CELLULOSE CHEMISTRY AND TECHNOLOGY

SWELLING BEHAVIOUR AND METHYLENE BLUE ABSORPTION OF CARBOXYMETHYL CELLULOSE HYDROGELS PREPARED FROM MALAYSIAN AGRICULTURAL WASTES BY ELECTRON BEAM IRRADIATION

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Malaysia is the second largest producer of palm oil and generates 18 million tons of empty fruit bunches annually. Sugarcane is another important crop that is widely planted throughout Southeast Asia for sugar production. Both crops generate large amounts of lignocellulosic waste biomass in the form of sugarcane bagasse (SCB) and oil palm fibres (OPF), which can be converted into carboxymethyl cellulose (CMC) and subsequently cross-linked into hydrogels using electron beam irradiation. The irradiated CMC yielded hydrogels with up to 40% gel fraction, which can be increased to 50% with the addition of acrylamide as copolymer. The addition of acrylamide increased hydrogel yields and protected the polymer from chain scission at high radiation doses, up to 40 kGy. Furthermore, the hydrogels produced were stable at pH 3-10, suggesting that pH had a minimal impact on swelling, which affects their performance as absorbents. The methylene blue absorption of all SCB and OPF hydrogels examined in this study ranged from 0.722-0.987 mmol/g, which far exceeded that of bamboo-based activated carbon (0.142 mmol/g). This makes these hydrogels suitable for cationic dye removal and may be applied for the absorption of fertiliser ions in the future.

Keywords: oil palm fibres, sugarcane bagasse, cationic dye removal, electron beam irradiation, carboxymethyl cellulose, hydrogel

INTRODUCTION

Malaysian agriculture is very productive and generates large amounts of biomass. Being the second largest producer of palm oil, Malaysia has 5.85 million hectares of oil palm, generating 21 million tons of empty fruit bunches and 3.5 million tons of palm kernel cake, yearly.[1] Sugarcane is another important cash crop in Malaysia, which ranks 57 globally in sugarcane production.[2] Every year Malaysia produces around 0.83 million tons of sugarcane. Much of the biomass ends up as waste after the extraction of sugar.

With the increasingly stringent regulations on waste discharges and emissions, there is renewed interest in the bioconversion of waste biomass into usable substances, such as carboxymethyl cellulose.[3] Carboxymethyl cellulose (CMC) is a bio-based polymer with a wide industrial usage. Its synthesis from Malaysian agricultural wastes has been previously reported.[4,5] Cellulose from these agricultural wastes was converted into CMC by etherification using sodium monochloroacetate (SMCA).

As CMC is most often derived from cellulosic materials that can be readily extracted from various natural sources, it can be employed as a cost-effective absorbent.[6] CMC exhibits higher adsorption capacities for various aquatic pollutants than unmodified cellulose. However, as CMC polymers derived from most plant sources are fairly water-soluble, they can be cross-linked to yield insoluble hydrogels. There is also a growing demand for hydrogels as three-dimensional scaffolds for expanding their applications in regenerative medicine, tissue engineering and cell culture techniques.[7] All of the applications described above, whether environmental or biomedical, require the resulting hydrogel to be free of toxic substances, which may be released over time. The advantage of hydrogel formation by electron beam irradiation is that the process takes place under mild conditions, *i.e.* room temperature and neutral pH.[8] Therefore, the use of reactive and toxic cross-linking reagents is avoided.

In our study, we determined the efficiency of electron beam irradiation in cross-linking CMC from sugarcane bagasse (SCB) and oil palm fibres (OPF). The synthesised CMC hydrogels were characterised based on their swelling behaviour at different pH, and their ability to function as a cation exchanger based on absorption and retention of methylene blue. Methylene blue is frequently used to measure cation exchange of soil and various soil conditioners, such as CMC hydrogels. The dye itself is also an environmental pollutant from the textile industry.

