

HYDROGEL OF *KAPPA*-CARRAGEENAN AS ADSORBENT FOR METHYLENE BLUE

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ABSTRACT

Dyes are often used in the textile, printing, paper production and cosmetic industries. Removal of dyes from industrial effluent through adsorption process has attracted many researchers. Methylene blue is one of the widely used dyes. Adsorbent based on *kappa*-carrageenan which can be categorized as an anionic polymer are expected to be able to interact with methylene blue which is a cationic dye. However, the adsorbent in the form of hydrogel was expected to improve the adsorption capacity due to its high density of functional group and the presence of cross linking in the hydrogel will slow down the solubilization of adsorbent in the aqueous solution. The presence of excess potassium ions during the extraction of *kappa*-carrageenan from seaweed is expected to assist in the process of forming a three-dimensional network in the *kappa*-carrageenan structure. Besides that, the removal of water will induce the formation of hydrogen bond between *kappa*-carrageenan chains. Therefore, the effect of temperature during the drying process of *kappa*-carrageenan based hydrogel has been studied. Three different temperatures were used which are room temperature, 90°C and 100°C. The functional group of *kappa*-carrageenan has been identified via Fourier Transform Infrared Spectroscopy (FTIR-ATR) whereas the analysis and distribution on the surface of *kappa*-carrageenan film were identified using Field Emission Scanning Electron Microscopy (FESEM). Swelling tests in distilled water is performed to determine the degree of swelling (DS) for all three methods. Hydrogel that provides highest swelling value are used as Methylene Blue adsorbent. The degree of swelling data showed hydrogel that was produced by drying at room temperature has the high degree of swelling compared to hydrogel produced by drying at 90°C and 100°C. Hydrogel produced at 90°C and 100°C are fragile compared to the rigidity of hydrogel produced at room temperature. For the adsorption of dye using hydrogel produced at room temperature, the highest adsorption capacity was 0.062 mg/g using 0.15 g *kappa*-carrageenan. This indicates that the hydrogel of *kappa*-carrageenan without using cross-linking agents has successfully been developed.

Keywords : *Kappa*-carrageenan; Hydrogel; Degree of swelling; Methylene Blue

INTRODUCTION

Hydrogels are three-dimensional polymer that are capable of storing the solvents and are not easily soluble. The ability of hydrogels to absorb water due to hydrophilic functional groups that attached to polymeric backbone, while resistance to dissolution are due to cross-links between network chains. Hydrogel appearance as matrix, film or microsphere depends on the technique of polymerization used. Hydrogel-forming natural polymers include proteins such as collagen and gelatine and polysaccharides such as starch, alginate and agarose. Synthetic polymers that form hydrogels are traditionally prepared using chemical polymerization methods [1].

Hydrogels can be divided into two categories based on the chemical or physical nature of the cross-links junctions that arise from either polymer chain entanglements or physical interactions such as ionic interactions, hydrogen bonds or hydrophobic interactions [2]. Hydrogels have received considerable attention in the past 50 years, due to their exceptional promise in wide range of applications [1]. Hydrogels are widely used in various applications such as agriculture, food, cosmetics, hygiene products, pharmaceuticals and health [2].

For removal of dyes from aqueous solutions, various techniques have been investigated and developed, among which adsorption is a widely used process within the field of advanced wastewater treatment. Particularly, hydrogel films, are typical adsorbents offering great utility in dye removal. Hydrogels based on polyacrylamide (PAM), polyacrylonitrile (PAN), methacrylic acid, chitosan (CS), polyvinylpyrrolidone (PVP), and their derivatives have been shown to form complexes with dyes. These types of hydrogels are usually used as adsorbents in water treatment owing to advantages including high swelling and wettability, easy loading, creation of chelated complex, and a capacity for semi-continuous operation [3].

Saber-samandari et al., [4] have developed a pullulan-graft-polyacrylamide porous hydrogel to remove methylene blue and reactive blue 2 and they claimed that the pullulan-graft-polyacrylamide porous hydrogel can uptake a maximum of 386.8 mg/g methylene blue compared to 273.3 mg/g reactive blue 2 due to effect of pH on adsorption. Kiani et al., [5] has synthesized copolymer of polyacrylonitrile (PAN) and monoethanolamine (MEA). The results showed that the adsorbent dose effect on the adsorption of 50 mg/L methylene blue where 0.1g PAN-MEA has higher adsorption capacity with 15.15 mg/g compared to 0.3 g with 3.04 mg/g. Bajpai et al., [6] has prepared poly(methacrylic acid) hydrogels by free radical aqueous polymerization of methacrylic acid (MAc) using N,N'-methylene bisacrylamide (MB) as crosslinker and potassium persulfate (KPS) as initiator. Their results showed maximum sorption capacity was found to be 169.43 mg/g while the equilibrium dye uptake was found to increase with the pH of the adsorbate medium and attained an optimum value of 77.8 mg/g for the initial dye concentration of 200 mg/L at 25°C at pH 5.2.

Wang et al., [7] managed to prepare chitosan-g-poly (acrylic acid)/attapulgitite composites (CTS-g-PAA/APT) as adsorbent to remove 2000 mg/L of methylene blue. Their results showed that the adsorption capacities of CTS-g-PAA/APT composites were higher with APT content of 2% (1896 mg/g) compared to CTS-g-PAA (1868 mg/g). Torun and Solpan [8] showed that poly(N-vinylpyrrolidone-co-methacrylic acid) (P(VP/MAA)) hydrogels prepared with gamma radiation were used for uptake of some cationic dyes which are Janus Green B (JGB) and Magenta (M). The adsorption capacity of P(VP/MAA) hydrogels are changed in the order of M are higher compared to JGB with 6.74 and 5.82 mg/g.

