Zinc (Zn) and lead (Pb).

4.3.1 Adsorption study of Cu, Zn and Pb

The effects of PVP concentration on the modified CS/PVA film on the adsorption of Cu, Zn and Pb irradiated at 10 kGy are presented in Figure 4.13. Each of heavy metals has been adsorbed individually from the initial concentrations of 20 mg/L at pH of 5.75 for Cu and pH of 5.0 for Zn and Pb. It was carried out for 24 hours and the results are presented in one graph for comparison. As can be seen different PVP concentration coated on CS/PVA film show little significant effect on the adsorption of metal ions.

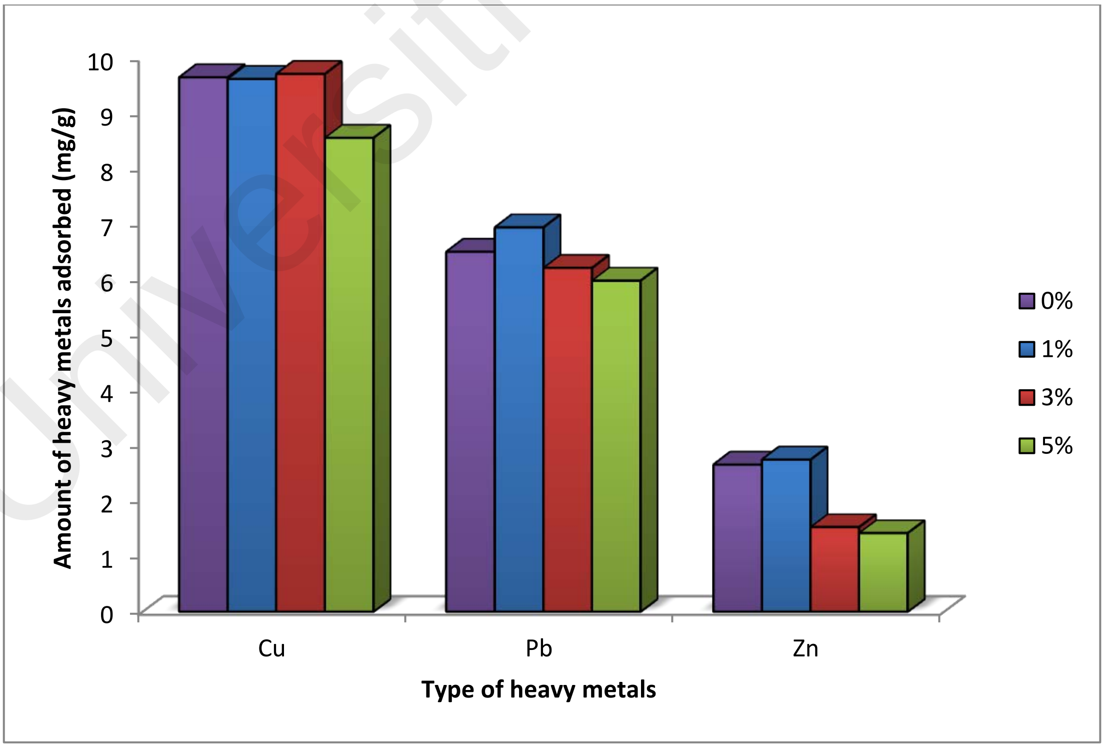


Figure 4.13: Effects of the concentration of PVP coated on the CS/PVA film irradiated at 10 kGy on the adsorption of Cu, Zn and Pb.