In the synthesis of cross-linked CMC hydrogels through electron beam irradiation, acrylamide was also grafted to the hydrogels as copolymer, aiming to improve their mechanical stability and water retention.[9] Although electron beam irradiation is able to cross-link CMC without additional reagents, irradiation often leads to chain scission of the polymer, especially at higher irradiation doses. The addition of acrylamide into an electron beam irradiated composite has been shown to improve physical properties and cross-linking efficiency. However, in many studies, acrylamide is a major component in the composite, comprising more than 50% w/w.[10,11]

In the present study, we demonstrated that the addition of a small quantity of acrylamide (10% w/w of CMC) can enhance cross-linking efficiency and protect against chain scission at higher irradiation doses. Furthermore, CMC produced from different agricultural wastes behaved differently when subjected to electron beam irradiation. We also noted that CMC from OPF can be separated into soluble and insoluble fractions. The latter is insoluble in aqueous media and can be directly applied as a methylene blue absorbent, without cross-linking into a hydrogel. This is a unique discovery.

EXPERIMENTAL

Materials

The agricultural wastes used in this study were sugarcane bagasse (SCB) and oil palm fibres (OPF). SCB was collected from vendors selling sugarcane juice at the Taman Connaught night market in Cheras, Kuala Lumpur. The sugarcane was cultivated in Hulu Langat, Selangor. OPF were obtained from the Heng Huat group of companies in Penang.

Preparation of CMC from SCB and OPF

CMC from SCB and OPF was prepared following the procedures described in our previous publications.[4,5] Briefly, 5 g of cellulose pulp were etherified with 6 g of sodium monochloroacetate (SMCA) in 80 mL of isopropanol and in 10 mL of 20% NaOH to yield CMC with a degree of substitution (DS) of approximately 0.7 for both types of CMC.

Separation of soluble and insoluble fractions of CMC from OPF

After etherification with SMCA, it was found that the resulting CMC from OPF could be separated into soluble and insoluble fractions. In contrast, the CMC from SCB was completely soluble. This presented an opportunity to directly utilise the insoluble fraction of CMC from OPF as a bio-based absorbent without the need for cross-linking.

To separate the insoluble fraction, 1 g of CMC from OPF was dissolved in 10 mL of 2% NaOH and heated in a microwave oven for 1 min. The solution was then centrifuged at 7,000 rpm for 5 min and the insoluble CMC fraction was recovered and dried overnight at 50 °C. Soluble oil palm CMC was recovered from the supernatant by precipitation in isopropanol adjusted to pH 7 using nitric acid. The isopropanol CMC mixture was chilled overnight to maximise recovery.

Approximately 70% of oil palm CMC was recovered from the insoluble fraction and the remaining 30% was recovered from the soluble fraction.

Preparation of CMC hydrogel

CMC hydrogel was prepared using electron beam irradiation using the procedures similar to those described by Ibrahim *et al.*[9] and Pushpamalar *et al.*[12] CMC from SCB and OPF was added into distilled water and homogenised using a pestle and mortar to make a paste with 60% w/w CMC.

The resulting mixtures were placed into vacuum-sealed polyethylene bags and sent for irradiation using an EPS-3000 electron beam machine (2 MeV; model EPS-3000, 10 mA current) at Malaysian Nuclear Agency in Bangi, Selangor. The radiation doses used ranged between 5-50 kGy. To determine the effects of acrylamide as a copolymer, the steps were repeated for the CMC samples with the substitution of CMC with 10% w/w acrylamide, as described by Ibrahim *et al.*[9]

The synthesised hydrogels were characterised based on their gel fraction, swelling ratio and cation exchange ability based on the absorption of methylene blue.

Gel fractions for CMC hydrogel

The gel fraction is an indicator of cross-linking efficiency based on the percent of insoluble hydrogel (% gel fraction) compared to the soluble fraction (% sol fraction), as shown in Equation 1 and Equation 2.[12] A total of 0.1 g of dried hydrogel (W_0) was immersed in 5 mL of deionised water for 24 h. The gel was then filtered and weighed. CMC hydrogel was oven dried again at 50 °C overnight to a constant weight (W_1). A high gel fraction indicates good cross-linking efficiency and a higher yield of hydrogel.

$$\% \text{ Sol fraction} = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

$$\text{Gel fraction} = 100 - \text{Sol fraction} \quad (2)$$

where W_0 = weight of hydrogels (g) before the test and W_1 = weight of hydrogels (g) after oven drying overnight, as modified from Pushpamalar *et al.*[12]

