

## Removal of Methylene Blue Dye in Aqueous Solution by Sorption on a Bacterial-g-Poly-(Acrylic Acid) Polymer Network Hydrogel

(Penyingkiran Pewarna Metilena Biru di dalam Larutan Aqueus dengan Serapan oleh Polimer Hidrogel Berasaskan Rangkaian Selulosa Bakteria-g-Poli-(Asid Akrilik))

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### ABSTRACT

*In this study, Bacterial cellulose (BC) grafted with Acrylic acid (AA) was prepared using Co<sup>60</sup>  $\gamma$ -rays source (30 KGy). Although many samples were prepared, BC: AA with ratio of 1:1 labelled as A1 and 2:1 labelled as A2 gave the most significant results. Hence these particular ratios have been selected and further investigated. AA was proven grafted onto BC by using ATR-FTIR due to the absent of C-O stretching (1040 cm<sup>-1</sup>) in both hydrogels. The SEM image of both hydrogels samples showed highly porosity networks structure have been produced. The physical properties of the hydrogels such as equilibrium water content (%) and swelling ratio (%) in different pH buffer solution were measured. It was found that the equilibrium water content (%) of A1 was 93.10% while A2 was 74.83%, respectively. The results indicated that the equilibrium water content (%) increased by gaining the AA concentration. At pH10, the A2 swelling ratio (%) was two folded with 3350% in comparison with the A1. For the removal of methylene blue (MB) from aqueous solution, the results from the UV-VIS spectroscopy demonstrated that the A2 sample hydrogel was also an effective absorbent material.*

*Keywords: Bacterial cellulose; gamma radiation; hydrogel; methylene blue*

### ABSTRAK

*Dalam kajian ini, hidrogel berasaskan selulosa bakteria telah dihasilkan dengan mencangkukkan molekul asid akrilik (AA) pada jaringan selulosa bakteria (SB). Teknik pempolimeran yang digunakan di dalam kajian ini adalah pempolimeran sinaran radiasi gama (sumber Co<sup>60</sup>, dos: 30 KGy). Walaupun banyak sampel disediakan, sampel hidrogel dengan nisbah SB: AA, 1:1 dilabel sebagai A1 dan 2:1 sebagai A2 memberikan keputusan yang paling baik. Oleh itu, kedua-dua sampel tersebut dikaji dengan lebih lanjut. AA telah terbukti ditambah kepada SB dengan menggunakan ATR-FTIR kerana regangan CO (1040 cm<sup>-1</sup>) dalam kedua-dua hidrogel telah disingkirkan. Imej SEM bagi kedua-dua sampel hidrogel menunjukkan struktur yang mempunyai keporosan yang tinggi. Selain itu, sifat-sifat fizikal bagi kedua-dua sampel seperti keputusan ujian kandungan air dalam keseimbangan (%) dan ujian pembengkakan dalam larutan penimbal dengan pH yang berbeza dikaji. Keputusan ujian kandungan air dalam keseimbangan (%) mendapati sampel A1 mencatatkan peratusan sebanyak 93.10% manakala sampel A2 mencatatkan peratusan sebanyak 74.83%. Hal ini membuktikan bahawa kandungan AA yang tinggi bagi setiap sampel akan meningkatkan peratusan kandungan air dalam keseimbangan. Dalam ujian pembengkakan dalam larutan penimbal dengan pH yang berbeza, keputusan menunjukkan kedua-dua sampel mempunyai kandungan serapan yang tinggi dalam larutan penimbal pH10. Sampel A2 mempunyai peratusan sebanyak 3350% berbanding sampel A1. Setelah kedua-dua sampel menjalani ujian penyingkiran pewarna metilena biru menggunakan spektroskopi UV-VIS, keputusan menunjukkan bahawa sampel A2 merupakan sampel hidrogel yang mampu menyerap pewarna metilena biru daripada larutan aqueus dengan baik berbanding sampel A1.*

*Kata kunci: Hidrogel; metilena biru; selulosa bakteria; sinaran gama*

### INTRODUCTION

Methylene blue (MB) is a cationic thiazine dye with a chemical name of tetramethylthionine chloride. Widely used as dye in textile industry, MB is easily being recognized due to its appearance as deep blue (at its oxidized state) with a maximum absorption at 609 and 664 nm (Oz et al. 2009). On contrary to its benefits, this stable compound (Figure 1) is very toxic and almost non-biodegradable which lasts for many years. MB not only pollutes the environment but also depletes the oxygen content and inhibits sunlight from reaching the water source.