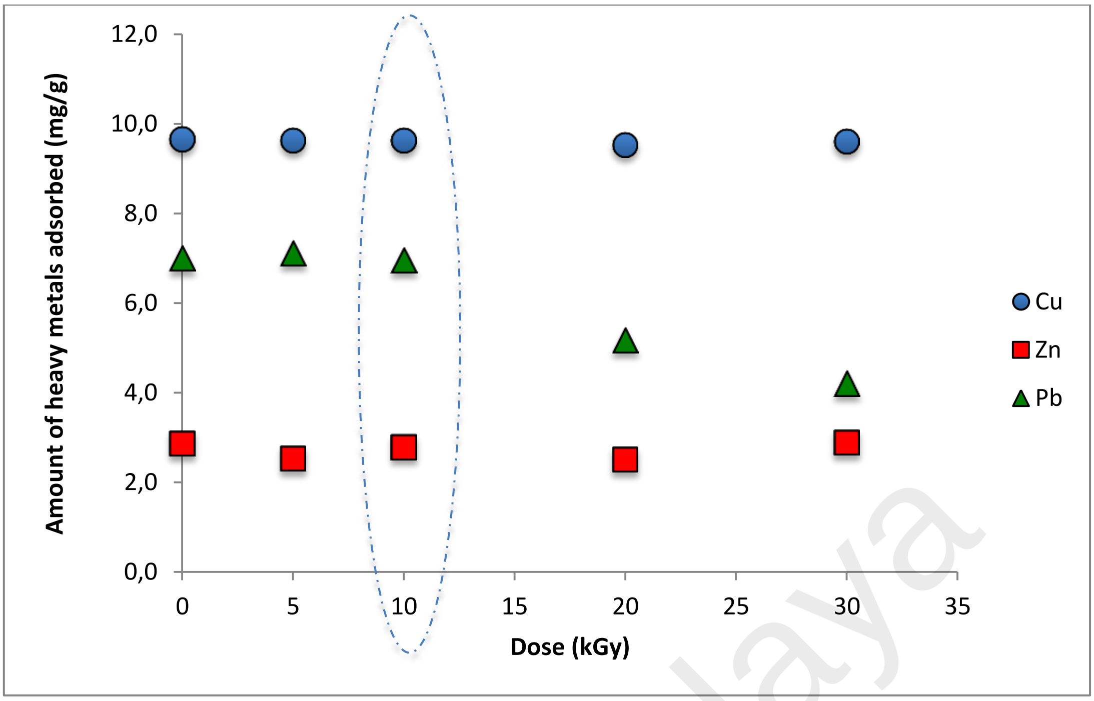


Figure 4.14 : Effect of irradiation dose on the modified film coated with 1% PVP for adsorption of heavy metals; copper, zinc and lead.

Metal ions adsorbed by the films were also not affected by the irradiation dose with 1% of PVP coating as can be seen in Figure 4.14. There were several studies using chitosan to absorb the heavy metals including blending chitosan with other polymer like PVA. However, due to the mechanical strength of the blend film, this study has been carried out. CS/PVA films were coated with PVP solutions and exposed to gamma irradiation. Modification of the CS/PVA film by coating and radiation induced, has improved mechanical strength. However, the modification of the CS/PVA film neither improved nor worsens the properties of the heavy metal ions adsorption.

Mainly, chitosan has the ability to adsorb heavy metals ion due to the presence of amine and hydroxyl functional groups in the structure that acted as the active sites. (Ghaee et al., 2010, Wu, et. al., 2009). Metal ions were attracted to chitosan by electrostatic attraction due to the protonation of amine groups in acidic solutions (Guibal, 2004). Based on this result, modification of CS/PVA film via radiation and PVP coating which involved crosslinking of polymer chains did not reduced the metal ions uptake efficiency. Commonly crosslinking procedure will involve with croslinking agents for example glutaraldehyde. This type of crosslinking method could cause sorption capacities as well as metal uptake efficiency reduced drastically. This kind of results specifically occurred when amine groups were involved in the chemical reactions (Erosa et al., 2001, Hsien & Rorrer, 1997).

Chitosan, which classify in natural polysaccharide group, when exposed to gamma ray will degraded either in solid form or dilute solutions (Khoylou & Naimian, 2009; C. Yang et al., 2010; Zhao et al., 2006). In this study, chitosan was in film form and degradation will also occurred when exposed to irradiation (Vanichvattanadecha et al., 2010). However, degradation of chitosan which involved reducing of chitosan molecular weight, does not really affected the sorption properties (Guibal, 2004).

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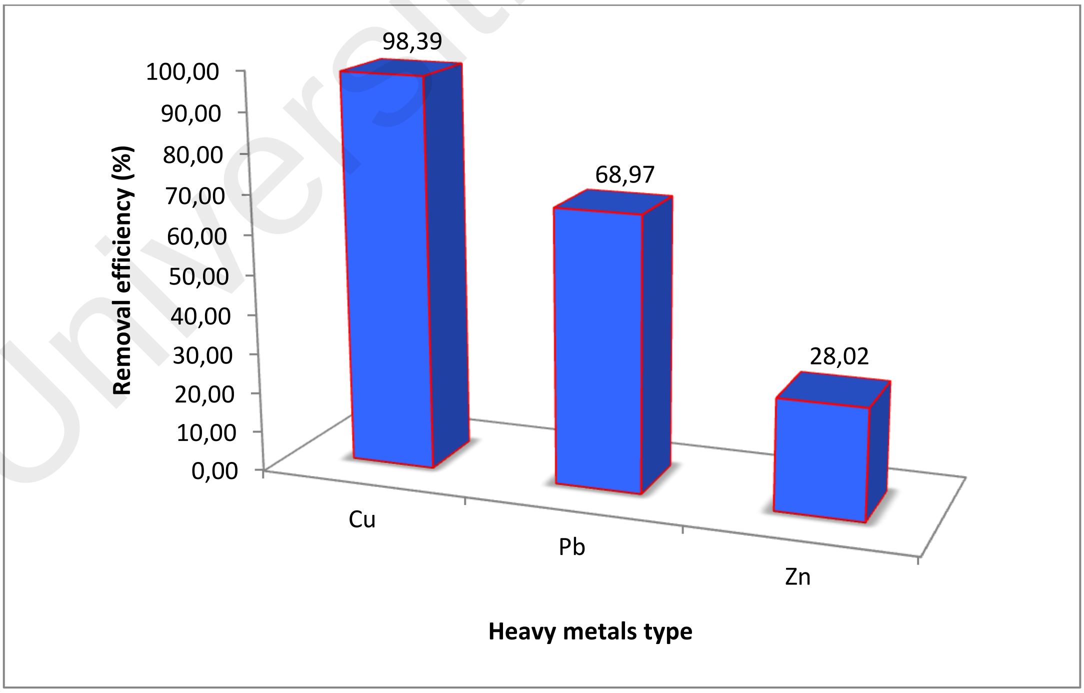

