

## Radiation Modified CS/PVA Film with PVP Coating as Cu Adsorbent Material

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### ABSTRACT

Chitosan/Polyvinyl alcohol (CS/PVA) films were coated with layer of polyvinyl pyrrolidone (PVP) to improve its mechanical strength. In this study, chitosan/PVA mixture was first cast into film. The films were later dipped into different concentrations of PVP solutions at 1%, 3%, and 5%. They were then exposed to gamma ( $\gamma$ ) radiation at 5,10,20 and 30 kGy. The tensile strength of chitosan/PVA films coated with 1% PVP was found to increase up to 31%. Elongation at break was improved by 1% PVP coating. The CS/PVA Removal Efficiency (RE) with or without PVP coatings were not affected by  $\gamma$  irradiation. Result shows that the best settings to enhance the tensile strength of CS/PVA films for Cu adsorption application was 1% PVP coating at 5 kGy  $\gamma$  radiation.

### ARTICLE INFO

#### Article history:

Received: 4 August 2020

Accepted: 10 February 2020

Published: 30 April 2021

*Keywords:* Chitosan, copper removal, polyvinyl alcohol, polyvinyl pyrrolidone, radiation

DOI: <https://doi.org/10.47836/pjst.29.2.23>

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### INTRODUCTION

Rapid industrial growth has immensely help to drive the country economy, but it comes at a cost where it causes massive environmental pollution. Water is among one of the most critical part of pollution that

requires utmost attention. Typical industrial wastewater pollutants include heavy metals such as copper (Cu), cadmium (Cd), zinc (Zn), and lead (Pb). These are toxic and harmful to the environment as they cause adverse effects to the health of human beings and other organisms due to their presence in drinking water and aquatic habitat (Barakat, 2011). The World Health Organization (WHO) (as cited in Y. Zhang et al., 2014) recommended that 1.5 mg/L was the maximum accepted value of Cu ion concentration in drinking water.

At present, several methods are employed for wastewater treatment and Cu ions removal such as membrane filtration, chemical precipitation, reverse osmosis, evaporation, oxidation, and adsorption (Chen et al., 2010; Sarioglu et al., 2009; Šćiban et al., 2008). Among these, adsorption method is the most common due to its economic factor, efficiency, simplicity, and environmental safety (Tripathi et al., 2009; Senthilkumar et al., 2011).

Chemical adsorption method depends on metal chelators, often they are prepared from commercial polymers such as poly(ethyleneimine) and poly(acrylic acid). Lately, naturally occurring polysaccharides such as chitosan (CS) is gaining attention due to its abundance and renewable sources (Kurita, 1998; Varma et al., 2004). CS possesses a few favorable properties (Xiao, 2007). Some of the more important properties are its capability to be shaped into films, chelate metal ions, and basic optical features (Kalantari et al., 2017; Kumar, 2000). 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; Alver et al., 2014). Despite all these useful properties, CS has strong intra- and inter-molecular hydrogen bonding along its polymeric chains. This makes CS partly crystalline and thus too brittle and has weak strain at break for adsorption films and castings applications (Huang et al., 2012).

To overcome the deficit in mechanical strength of CS films, it is commonly blended with other polymers (Tripathi et al., 2009; Ngah et al., 2004; J. M. Yang et al. 2004). Poly(vinyl alcohol) (PVA) is one candidate that has been extensively used to blend with chitosan. However, according to Huang et al. (2012), CS/PVA blend needs to be improvised in order to enhance the mechanical properties and water resistance of the film for practical applications. The objective of the present work is to further improvise CS/PVA film mechanical strength and properties with polyvinyl pyrrolidone (PVP) coating and  $\gamma$  irradiation to introduce cross-linkages on the coated film. Interactions between polymer materials and radiation from sources like  $\gamma$  ray will produce free radicals. This is due to the energy of irradiation which has been absorbed by the backbone of polymer materials. This reaction can occur without the presence of catalyst, initiator, monomers, or other cross-linkers (Bhattacharya, 2000; Idris, 2008). Radiation technique was chosen due to the its effective, clean, and versatile process which can be done in convenient temperature, in any physical form and no initiator needed in this process (Al-Assaf et al., 2016).