Many techniques have been developed and applied to overcome the un-dissolved dye problems including biological, air flotation and chemical treatments (Sajab et al. 2011). Although all techniques offered some solutions however major disadvantages occurred such as low decolourization rate and producing secondary pollution of adsorbing materials. Moreover they were costly, non-portable and complicated.

Recently, dye removal using functional polymers become new approach for environmental applications. Different polymeric adsorbents in particular hydrogels

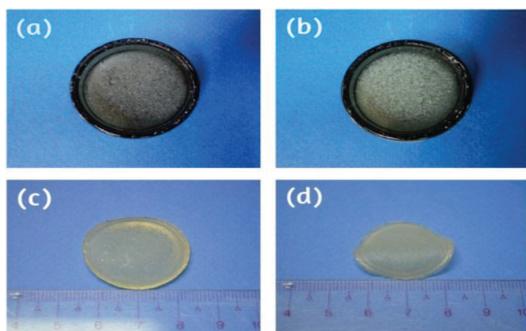


FIGURE 1. Images of (a) sample A1 (b) sample A2 before drying process and (c) Sample A1 (d) sample A2 after purifying and drying process

with different functional groups with ability to complex with dyes gained much attentions and further investigated (Jeon et al. 2008).

In general, hydrogel is three-dimensional networks of hydrophilic polymer chains with intermediate properties between liquids and solids (Sahera et al. 2012). It has excellent hydrophilic properties, high swelling ratio and biocompatibility, which have been widely used in various areas including water purification (La et al. 2011) agriculture (Koupai et al. 2008; Narjary et al. 2012) and biomedical (Campbell & Hoare 2014; Jaiswal et al. 2013; Tamura et al. 2011). As example, hydrogel has been used as a smart controller of fertilizer (Pourjavadi et al. 2012), antibacterial materials (Ding et al. 2013; Murthy et al. 2008), mimicking as muscles in tissue engineering (Mirahmadi et al. 2013; Ng et al. 2012; Zhang et al. 2014), biosensors (Endo et al. 2008; Liu et al. 2011; Wang et al. 2010), sorbents for the removal of heavy metals from water (Huang et al. 2013; Ningmei & Zhengkui 2013; Nurettin et al. 2010; Ozgur et al. 2009; Sahiner et al. 2011; Wang et al. 2014) and as efficient carrier for drug delivery (Masteiková et al. 2003; Qiu & Park 2012).

Most hydrogels were prepared from synthetic polymers by radical copolymerization (Sand et al. 2012), graft copolymerization (Nasef & Güven 2006), cross-linking and ionizing radiation (An 2010; Sáfrány et al. 2010). Since pure synthetic hydrogels are not green, slightly toxic and incompatible to human body, therefore to date research was made by combining natural sources such as starch (Abdel-Halim 2013; Zhong et al. 2013), cellulose (Kentaro & Hiroyuki 2012; Sannino et al. 2009) and lactic acid (Hu et al. 2008; Wang & Wu 1998). As example, bacterial cellulose hydrogels have excellent biocompatibility biomaterial and less latent toxic effect compare to the synthetic polymer (Cherian et al. 2011; Kentaro & Hiroyuki 2012; Wendler et al. 2013).

Bacterial cellulose (BC) is an organic compound which produced by bacteria called *Acetobacter xylinum* (Lee et al. 2011). In food industry, BC becomes the main source of producing *Nata de coco*, a local sweet Malaysian dessert. As it is free from wax, hemicellulose, lignin and pectin, which present in most plant based cellulosic materials,

this characteristic has put BC in great advantages for more extensive applications.

In this study, a pH-responsive BC-hydrogel was prepared by using gamma radiation polymerization. The grafted acrylic acid (AA) monomer onto the BC at two different of ratios was determined, compared and analysed using ATR-FTIR. Their morphology were analysed by using SEM while their absorption ability was carried out in different pH buffers. Finally, the absorption of MB was determined by using UV-VIS spectroscopy.