Figure 4.15: Removal efficiency of Cu, Pb and Zn for CS/PVA film coated with 1% PVP, irradiated at 10 kGy.

Figure 4.15 shows removal efficiency of CS/PVA film coated with 1% PVP and irradiated at 10 kGy for copper, lead and zinc. As can be seen, removal efficiency for three heavy metals shows that removal of copper is the highest followed by lead and zinc. In the same condition, copper is the most metal ion to be bind to the film compared to other metal ions is because Cu^{2+} is the most easy metal ion to be complexed with ligands which contains nitrogen and oxygen (Essawy & Ibrahim, 2004). Similar trend of result has been obtained by Dean & Dixon, 1992 where Cu^{2+} has been adsorbed more than Pb^{2+}, which may due to the size of metal ions. In other study, it was reported that adsorption of chitosan favorable selected towards Cu^{2+} over other metal ions such as Zn^{2+},Cd^{2+} and Ni^{2+} (Chauhan, 2015).

The result of selectivity of the film towards Cu^{2+} when compared with other metal ions might be due to the presence of PVP in the film. As known that chitosan has the ability to adsorb heavy metals. However, PVP presence in the film may attribute some positive effect on adsorption of copper ion where, the functional groups of PVP which consist of C=O and C-N have interacted with Cu ions and were capable to remove Cu ions (Zhang et al., 2014).

PVP coated onto the CS/PVA film not only help improve mechanical strength of the film, but also help to maintain the heavy metals absorption capability. PVP has the characteristic of reversibly coordinating to various metal ions and has been used in the wastewater treatment (Lu et. al., 2011). PVP also consist of oxygen in the carbonyl group, which may attribute to the attraction of the metal ions with the film (El-Hag Ali et. al., 2003).

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

At first 2% (w/v) of chitosan (CS) and 5% (w/v) of PVA were blended at different CS: PVA weight ratios which were, 50:50, 70:30 and 90:10 to form thin film by solution casting method. CS:PVA with 70:30 ratio was chosen as optimum parameter based on mechanical strength.

Modification of CS/PVA film was done with PVP coating and exposure to gamma irradiation. PVP at different concentrations of 1%, 3% and 5 % (w/v) were coated onto CS/PVA film and irradiated with gamma radiation at dose of 5-30kGy. Mechanical test (tensile and elongation at break) was carried out to optimize the concentration of PVP coating. The result shows at 1% of PVP coating gave the best in mechanical strength. Further characterizations were directed on this particular PVP concentration.

Characterizations on modified CS/PVA films were carried out with FTIR, XRD, AFM gel content and swelling test. From swelling test, swelling value increase up to 10kGy and decreased as the irradiation dose increased. FTIR and XRD analysis proved the formation of C-C linkages due to crosslinking by gamma irradiation. Morphology of the film showed irradiation dose increase the surface roughness.

Adsorption study was carried out with three types of metal ions; Cu, Zn and Pb. Modification of CS/PVA film with PVP coated and gamma irradiation did not affect the adsorption of heavy metal ions. It can be concluded that modification of CS/PVA film with PVP coating and gamma irradiation had improved the mechanical strength and, at the same time sustained the adsorption capability towards Cu, Zn and Pb. Although the film was coated with layer of PVP but it does not reduce the capability of chitosan to absorb heavy metal ions. Therefore, modification of CS/PVA film with PVP coating and gamma irradiation successfully enhance the mechanical properties and sustained the properties to adsorb heavy metals.

5.2 Recommendation

This study has been carried out to improve the properties of chitosan membrane as adsorbent for heavy metals removal. However, further improvement can be conducted as follows:

i. Different methods to produce chitosan film can be used such as electrospinning method.
ii. Different radiation source like electron beam can be used to study and compare the effectiveness the crosslinking process between different radiation sources.
iii. PVP can be blended together with chitosan and PVA and to study the performance of the mechanical strength as well as heavy metal ions adsorption property.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

1. Norhashidah Talip, presented “Gamma Irradiated PVP Coated Chitosan/Poly Vinyl Alcohol Membrane for Potential Water Treatment Application”, International Conference on Advances in Materials and Processing Technologies (AMPT 16) 0n 8-11 November 2016 at Kuala Lumpur