Natural polymer-based hydrogels have also been used as an adsorbent due to their safety, biocompatibility, and eco-friendly properties. Carrageenan with a linear chain of sulfonic group (SO_3^-) presents high potential as film forming materials [9]. *Kappa*-carrageenan is a suitable adsorbent for methylene blue since it is an anionic polymer while methylene blue was categorized as a cationic dye. Few studies showed that *kappa*-carrageenan has already been used as an adsorbent of methylene blue. Jo et al., [10] used cellulose/carrageenan/TiO₂ nanocomposites film as an adsorbent. Their study showed that the presence of carrageenan in cellulose/TiO₂ film has increased the adsorption capacity from only 0.8 mg/g to 115.3 mg/g. Mahdavinia et al., [11] has developed nanocomposite hydrogel based on *kappa*-carrageenan and their research showed that the clay content affected the dye adsorption. Nanocomposite hydrogel with 0.2 g of composition has higher methylene blue removal (99%) compared to

pristine hydrogel based on *kappa*-carrageenan (88%). However, in their studies, the pristine hydrogel based on *kappa*-carrageenan were prepared by adding acrylamide and methylene blue inside the *kappa*-carrageenan solution. Besides that, the ammonium persulfate (APS) was added inside the solution as initiator for cross-linking to occur.

Based on previous studies, filler or crosslinking agent had been used for the formation of the hydrogel. However, some of the crosslink agents are usually avoided due to their toxicity. In this research, we focused on the cooling temperature for the development of hydrogel based on *kappa*-carrageenan without using cross-linking agent or filler. The effect of temperature and the presence of cations are the factor that influence the thermo-reversible gel formation of carrageenan. Carrageenan will exist as random coil structure at above 75–80 °C as a result of electrostatic repulsions between adjacent polymer chains. However, the polymeric chains will change conformation to helix structure when the hot solution cooled [12]. These were due to the formation of multiple hydrogen bonds between *kappa*-carrageenan chains as removal of water [13].

Since commercial carrageenan are extracted from the red seaweed using hot alkali solution such potassium hydroxide (KOH) solutions, there is possibility of excess potassium ion present inside the *kappa*-carrageenan samples. Based on Figure 1, in the presence of potassium ion, *kappa*-carrageenan will be able to form strong, rigid hydrogels as it promotes cation-dependent aggregation between carrageenan helices [12]. Besides, the presence of potassium ion will be able to form stiff *kappa*-carrageenan gel as its function is to stabilize the junction zones between the two helices by binding to the negatively charged sulfate groups without hindering cross-linking of the two helices. Therefore, this paper will discuss the effect of cooling temperature on the development of hydrogel of *kappa*-carrageenan and its application on methylene blue removal.

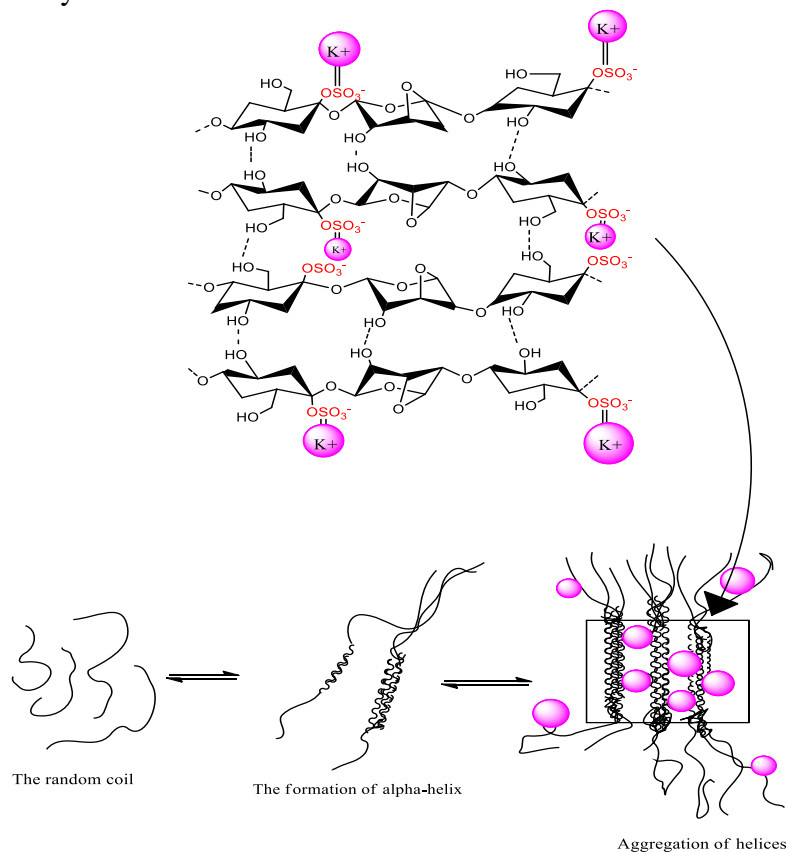


Fig. 1 The gelation mechanism of *kappa*-carrageenan in the presence of potassium ion [12]

EXPERIMENTAL

Preparation of Kappa-Carrageenan Hydrogels

Kappa-Carrageenan based hydrogel was prepared according to report by Wathoni et al., [14]. Hydrogels were prepared by stirring *kappa*-carrageenan and 50 mL distilled water for 12 hours at 80°C. However, a slight modification was made in the drying method for the production of hydrogel films. In Method 1, the material was heated at 90°C, while in Method 2 the heating temperature used was 100°C for 2 hours after the solution was poured into a Teflon mold. For Method 3, the solution was dried in a fume hood at room temperature until film formed.