## METHOD

### PREPARATION OF HYDROGEL

The BC powder was dispersed in 2.0 M hydrochloride acid. AA was then added to this dispersion to make ratios of BC: AA, (1:1) and (2:1) in every 20 mL of solution mixture. The mixture then stirred using a homogenizer (Mechanical Stirrer IKA® RW 20 Digital, India) for 2 h. After 2 h of stirring, the mixture was poured into plastic tray and sealed using Para film. Both hydrogel samples were labelled as A1 for ratio (1:1) and A2 for (2:1). The mixture was then subjected to gamma radiation with dosage of 30 kGy by using Gamma Cell 220 Excel instrument (MDS Nordion, Canada).

### PREPARATION OF METHYLENE BLUE

In a 100 mL volumetric flask, 0.1 g of methylene blue powder was dissolved up to the mark by adding deionized water. For dilution, 1.0 mL of the stock solution was pipetted in a 250 mL volumetric flask before adjustment was made by adding deionized water to get a concentration of 4.0 mg/L solution (Rahman et al. 2012).

### DETERMINATION OF EQUILIBRIUM WATER CONTENT (%)

Water in hydrogels not only provides a moist environment but also controls the permeation of nutrients into the cells and of cellular products out of the hydrogels. The amount of absorbed water is usually expressed as the equilibrium water content (EWC). After subjected to gamma radiation, both hydrogel samples (A1 and A2) were dried in oven at 45°C for 24 h. The dried hydrogel samples with constant weight were immersed in distilled water for 24 h to remove sol fraction. The samples were taken out from the distilled water and dried to get a constant weight in an oven. The EWC was calculated as follows:

$$EWC = \frac{A}{B} \times 100,$$

where A is the weight hydrogel with water absorbed and B is the initial weight of dry hydrogel. EWC is the most significant property of hydrogels, since the water in a hydrogel structure lends them unique properties and potential further applications in biomedical fields (Gibas & Janik 2010).

#### ATTENUATED TOTAL REFLECTANCE-FOURIER TRANSFORM INFRARED SPECTROSCOPY (ATR-FTIR) ANALYSIS

The ATR-FTIR spectra of the hydrogel A1 and A2 were recorded using ATR-FTIR Spectra 2000 (Perkin Elmer) at room temperature. The samples were analysed by directly placing the dried hydrogels on the top plate of Diamond attenuated total reflectance (DTAR) and analysed over range of 4000-650  $\text{cm}^{-1}$ .

#### SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS

The morphology of the samples was investigated by using a Quanta 200 type scanning electron microscope, operating at 30 kV with secondary electrons, in low vacuum mode. For a better observation of the pores, the hydrogels were previously freeze-dried in an ALPHA 1-2/LD device (Martin Christ GmbH, Germany), for 15 h, at  $-65^\circ\text{C}$ . The cross-sections were prepared by cutting the dry hydrogels with a sharp razor blade, in order to expose the internal structures.

#### SWELLING TEST IN DIFFERENT BUFFER PH SOLUTION

In order to determine the pH sensitivity of hydrogel, both dried samples hydrogel A1 and A2 were immersed (at room temperature) into pH buffer solutions (4, 7 and 10) and kept for 120 min. In every 10 min, samples were taken out and weight. The swelling degree (%) in pH solution was calculated from the following relation:

$$\text{Swelling ratio}(\%) = \left( \frac{W_i - W_o}{W_o} \right) \times 100,$$

where  $W_i$  is the mass of the swollen gel at time  $t$  and  $W_o$  is the mass of the dry hydrogel at time 0 to 120 min.

#### ADSORPTION OF METHYLENE BLUE

Both dried samples A1 and A2 immersed in 40 mL of aqueous solution of MB at room temperature ( $27^\circ\text{C}$ ). Every 24, 48, 72, 96 and 120 h, the residual concentration of MB solution was determined using UV-VIS spectroscopy (UV-2401PC, Shimadzu, Japan) using the standard curves.

## RESULT AND DISCUSSION

After the mixture of BC: AA was subjected to the gamma radiation, the mixtures were still in the liquid formed. Then, all mixture was treated with drying process using oven. In order to remove the unreacted AA, the hydrogel was treated with purification process. The hydrogels were soaked into distilled water in 2 h. After that, the hydrogel were washed with distilled water and dried in oven. All of those steps repeated until a constant dried weight was achieved. Figure 2 shows the hydrogel A1 and A2 samples before drying process, after purifying and drying process.