PVP is one of the polymers that will undergo cross-linking with radiation technique (Rosiak et al., 1990). PVP solutions when exposed to  $\gamma$  ray irradiation, it will induce the formation of free radicals from both carbon atoms in PVP and hydrogen atoms from water that promotes cross-linking by forming C-C bonding (Demeter et al., 2017; Jeong et al., 2020). Besides, PVP has excellent properties of bonding to various metal ions such as Cu(II), Pb(II), and Cd(II), low cytotoxicity, and biocompatibility (Lu et al., 2011). Cu ions adsorption capability of this film is also discussed to evaluate the possibility/effectiveness of PVP coated chitosan as wastewater treatment membrane.

## **MATERIALS AND METHODS**

Chitosan, (Molecular weight 190,000 – 310,000 Da) and degree of deacetylation (DD) of 75-85% was purchased from Sigma Aldrich. 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. Acetic acid (glacial) and sodium hydroxide (analytical reagent) were purchased from HmbG Chemicals and Fisher Scientific, respectively. Materials were used without further purification.

### **Preparation of CS/PVA Film Modified with PVP and Gamma Irradiation**

Chitosan (2%, w/v) was dissolved in 1% (v/v) aqueous acetic acid and stirred overnight at room temperature. The solution was then filtered to remove dust and other impurities. PVA solution with a concentration of 5% (w/v) was prepared by dissolving PVA powder in ultra-pure water and autoclaved at 121°C for 15 minutes. CS and PVA solutions were mixed at weight ratio of 70:30. The mixed solutions were stirred at room temperature for 30 minutes. Films were obtained by casting method, where 7 ml of the solutions were poured onto polystyrene petri dishes followed by drying at room temperature for 48 h. The dried films were then soaked in 1N of NaOH for 1 h, then, washed four times with 250 ml of Reverse Osmosis (RO) water to remove the excess of acid and NaOH, respectively. The films were then soaked in 1, 3 and 5% (w/v) PVP solutions for 15 – 20 minutes and immediately kept in plastic bag prior to irradiation. The films were irradiated at 5, 10, 20, and 30 kGy from Co-60 source facility at Sinagama, Malaysian Nuclear Agency. Dose rate of the irradiation was 1.62kGy/h. Upon completion of irradiation process, the films were dried again at room temperature for 24 h. Dried films were kept in desiccator until further use. All films obtained were transparent, uniform, and free of air bubbles.

### **Characterization of CS/PVA Films**

The Fourier Transform Infrared Spectroscopy (FTIR) analysis of blended film and modified film were performed using Bruker TENSOR FTIR. The spectrums were obtained at a frequency range of 3600  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and 16 times scanning.

Mechanical properties of films were tested using Instron Universal machine model 4201 according to ASTM Standard Method D 882 (ASTM D882-12, 2012). Testing specimens were cut into strips with 40 mm length and 10 mm width. Thickness of the films was measured at seven various positions using Digital Thickness Gauge model Mitutoyo Crop (Japan). Gauge length and crosshead speed were set at 20 mm and 5 mm/min, respectively with load cell of 1kN. Minimum of five specimens were tested for each sample and average were calculated.

Gel fractions of irradiated films were carried out. The films were cut into small pieces and placed in the tea bags. The tea bags were 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 fraction was measured by the insoluble part after immersion in water. A minimum of five specimens were tested for each sample and average were calculated. Gel fraction was calculated using Equation 1.

$$\% \text{ Gel fraction} = \frac{W_2}{W_1} \times 100 \quad [1]$$

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

Surface roughness and morphology of the films were studied using Atomic Force Microscope (AFM) from JPK Instruments. Samples were cut into small size and located on glass slide. Measurement was done by using contact mode cantilever.