Gelation dose

The P_o/Q_o ratio is the extent of chain scission against cross-linking.[12] This ratio influences the mechanical strength of the gel. A higher P_o/Q_o ratio would therefore mean lower cross-linking and *vice versa*. The gelation dose (D_g) is the minimum amount of radiation required to form cross-links. Hence, these two factors affect the entire gelation process. The yield of both these variables is estimated by gel-sol analysis based on the Charlesby-Pinner equation.[12,13] The values of P_o/Q_o and D_g were estimated with the computer tool GelSol95 based on Equation 3, which allows plotting the relationship between sol fraction and gelation dose in the form of a straight line:

$$S + \sqrt{S} = P_o/Q_o + (2 - P_o/Q_o)\,(D_g + D_v) / (D_v + D) \quad (3)$$

where S = sol fraction, P_o = degradation density or the average number of chain scissions per monomer unit and per unit dose, Q_o = cross-linking density or the proportion of monomer units cross-linked per unit dose, D_g = gelation dose, D_v = virtual dose or the dose required for changing the distribution of the molecular weight of the polymer in such a manner that the relationship between weight-average and number-average molecular weight would be equal to 2, and D = radiation dose or cross-linking agent concentration (in the case of chemical cross-linking).[12]

Swelling ratio in various pH media

The swelling ratio was estimated based on the water retention of the respective hydrogels. 0.1 g of dried CMC hydrogel was weighed (W_0) and immersed into 5 mL of distilled water and in phosphate buffer of varying pH (3, 7 and 10) for 24 h, before being filtered and weighed again. Then, the gel was oven dried overnight at 50 °C to a constant weight (W_1). The swelling ratio was calculated using Equation 4 as shown below:

$$\text{Swelling Ratio} = \frac{W_{solution} - W_0}{W_1} \quad (4)$$

where W_0 = weight of hydrogel (g) before test, W_1 = weight of hydrogel (g) after the test, and $W_{solution}$ = weight of hydrogel (g) after immersing into water/solution overnight as modified from Ibrahim *et al.*[9]

Methylene blue absorption

To test the ion absorption and release capability of each CMC hydrogel, 0.1 g of dried CMC hydrogel was placed into a test tube with 1 mL of 0.15 M methylene blue solution and swirled in an orbital shaker for 30 min to facilitate the absorption of ions. To recover the unabsorbed dye, 5 mL of distilled water was then added and swirled for another 30 min. The mixture was filtered into beaker using a mesh. The solution was transferred into a 10 mL volumetric flask for dilution with distilled water to a measurable absorbance range. After standing for 5 min, the absorbance was measured at 668 nm against distilled water as blank. The measurement of the absorption of ions was based on the estimation of unabsorbed ions present in the leftover methylene blue solution.

Methylene blue retention

The hydrogel loaded with methylene blue was recovered and oven-dried overnight. The dried hydrogel was immersed in distilled water for 24 h at room temperature. The release of methylene blue ions was estimated based on the amount of dye present in the distilled water. The absorbance was measured at 668 nm against distilled water as blank.

Statistical analysis

Statistical analyses of all data were performed using SPSS (version 20.0) with one-way ANOVA. Significant differences were determined using Student's t-test for comparisons between two means and Tukey HSD test for comparisons between three or more means. Values were expressed as mean ± S.D. based on three authentic replicates from multiple batches of hydrogels cross-linked *via* electron beam irradiation.

RESULTS AND DISCUSSION

Gel fraction

Results showed that increased CMC concentration reduces the gelation dose of electron beam irradiation, with 60% w/v CMC showing reduced dosages compared to 40% w/v CMC (Table 1). The gelation dose or minimum amount of radiation for cross-linking to occur is an indicator of cross-linking efficiency. Cross-linking efficiency is higher at increased CMC concentration. This is consistent with most previous studies.[12] Blending CMC with 10% w/w of AA was reported to protect against chain scission and increase cross-linking efficiency, as shown by reduced P_o/Q_o values and D_g values, respectively. It was observed that hydrogels produced at 40% w/v CMC tend to be mechanically weak and thus not very suitable to serve as methylene blue absorbents.

The gel fraction is another measure of hydrogel yield as well as cross-linking efficiency. Figure 1 shows that the gel fraction is highly dependent on radiation dose. At lower dose, the density of CMC radicals produced may not be sufficient to form cross-linking bonds, therefore resulting in a low gel fraction. However, chain scission resulted in a lower gel fraction at higher radiation doses, with marked reduction at 30 kGy for CMC from SCB and 50 kGy for CMC from OPF.