Characterization of Kappa-Carrageenan Hydrogel

Kappa-Carrageenan hydrogel was characterized by Fourier Transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM). The infrared spectrum analysis was done to determine the functional group on *kappa*-carrageenan and the hydrogel while the scanning electron microscopy to determine the morphology of hydrogel.

Swelling Test

Effect of different drying methods

The degree of swelling of hydrogel was determined by immersing 1.0 g of hydrogel from Method 1, Method 2 and Method 3 in 25 mL of distilled water at room temperature for 30 minutes. The hydrogel films then were extracted and weighed. The degree of swelling was calculated by the following equation:

$$\text{Degree of Swelling (g/g)} = \frac{W_S - W_D}{W_D}$$

where W_S and W_D are the weight of hydrogel after and before the swelling test.

Effect of continuous time based on different methods

A hydrogel film of Method 1, Method 2 and Method 3 was submerged in 25 mL distilled water for 30 minutes at room temperature. After that, the films were removed and weighed before drying. After drying, the film then re-immersed in the water for next time impression. The time taken was 30, 60, 90, 120 and 150 minutes. The degree of swelling calculated using degree of swelling equation.

Effect of non-continuous time based on different methods

Five hydrogel films from Method 1, Method 2 and Method 3 was submerged in 25 mL distilled water at room temperature at different times (30, 60, 90, 120 and 150 minutes). The films were removed and weighed. The degree of swelling calculated using degree of swelling equation.

Effect of different weight for Method 3

0.15, 0.20, 0.25, 0.30, 0.35 and 1.0 g hydrogel from Method 3 was soaked in 25 mL distilled water at room temperature for 30 minutes. Hydrogel films were then extracted and weighed. The degree of swelling was calculated using degree of swelling equation.

Effect of continuous time based on different film weights for Method 3

A hydrogel film of 0.15, 0.20, 0.25, 0.30, 0.35 g was submerged in 25 mL distilled water for 30 minutes at room temperature. After that, the film was removed and weighed before drying.

After drying, the film is re-immersed in the water for a next time impression. The time used was 30, 60, 90, 120 and 150 min. The degree of swelling calculated using degree of swelling equation.

Effect of non-continuous time based on different film weights for Method 3

Five films of 0.15, 0.20, 0.25, 0.30 and 0.35 g were soaked in 25 mL distilled water at room temperature. The time taken is 30, 60, 90, 120 and 150 minutes. Hydrogel films are then extracted and weighed. The degree of swelling was calculated using degree of swelling equation.

Adsorption Studies of Methylene Blue for Method 3

The effect of hydrogel film weight on dye adsorption was carried out at different mass (0.15, 0.20, 0.25, 0.30 and 0.35 g) in 25 mL dye solution (2.0 mg/L) for 30 minutes. The absorbencies of sample were measured using UV-Vis Spectrophotometer at 664 nm corresponding to maximum absorbent of methylene blue. The adsorption capacity, q (mg/g) was calculated using the following equation:

$$\text{Adsorption capacity, } q \text{ (mg/g)} = \frac{(C_i - C_f)V}{w}$$

where C_i and C_f (mg/l) are the concentration of dye at initial and at time respectively. V is the volume of solution (L) and W is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

FESEM Analysis

Fig. 2 (a) showed the EDX mapping on the cross-section of *kappa*-carrageenan hydrogel. Based on this figure, it can be concluded that the distribution of the *kappa*-carrageenan hydrogel on the cross section composition was dominated by potassium sulfate group. Whereas Fig. 2 (b) showed the spectrum with composition value of the element present in the hydrogel during characterization. Based on the EDX composition value, the presence of potassium ion, K^+ (8.2 wt%) was observed. Therefore, it is expected that the physical cross-linking of the hydrogel can be formed through ionic bond between K^+ ion and sulfate ion that present on β -D-galactose group of *kappa*-carrageenan during the drying process.

Fig. 2 (c) showed the morphology of *kappa*-carrageenan hydrogel cross section. The morphology shows a smooth appearance which indicates that the films were homogenous and compact microstructures, which likely caused by strong cohesion forces that appear during the slow drying of the films [15].