### Adsorption Study of the Film

Removal of copper ions was performed via batch adsorption analysis. This experiment was carried out by soaking 0.1 g of film in 50 ml of copper (II) nitrate solution with initial concentration of 20 mg/L for 24 h at room temperature with 120 rpm. pH value of the solution was adjusted to 5.75 by adding 1% of ammonium hydroxide or 1% of HCl. Atomic Absorption Spectrophotometer (Perkin Elmer 800 Analyst) was employed for determination of copper ions. The amount of copper adsorbed onto the film was calculated by using Equation 2.

$$q = \frac{(C_o - C_t)}{m} \times V \quad [2]$$

where,  $C_o$  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 using Equation 3 as describe by Lee et al. (2015).

$$RE (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad [3]$$

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

## RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of (a) CS film (b) CS/PVA film, (c) PVP, modified CS/PVA film with 1% of PVP and irradiated at (d) 0 kGy and (e) 5 kGy. The broad band for all films observed at 3450 - 3200  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  which was caused by -CH-OH bending vibration of PVA (Zhuang et al., 2012). The shifts of absorption peaks to 3357 and 3283  $\text{cm}^{-1}$  indicate introduction of -OH group from PVA. Increment in peak intensity at 1650  $\text{cm}^{-1}$  indicates the interaction between amine from CS and -C-OH from PVA. A reduction in peak intensity at 1576  $\text{cm}^{-1}$  indicates a reduction in -NH<sub>2</sub> group where, some degradation took place. Figure 1(b) shows PVP spectra, strong band at 1645  $\text{cm}^{-1}$ , 1421  $\text{cm}^{-1}$ , 1281  $\text{cm}^{-1}$  and weak band at 2917  $\text{cm}^{-1}$  are attributed to C=O stretching, C-N stretching, O-H bending and C-H stretching vibrations, respectively (Can, 2005; Singh & Pal, 2011; C. Yang et al., 2010).

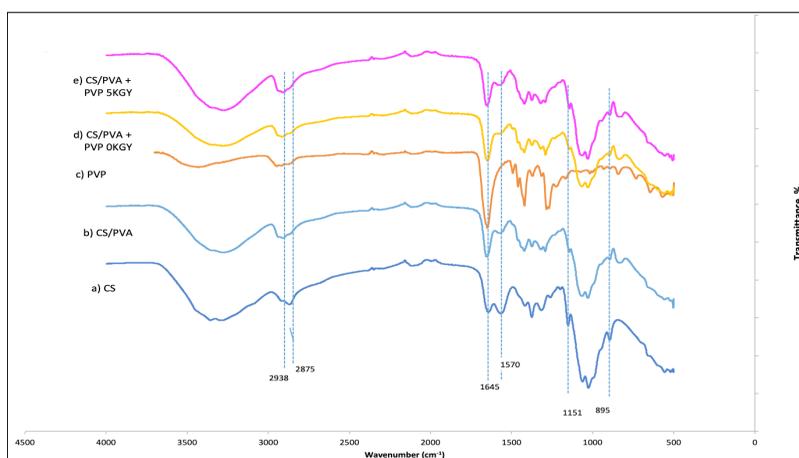


Figure 1. FTIR spectra of (a) CS, (b) CS/PVA, (c) PVP, (d) CS/PVA + PVP 0 kGy, (e) CS/PVA + PVP 5 kGy

As shown in Figure 1(c), 1(d) and 1(e), carbonyl group from PVP at peak 1645  $\text{cm}^{-1}$  is very intense. However, this reduced 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  $\text{cm}^{-1}$ , 2909  $\text{cm}^{-1}$ , and 2875  $\text{cm}^{-1}$  become more intense and shifted to lower wavenumbers. These

indicate formation of C-C linkages that may be formed from chemical cross-linking by  $\gamma$  irradiation.

Chitosan in the mixture of CS/PVA films when exposed to  $\gamma$  irradiation will undergo degradation. It can be shown in decreasing of peaks intensity at 895 and 1151  $\text{cm}^{-1}$  as suggested by Casimiro et al. (2016) that some degradation by cleavage of  $\beta$ -glucosidic linkages due to reaction by OH radicals.