#### EQUILIBRIUM WATER CONTENT (%)

Figure 3 shows the EWC of hydrogel for sample A1 and A2. The EWC of sample A1 was 93.10% while the EWC of sample A2 was 74.83%. The differences occurred due to the amount of AA utilized in both samples where in sample A1 more AA being used compared with sample A2. As a result, water content of hydrogel (BC-g-AA) varied. The single molecule of acrylic acid was polymerised into poly-acrylic acid chain increased when amount of AA increased. Therefore, the EWC in hydrogel has increased.

#### ATR-FTIR ANALYSIS

Figure 4 shows the ATR-FTIR spectrum of pure BC, poly-(acrylic acid) and the formation of hydrogels sample. The interaction between AA and BC molecule can be determined by comparing both hydrogel samples with pure BC spectrum. As can be seen, the pure BC spectra exhibited a C-O stretching vibration at  $1040\text{cm}^{-1}$ , C-O-C stretching of the ether linkage (1, 4- $\beta$ -D glycoside) of cellulose at  $1163\text{cm}^{-1}$  and O-H stretching of intermolecular hydrogen bonding at  $3338\text{cm}^{-1}$ . Whereas the poly-(acrylic acid) spectra exhibited distinctive peaks at  $1701\text{cm}^{-1}$  due to C=O stretching and at  $1166\text{cm}^{-1}$  due to C-O stretching, as well as a broad peak at  $3400\text{-}2575\text{cm}^{-1}$  due to O-H stretching. Although different ratio of AA has been used, all peaks present in both hydrogels spectra are comparable, suggesting that the formation of hydrogels involved the same interaction between BC and AA polymer chain. The