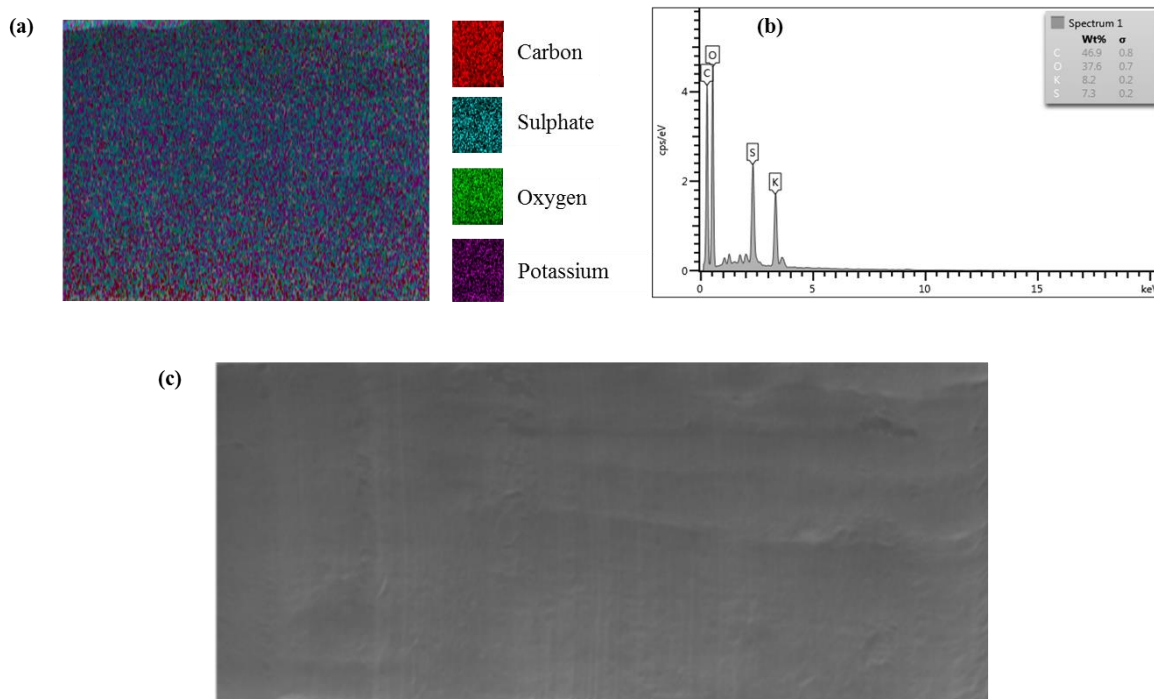


Fig. 2 (a) EDX mapping on cross-section of *kappa*-carrageenan hydrogel film, (b) cross section of *kappa*-carrageenan hydrogel film element analysis, (c) morphology of *kappa*-carrageenan hydrogel cross section

FTIR Analysis

Based on the spectrum of *kappa*-carrageenan powder that shown in Fig. 3, the S-O asymmetry stretches at 1228 cm^{-1} and the peak at 1156 represents the C-O-C asymmetry stretch by the ether group. For the *kappa*-carrageenan hydrogel spectrum, the S-O asymmetry stretches at peak 1225 cm^{-1} shifted from the original peak. This indicate that there is interaction between potassium ions and sulfate ion from β -D-galactose group found in *kappa*-carrageenan. While 1158 cm^{-1} peak represent the C-O-C asymmetric stretching of ether group also shifted from the original peak. Besides, at 927 cm^{-1} peak it shows 3,6-anhydro-D-galactose on a 0.35 g hydrogel spectrum. The broad peak at $3200\text{-}3400\text{ cm}^{-1}$ showed the stretching of the O-H group.

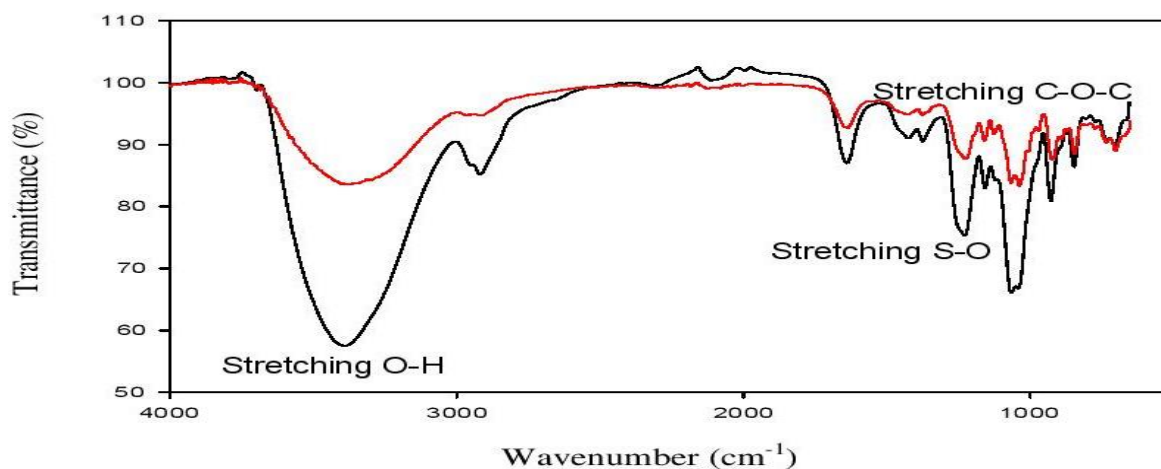


Fig. 3 FTIR spectrum of *kappa*-carrageenan powder and *kappa*-carrageenan hydrogel

Effect of different drying methods

The degree of swelling at different drying method was investigated at 25°C for 30 min and the results were shown in Fig. 4. It was observed that the hydrogel that drying using Method 3 have high degree of swelling (30.63 g/g) compared to Method 1 and Method 2 respectively, having similar degree of swelling (13.34 and 13.10 g/g). This indicate that the cross-links generated by Method 3 are lower compared to Method 1 and Method 2.