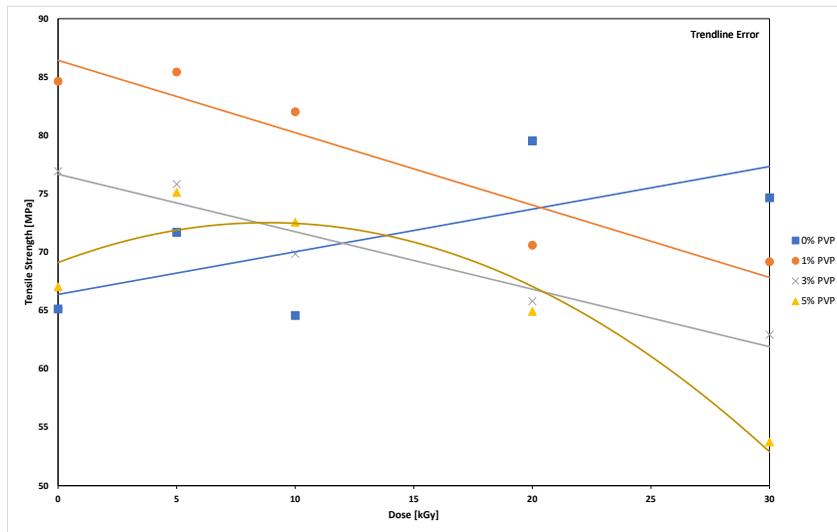


Figure 2. The effect of concentrations of PVP used for coating on tensile strength of CS/PVA films as a function of gamma irradiation dose.

Table 1

Thickness of CS/PVA film and CS/PVA films with PVP coating

| Concentration of PVP (%) | Thickness (mm) |
|--------------------------|----------------|
| 0                        | 0.015          |
| 1                        | 0.016          |
| 3                        | 0.017          |
| 5                        | 0.018          |

Concentrations of PVP used for coatings up to 5% showed no significant impact on the final thickness of the films where, bare CS/PVA film at 0.015 mm while, coated with 5% at 0.018 mm as can be seen in Table 1. Figure 2 shows the tensile strength of bare CS/PVA films and PVP coated CS/PVA film, irradiated with  $\gamma$  irradiation at 5, 10, 20, and 30 kGy. Generally, for non-irradiated samples, addition of PVP enhanced the CS/PVA film

tensile strength. This is expected as coating of PVP provides physical support on CS/PVA films. Bare CS/PVA films generally improved upon irradiation, suggesting that the PVA chains in the CS/PVA mixture have formed cross-linkages that can support the structure. However, this is still lower than the tensile strength provided by PVP coatings especially below 10 kGy. Coating of 1% PVP at 5 kGy, improved the tensile strength as much as 31% compared to the bare CS/PVA film. This can be attributed to PVP-PVP chain cross-linking that provide support on the coated CS/PVA film. However, a slight decrease could be observed at 10 kGy, where the tensile strength improved at only 26% compared to the bare CS/PVA film. This improvement, although lower than that of 5 kGy, was caused by the competing nature between cross-linking and degradation when polymers were subjected to ionizing radiation (Rosiak, 1998). At this dose, the chains degradation effect was more predominant than that of cross-linking compared to the one at 5 kGy as shown in Figure 3.