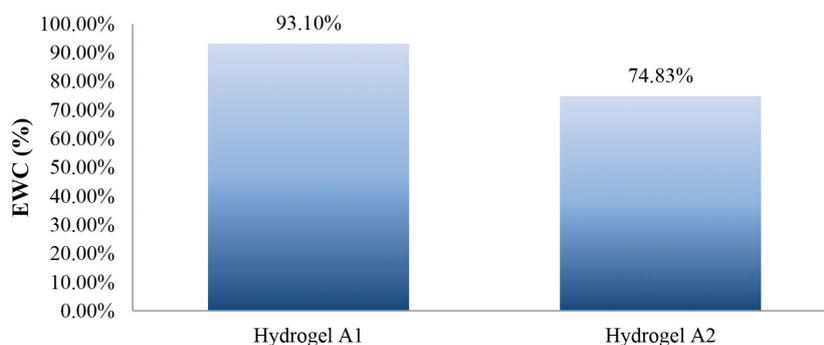


FIGURE 2. EWC (%) of sample hydrogel A1 and A2

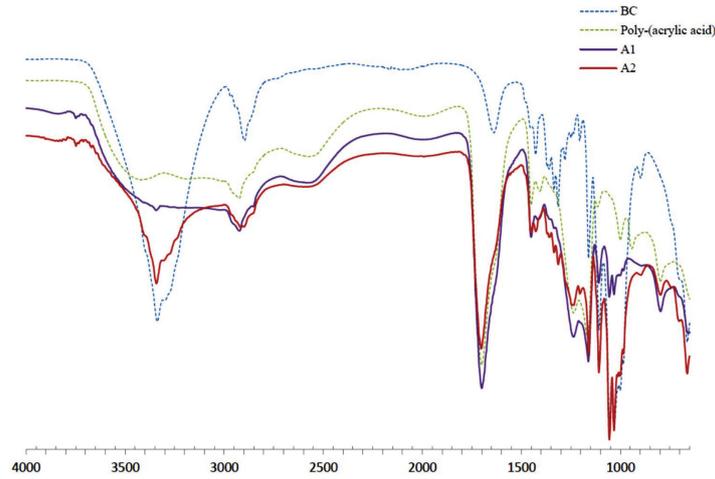


FIGURE 3. The comparison of all ATR-FTIR spectrums

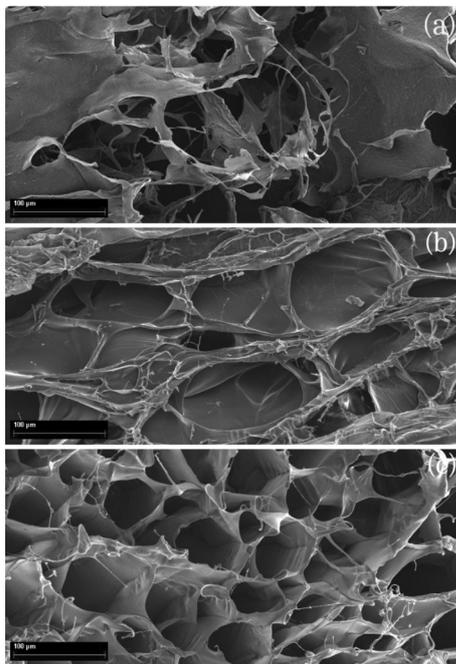


FIGURE 4. SEM images of (a) freeze dried bacterial cellulose, (b) hydrogel A1 and (c) hydrogel

formation of C-O stretching vibrations in the hydrogel sample A1 and A2 spectra indicated the grafting of AA onto BC (Amin et al. 2012).

SEM ANALYSIS

Figure 5 shows the SEM images of pure bacterial cellulose, samples A1 and A2. The images showed highly porous hydrogel was produced due to AA grafted onto BC as a result of the cross-linked networks (Saha et al. 2011). By having this structure hence, numerous amount of water are able to be retained in the structure of hydrogels. A super-hydrophilic/super-absorbent hydrogels was produced with ability to absorb high capacity of water. Although both

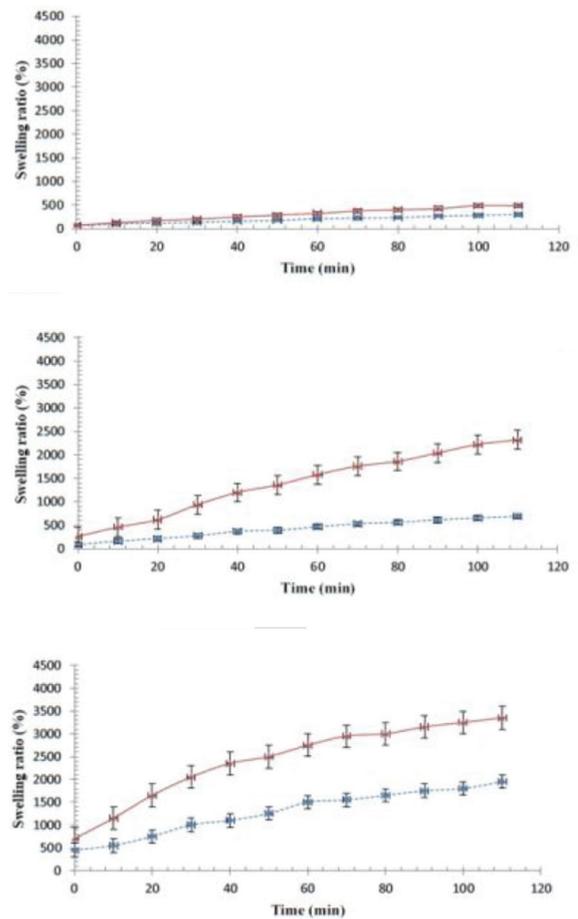


FIGURE 5. Swelling ratio (%) for hydrogel (blue-dotted line)-sample A1 and (red-continue line)-sample A2 at different pH buffer solution (a) pH4, (b) pH7 and (c) pH10

samples produce porous structure, however the distribution of pores in sample A2 also appeared more even and homogeneous throughout the surface area. This will affect the swelling degree of both hydrogels. The homogenous distribution and uniformed pores of A2 may enable water

molecules to be absorbed in every direction with faster time (Johari et al. 2012).

#### SWELLING TEST IN DIFFERENT BUFFER PH SOLUTION

The variations of the swelling ratio (%) for all samples in pH4, 7 and 10 buffer solutions are presented in Figure 6. At pH4 buffer solution, the maximum swelling ratio for sample A1 after 110 min was 300.00% but slightly higher for sample A2 with 487.50%. A different phenomenon was observed when the samples were placed in pH7 buffer solution. Both samples were swelling greatly where A1 swelled with 692.31% while A2 after 110 min swelled up to 2320.00%. Both samples demonstrated that they were able to be a super-absorbent hydrogel where the swelling ratio for A1 was 1950.00% (%) in pH10 buffer solution whereas the A2 was 3350.00% after a period of 110 min, respectively.