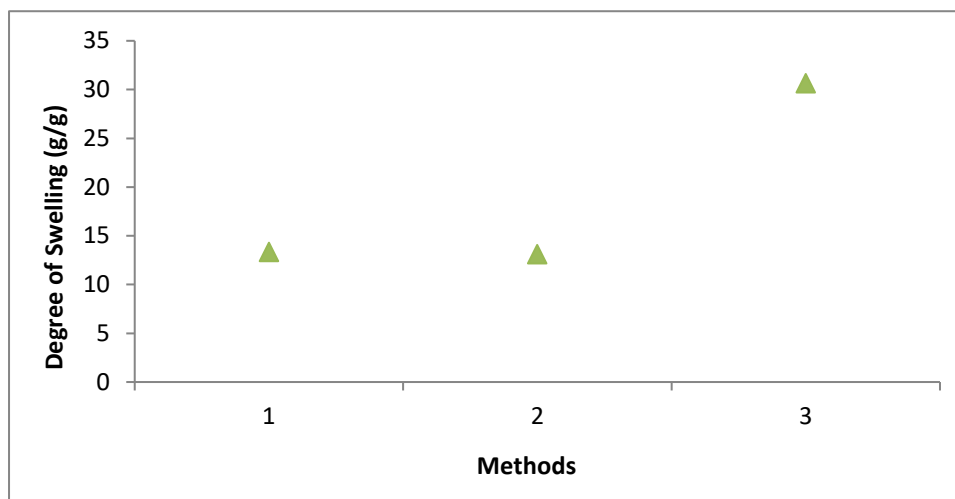


Fig. 4 Effects of different drying methods

Effect of continuous time on different methods

Fig. 5 (a) showed the high-water absorption capacity at the first 30 minutes for hydrogels produced using Method 3 (41.47 g/g) compared to Method 1 (20.82 g/g) and Method 2 (30.82 g/g). However, it can be observed that degree of swelling at 60 minutes was lower compared to 30 min. This showed that *kappa*-carrageenan chains formed multiple hydrogen bond with one another as water is removed during heating process before re-soaking at 60 minutes [13]. This causes rate of water infusing inside the hydrogel becomes slower. However, the increase in the degree of swelling at 120 min showed that the amount of water that infuses inside the *kappa*-carrageenan chains can disrupt the physical cross-links. This has been proven since hydrogel prepared by Method 3 was soluble in water after being soaked for 120 minutes.

Hydrogels that prepared by Method 1 and 2 can still maintain as it has higher cross-links compared to hydrogel that prepared by Method 3. Thus, it reduced the free space between the polymeric chain and limit the water uptake [16]. However, it showed that the physical cross-links for hydrogel that prepared by Method 1 and 2 was reduce as it allowed the more water uptake at 150 min. Overall, the prepared hydrogel based on *kappa*-carrageenan can be reused after being removed from aqueous solution.

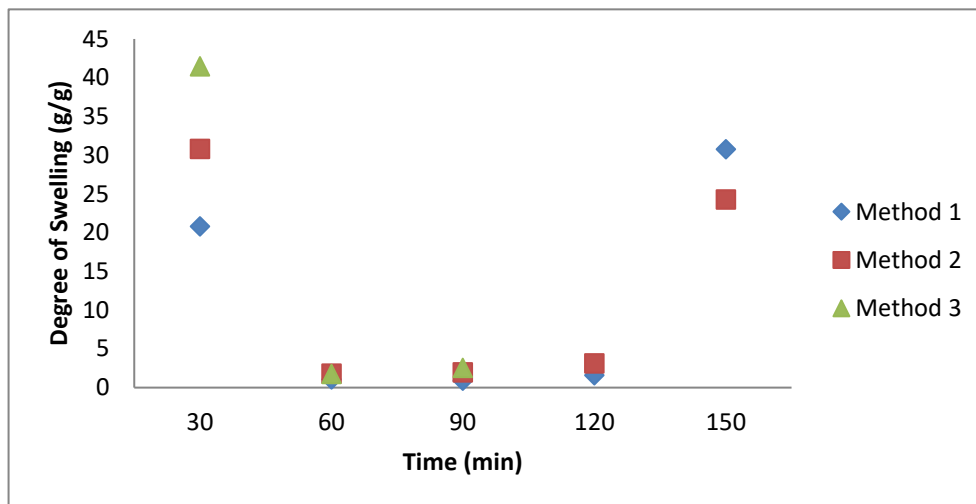


Fig. 5 (a) Effect of continuous time based on different methods

Effect of non-continuous time based on different methods

The effect of non-continuous time based on different methods are shown in Fig. 5 (b). The trends are different when the hydrogel we tested at continuous time. The highest degree of swelling was obtained using Method 2 (99.91 g/g) while soaking the hydrogel film in distilled water for 150 minutes compared to Method 1 (27.64 g/g) and Method 3 (53.59 g/g). According to Okajima et al., [13] drying temperature is very effective in controlling hydrogel volume. Drying temperature below 100°C will lowering the degree of swelling and resulting higher cross-links. Therefore as Method 2 in this research was used 100°C for drying process, increase in degree of swelling can be observed compared to Method 1 which used 90°C. Based on Fig. 5 (a) and (b) showed that the optimum swelling capacity for hydrogel prepared using Method 3 was only around 45-55 g/g. As comparing to the results at 30 min, the hydrogel from Methods 3 was chosen for the effect of different weights.