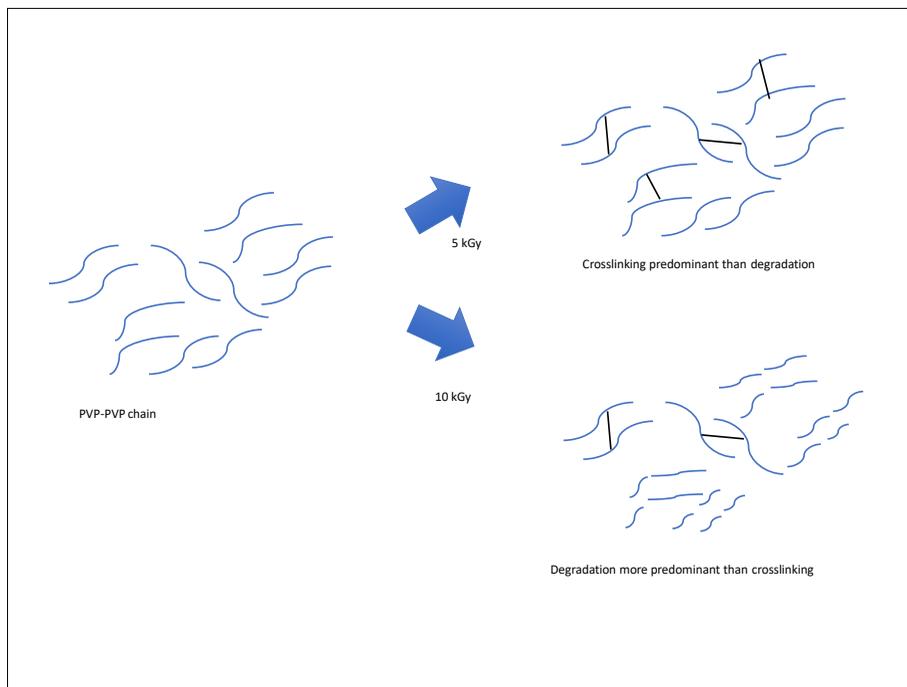


Figure 3. Schematic diagram of competing nature between crosslinking and degradation.

The same trend was observed for CS/PVA films coated with 3% and 5% at greater degradation rates. The stronger decline in the tensile strength at higher PVP concentration coatings can be discussed in term of number of radicals generated by water radiolysis when the coated films are subjected to ionizing radiation. At higher solution concentration

regime, the required dose to form gel phase is proportionate to the concentration of polymer (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 cross-linking point of view, lower numbers of cross-linking networks are formed on CS/PVA film coated at higher concentration of PVP at the same irradiation dose. The lower amount of cross-linkages means lower strengthening effect from PVP, hence the lower tensile strength values.

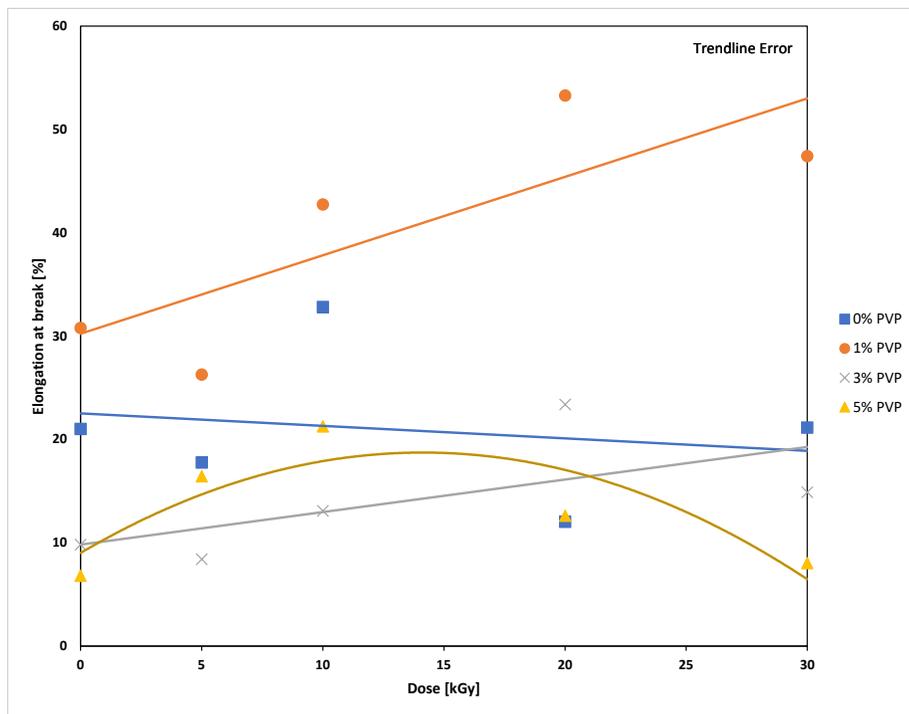


Figure 4. The effect of PVP coated concentration and radiation dose on elongation at break of CS/PVA films

Figure 4 shows the elongation at break data for bare CS/PVA films and its PVP coated form, 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 lacks elasticity throughout the dose range. This is expected due to the partial crystallinity of CS. Coating of 1% PVP improves the elongation at break throughout the irradiation doses up to 53%. This suggests that PVP-PVP cross-linking provides a useful flexible support to CS/PVA films. PVP coatings at higher concentration 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 gave the best tensile strength and elongation at break, thus further characterization and testing were directed on this particular concentration.

Gel fraction was used to estimate the degree of cross-linking of the polymers. Gel fraction of CS/PVA film coated with 1% of PVP and irradiated at various  $\gamma$  doses (5, 10, 20, and 30 kGy) is shown in Figure 5.