From the observation, all samples exhibited greater swelling ratio against time. When the pH buffer solution increased, the swelling ratio of all hydrogels sample increased. On top of that, A2 hydrogel sample has greater swelling ratio compared with A1 sample in all three different pH buffer solutions. It showed that the hydrogels was very sensitive of the pH changes (from pH4 to 10) due to the hydrophilicity contributed by the carboxylic

group in the hydrogel. By increasing the pH the negative charges rise, while the carboxylic group of AA is also deprotonated to negatively charged of carboxylate ion which resulting electrostatic repulsion and causes the hydrogel swells (Spagnol et al. 2012).

#### ADSORPTION OF METHYLENE BLUE

In this experiment, the concentration of MB declined over a period of time as shown in Figure 7. For A1, MB was absorbed 1.29 mg/L at the first 24 and 48 h, 0.76 mg/L for 72 h, 0.52 mg/L for 96 h and finally about 0.34 mg/L for 120 h. The trend was quite similar showed by sample A2 where the MB absorbed was 1.23 mg/L after 24 h, 0.96 mg/L for 48 h, 0.66 mg/L for 72 h, 0.47 mg/L for 96 h and 0.35 mg/L lastly for 120 h. As the comparison made, the results showed in Figure 8 that A2 hydrogel sample adsorbed more MB compared with sample A1. The absorption of MB by both sample occurred because of the imine groups of MB and carboxyl groups of hydrogel may form ionic complexes (Defader et al. 2012). The absorption ability of hydrogel A2 is higher than hydrogel A1 because of the porosity of hydrogel itself as shown in SEM image before. Therefore, more amount of MB was absorbed in hydrogel with high porosity in their structure.