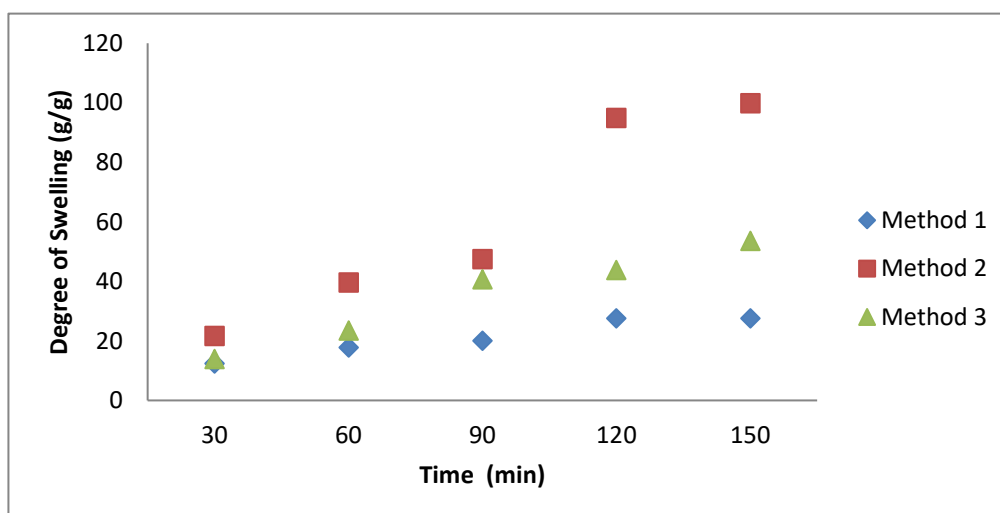


Fig. 5 (b) Effect of non-continuous time based on different methods

Effect of different weight for Method 3

Fig. 6 shows that 0.15 g film hydrogel can absorb more water (41.84 g/g) than 1.0 g film hydrogel (25.57 g/g). This is because, the cross-links formed at 1.0 g are higher compared to 0.15 g causing 1.0 g absorb water at low rate than 0.15 g. This is due to the interaction between potassium ions and sulfate group which causes the cross-linking to increase with the increase in weight of *kappa*-carrageenan [17]. Therefore, increasing the mass of hydrogels will increase the amount potassium ions thus increased the cross-links formation.

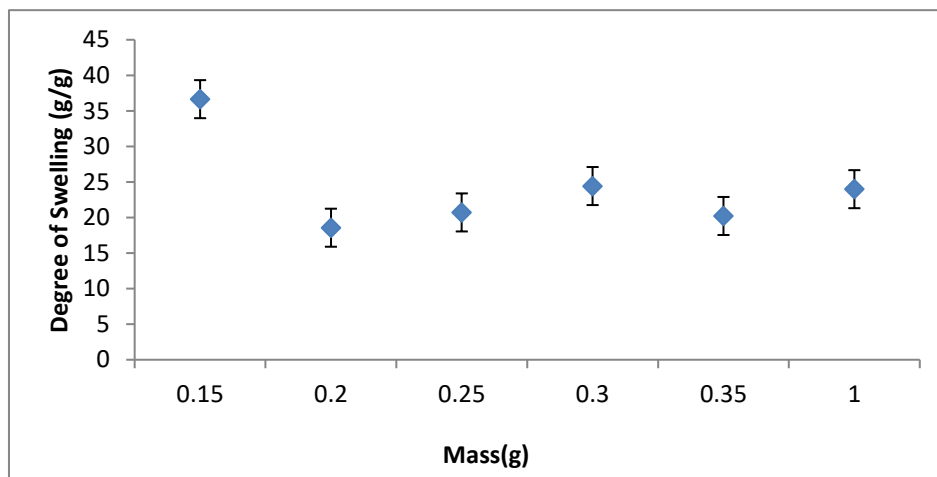


Fig. 6 Effect of different weight for Method 3

Effect of continuous time on different film weights-based on hydrogel prepared by Method 3

Based on Fig. 7 (a), the degree of swelling decreases with increasing time. However, the degree of swelling for hydrogel film of 0.15 g can only obtained the value for 30 minutes because in the next 60 minutes, the hydrogel film dissolves in water. Other hydrogel weight can last for the next 60 minutes with hydrogel films of 0.20 g having the highest cross-linking. 0.15 g shows a high degree of swelling (37.83 g/g) compared to 0.35 g (22.68 g/g) in 30 minutes. This is because, low cross-links were able to absorb large amounts of water compared to high cross-links due to the presence of large cross-linking that reduced the free space between the polymer chains and prevented the entry of the solvent [16]. This also proves that hydrogel from 0.2, 0.25, 0.3 and 0.35 g has higher degree of cross-links compared to hydrogel of 0.15 g as Fig. 6 also showed the lower degree of swelling.