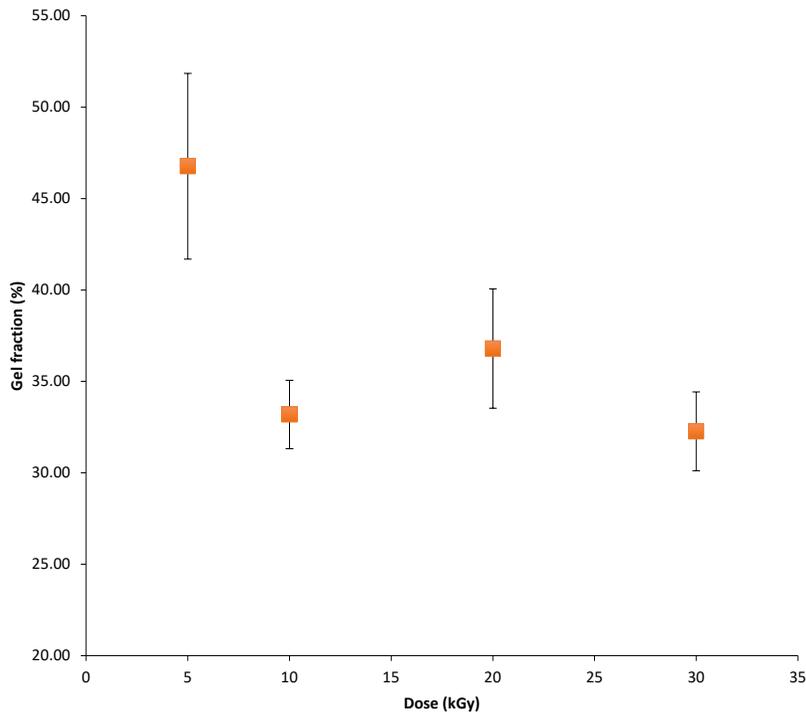


Figure 5. Gel fraction of CS/PVA film coated with 1% PVP and irradiated at various dose.

At 5 kGy of gamma irradiation dose, the value of gel fraction was the highest when compared to other irradiation doses. At this particular dose, it was the highest cross-linking formation between PVP-PVP chains, and this can support the results obtained from the tensile strength where, CS/PVA film with 1% PVP coating irradiated at 5 kGy dose gave the highest value in strength. The mechanism of PVP crosslink by  $\gamma$  irradiation is that, water molecules have absorbed the ionizing radiation and formed free radicals such as hydroxyl radicals and hydrogen atoms which were responsible for macroradicals formation (Demeter et al., 2017). In general, macroradicals may involve in the inter- and intramolecular reactions (Rosiak et al., 1990).

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 et al., 2006). Therefore, CS/PVA coated with 1% PVP and irradiated at 5 kGy successfully improved the mechanical strength of the film. This can support the statement by Q. G. Zhang et al. (2013) and Can (2005) where, crosslinking between PVP chains can be produced through irradiation and it is one of the convenient methods to improve mechanical strength.