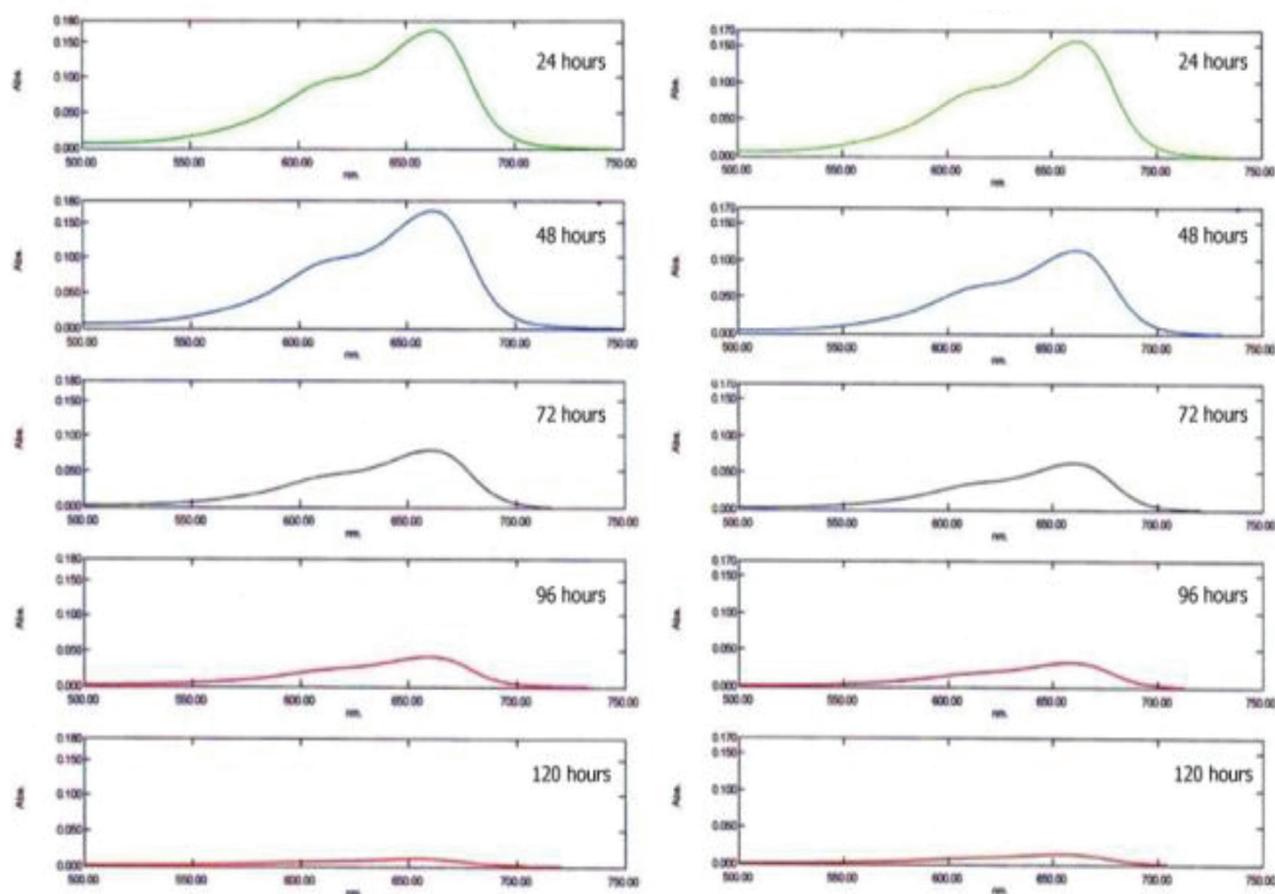


FIGURE 6. UV-VIS spectrum of hydrogel (a) sample A1 and (b) Sample A2 at specific time: 24, 48, 72, 96 and 120 h

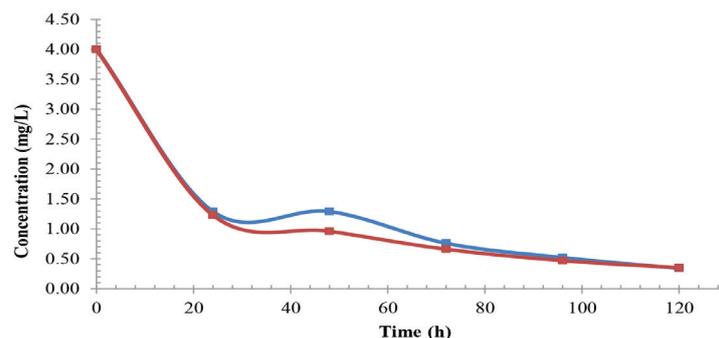


FIGURE 7. Graph concentration (mg/L) vs. time (h) of hydrogel (blue) sample A1 and (red) sample A2

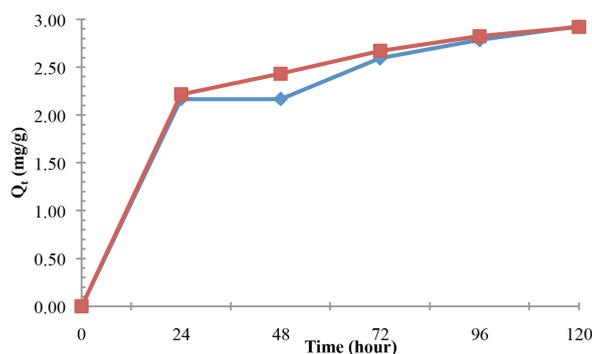


FIGURE 8. Graph of the amount of dye adsorption per unit mass of hydrogel at  $t$ ,  $Q_t$  (mg/g) vs time (hours) of hydrogel (blue) sample A1 and (red) sample A2

### CONCLUSION

Hydrogels were successfully prepared from aqueous mixture of BC and AA by irradiation using  $\text{Co}^{60}$  gamma source (dose: 30 KGy) at room temperature. The ATR-FTIR spectrum showed the existence of peak of C-O which proved the molecules of AA was grafted to BC molecules. The SEM images showed the surface structure of hydrogel with different porosity may affect the swelling degree and adsorption of MB. The hydrogel with high porosity exhibits high swelling degree and high ability adsorption of MB. For swelling test, both samples swelled as the pH of buffer was adjusted to basic hence the percentage of swelling ratio A1 and A2 were also increased. The adsorption of MB in 120 h showed A2 able to absorb more compared with A1. The findings give an overview that BC-g-AA hydrogel is highly potential to be used for MB removal in water.

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