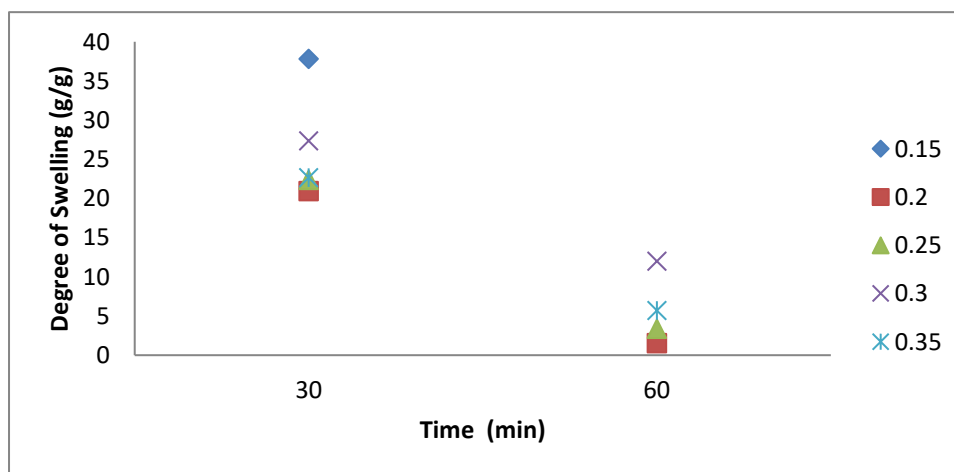


Fig. 7 (a) Effect of continuous time based on different hydrogel film weights

Effect of non-continuous time on different film weights-based on hydrogel prepared by Method 3

Based on Fig. 7 (b), the degree of swelling for 0.15 g hydrogel was the highest (44.06 g/g) compared to other samples and 0.35 g (22.63 g/g) in 30 min to 90 min. This was due to lower cross-links formation inside the 0.15 g hydrogel. The presence of free space between the polymer chains as lower amounts of cross-links will allow more water uptake [18]. However, 0.15 g hydrogel becomes fragile and dissolved in water at 120 minutes. Overall, the increase of *kappa*-carrageenan weight will lead an increase of cross-linking inside the hydrogel as increase of potassium ions and number of functional groups such as hydroxyl and sulphate ion.

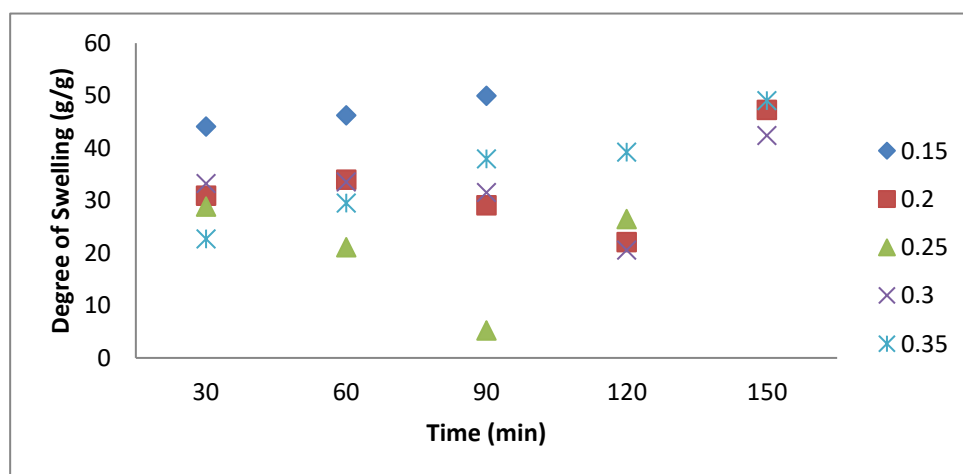


Fig. 7 (b) Effect of non-continuous time based on different hydrogel film weights

Effect of hydrogel film weight on Methylene Blue sorption

Effect of hydrogel film weight on adsorption capacity of methylene blue was investigated using different mass of *kappa*-carrageenan hydrogel such as 0.15, 0.20, 0.25, 0.30 and 0.35 at 25°C for 30 minutes and shown in Fig. 8. It was observed that the adsorption capacity decreases as the mass of adsorbent increases. The highest capacity adsorption of methylene blue was 0.062 mg/g by using 0.15 g of *kappa*-carrageenan hydrogel as the previous swelling test showed that 0.15 g has lower cross-linking compared to other weights.

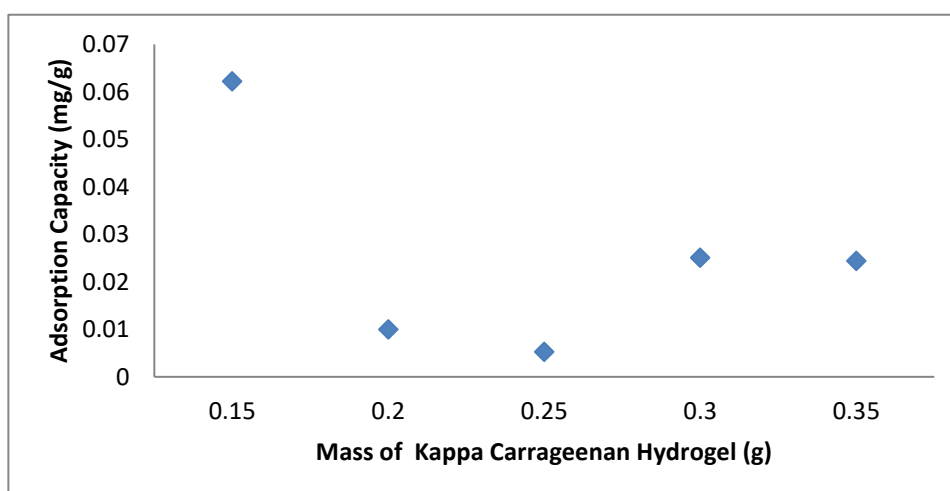


Fig. 8 Effect of hydrogel film weight on Methylene Blue sorption

CONCLUSION

Based on the results, it can be concluded that the hydrogel of *kappa*-carrageenan had successfully been developed. It was observed that the degree of swelling is dependent on the drying temperature used, the weight and contact time that being used.