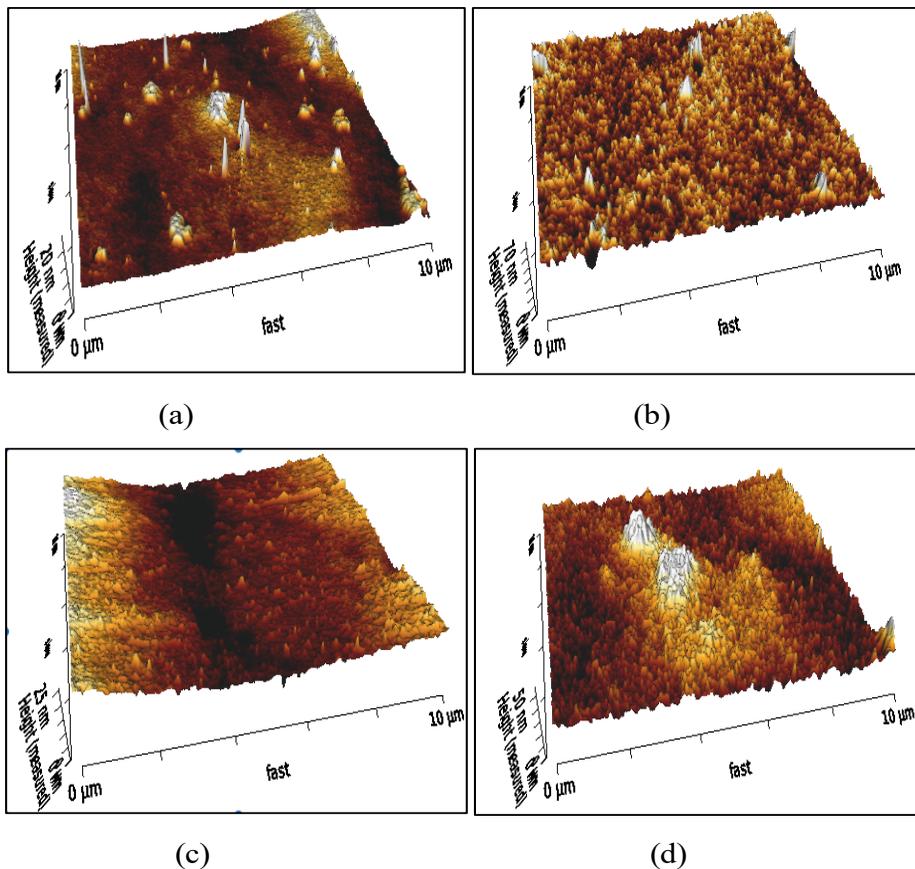


Figure 6. AFM images of (a) CS/PVA/1%PVP – 0 kGy, (b) CS/PVA/1%PVP – 5 kGy, (c) CS/PVA/1%PVP – 10 kGy and (d) CS/PVA/1%PVP – 30 kGy

Figure 6 shows the surface condition of the bare and PVP coated films and the effect of irradiation on its surface roughness. PVP coatings and  $\gamma$  irradiation increases the surface roughness of the films. According to Salehi et al. (2013), surface roughness enhances the reactivity for ions adsorption, however, as seen in Figure 7, this is not true in this study. Although the roughness of the 1% PVP coated CS/PVA films increase with increasing irradiation doses, the adsorption values remain almost unchanged at around 9.6 mg/g. This shows that the adsorption performance does not depend on the surface roughness of the coated films.

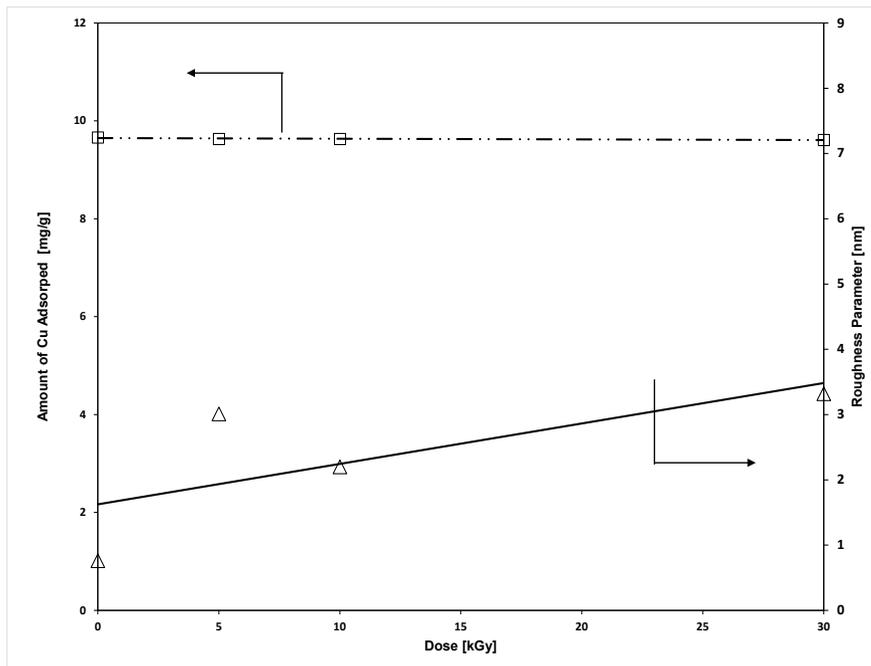


Figure 7. The relation of amount of Cu adsorption and surface roughness of CS/PVA films coated with 1%PVP at different gamma irradiation doses.