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REFERENCES

1. Ahmed, E. M. 2015. Hydrogel : Preparation , characterization , and applications : A review. *Journal of Advanced Research* 6(2): 105-121.
2. Mampho, C., Pandey, S., Ramontja, J., Fosso-kankeu, E. & Waanders, F. 2016. Synthesis and Characterization of Superabsorbent Hydrogels Based on Natural Polymers : *Kappa Carrageenan*.
3. Van Tran, V., Park, D. & Lee, Y. 2018. Hydrogel applications for adsorption of contaminants in water and wastewater treatment. *Environ Sci Pollut Res* **25**, 24569–24599.
4. Saber-Samandari, S., Gulcan, H.O., Saber-Samandari, S. *et al.* 2014. Efficient Removal of Anionic and Cationic Dyes from an Aqueous Solution Using Pullulan-graft-Polyacrylamide Porous Hydrogel. *Water Air Soil Pollut* **225**, 2177.
5. Kiani, G., Khodagholizadeh, M. & Soltanzadeh, M. 2013. Removal of methylene blue by modified polyacrylonitrile from aqueous solution.
6. Bajpai, S. & Chand, N. & Mahendra, M.. 2012. The adsorptive removal of cationic dye from aqueous solution using Poly (methacrylic acid) Hydrogels: Part-I. Equilibrium studies. *Agris On-line Papers in Economics and Informatics*. 2. 1609-1624.
7. Wang, Q., Gao, D., Gao, C., Wei, Q., Cai, Y., Xu, J., ... Xu, Y. 2012. Removal of a Cationic Dye by Adsorption/Photodegradation Using Electrospun PAN/O-MMT Composite Nanofibrous Membranes Coated withTiO₂. *International Journal of Photoenergy*, 2012, 1–8.
8. Torun, M., Şolpan, D. 2015. The removal of cationic dyes from aqueous solutions by using poly(N-vinylpyrrolidone-co-methacrylic acid) hydrogel adsorbents: Effects of pH and composition on adsorption. *Fibers Polym* **16**, 735–743.
9. Siti Zarina, Z., Ishak, A. & R. Nazaruddin. 2014. Preparation of Hybrid Nano Biocomposite κ-Carrageenan/Cellulose Nanocrystal/Nanoclay. *The 2013 UKM FST Postgraduate Colloquium* ; 738-743
10. Jo, S., Oh, Y., Park, S. *et al.* 2017. Cellulose/carrageenan/TiO₂ nanocomposite for adsorption and photodegradation of cationic dye. *Biotechnol Bioproc E* **22**, 734–738.
11. Mahdavinia, G. R. & Asgari, A. 2013. Synthesis of kappa-carrageenan-g-poly(acrylamide)/sepiolite nanocopasite hydrogels and adsorption of cationic dye. *Polymer Bulletin* 70(8): 2451-2470.
12. Rhein-Knudsen N, Ale MT, Meyer AS. 2015. Seaweed hydrocolloid production: an update on enzyme assisted extraction and modification technologies. *Mar Drugs*. 2015;13(6):3340–3359.
13. Okajima, M. K., Mishima, R., Amornwachirabodee, K., Mitsumata, T., Okeyoshi, K., & Kaneko, T. 2015. Anisotropic swelling in hydrogelsformed by cooperatively alignes megamolecules. *RCS Advances*, 5(105), 86723-86729.

14. Wathoni, N., Motoyama, K., Higashi, T., Okajima, M., Kaneko, T. & Arima, H. 2016. Physically crosslinked-sacran hydrogel films for wound dressing application. *International Journal of Biological Macromolecules* 89 : 465-470.
15. Ili Balqis, A.M., Nor Khaizura, M.A.R., Russly, A.R., & Nur Hanani, Z.A.. 2011. Effects of Plasticizers on the Physicochemical Properties of Kappa-Carrageenan Films Extracted from *Eucheuma cottonii*
16. Bertoli, G., M. Gindri, I., O. Cubillos, P., R. M. Roesler, C. & V. Salmoria, G. 2018. Investigation on the structure, cross-link, and oxidation index of ultra-high molecular weight polyethylene acetabular liners. *The International Journal of Advanced Manufacturing Technology* (101) : 235-241.
17. Mahdavinia, G. R., Massoudi, A., Baghban, A. & Massoumi, B. 2012. Novel carrageenan-based hydrogel nanocomposites containing laponite RD and their application to remove cationic dye. *Iranian Polymer Journal (English Edition)* 21(9) : 609-619.
18. Lapwanit, S., Sooksimuang, T., & Trakulsujaritchok, T. 2018. Adsorptive removal of cationic methylene blue dye by kappa-carrageenan/poly(glycidyl methacrylate) hydrogel beads: Preparation and Characterization. *Journal of Environmental Chemical Engineering*.