Figure 8 shows the removal efficiency (RE) of copper by CS/PVA films coated with 1% PVP and the effect of irradiation. The RE values remain high, in excess of 95% for PVP coated films at doses from 5 to 30 kGy. Note that the RE value for bare CS/PVA has a value of 98%. Heavy metals adsorption ability of chitosan is due to the existence of amine and hydroxyl functional groups in the structure. Although through  $\gamma$  irradiation process chitosan undergo some degradation, but in this study, the RE has no significant change up to 30kGy of irradiation dose when compared with un-modified CS/PVA film with  $\gamma$  irradiation and PVP coatings.

PVP coated on the film might also contribute to this minor change of RE because PVP has the characteristic of reversibly coordinating to various metal ions and has been used in wastewater treatment (Lu et al., 2011). This may be caused by the presence of oxygen in the carbonyl group in the PVP structure that attributes to the attraction of the metal ions with the film (Ali et al., 2003). According to Çaykara and İnam, (2002) there are few non-specifically ways of metals ions that can be adsorbed either by physical or chemical adsorption. In the case of film containing PVP, the adsorption may be attributed by chemical adsorption, which related to exchange of electrons and formation of chemical bond between metal ions and most likely with carbonyl groups of the PVP.

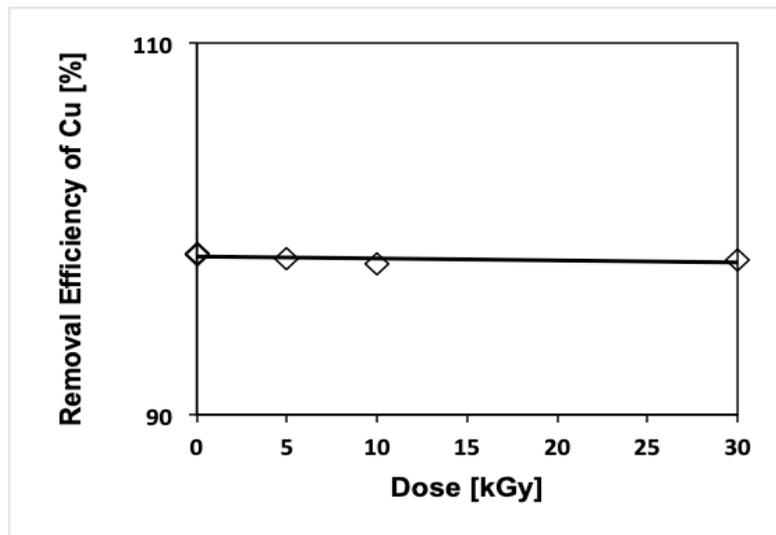


Figure 8. Removal efficiency of 1% PVP coated CS/PVA films copper as a function of gamma irradiation dose.

## CONCLUSION

PVP coatings and irradiation method successfully improved the deficit in mechanical strength of CS/PVA films. Coating of PVP even at 0 kGy, enhanced the CS/PVA film tensile strength. Although, with irradiation only (without PVP coating) may help strengthen bare CS/PVA films, the effect is lower compared to the ones with PVP coatings, which is evident for dose below 10 kGy. Elongation at break, however, was only improved by 1% PVP coating. Surface roughness was improved by irradiation; however, it did not improve the Cu ion adsorption. This is because Cu adsorption is very much dependent on the CS portion. RE values were similar for both bare and coated CS/PVA films and were not dependent on irradiation doses. This proves that radiation method can be used to improve the strength

of CS/PVA films without compromising its RE. The result shows that the best settings to improve the mechanical strength of CS/PVA films for Cu adsorption application are 1% PVP coating at 5 kGy.

## ACKNOWLEDGEMENTS

The first author would like to thank Assoc. Prof. Dr. Amalina M. Afifi for supervising and assisting this research work. Also, big appreciation to colleagues and supporting staff of Malaysian Nuclear Agency for their expert advices, guidance, and valuable knowledge while conducting this research work.

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