Generally, CMC hydrogels at lower radiation doses have lower percentage of gel fraction. The increasing trend of both gel fraction and radiation dose may be due to the increased number of free radicals on the CMC chain, which can easily form more cross-linking between chains.[14] Irradiation creates CMC radicals by the removal of hydrogen.[12,15] These radicals may undergo chain scission, hydrogen transfer, inter-molecular and intra-molecular recombination and disproportionation. Cross-linking occurs when CMC radicals on separate chains are linked together.

The addition of acrylamide as copolymer increased gel fraction and protected against chain scission. As shown in Figure 1, chain scission tends to reduce the gel fraction by about 30 kGy. CMC from both sources exhibited much higher gel fractions, even at high radiation doses, beyond 30 kGy, with the addition of acrylamide. Hydrogels from both sources were cross-linked at 60% w/v carboxymethyl cellulose (CMC), and comparisons were made between hydrogels with and without acrylamide (AA) as copolymer.

Table 1
Gelation dose (D_g) and chain scission (P_o/Q_o) of SCB and OPF hydrogels irradiated at different concentrations

CMC hydrogel	P_o/Q_o	D_g (kGy)	CMC hydrogel	P_o/Q_o	D_g (kGy)
SCB hydrogel					
40% with AA	1.29	2.61	40% without AA	1.42	2.26
60% with AA	1.26	1.25	60% without AA	1.25	1.74
OPF hydrogel					
40% with AA	1.36	3.03	40% without AA	1.75	3.75
60% with AA	1.23	2.36	60% without AA	1.56	2.73

*% values are w/v CMC in water; hydrogels with AA were blended with 10% AA per weight of CMC

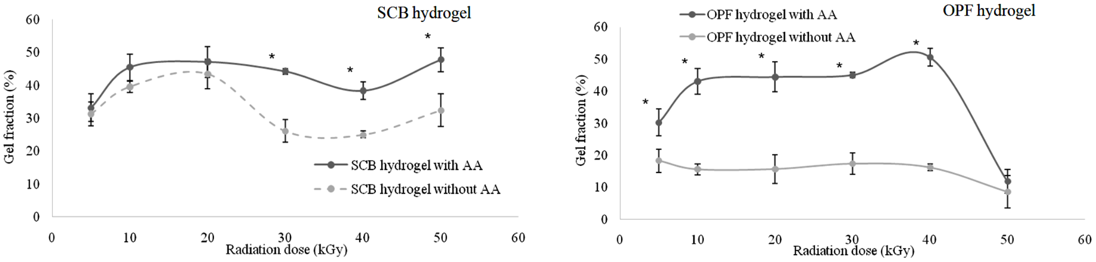

Figure 1: Swelling ratio against radiation dose of sugarcane bagasse (SCB) hydrogel and oil palm fibre (OPF) hydrogel (significant differences at $P < 0.05$, as measured by the Student's t-test between hydrogels with AA and without AA were indicated with an asterisk)

Fewer radicals are formed at lower radiation doses and when the distance between radicals is too great, degradation predominates. It was also reported by Fekete *et al.*[16] that the solubility of CMC is a function of reduced molecular weight, and gelation would be reduced because of shorter polymer chains. The addition of acrylamide as a copolymer would help bridge shorter polymer chains and increase cross-linking efficiency. However, the gel fraction was found sharply lowered at 50 kGy for OPF CMC with acrylamide, which could be due to the formation of some polyacrylamide homo-polymers.[9]

AA has been shown to improve the mechanical properties of carbohydrate composites upon electron beam irradiation. Many of such studies use a much higher composition of AA. Dai *et al.*[10] studied polymerisation of 0.2 g of CMC from pineapple peel with 4 g of AA. Moghaddam *et al.*[11] studied irradiation of tragacanthin, a carboxymethylated carbohydrate, with AA at a 1:1 ratio.

Our study is unique since we showed that a 10% w/w of AA is enough to protect CMC from chain scission at higher irradiation doses. Ibrahim *et al.*[9] studied electron beam irradiation of CMC and AA blends from 10% w/w to 30% w/w of AA. However, because they used a very dilute CMC concentration of about 10% w/v CMC, the protective effect of AA was not observed. In their study, all blends showed reduction of the gel fraction at above 30 kGy.

Swelling behaviour

The swelling behaviour of CMC hydrogels is dependent on cross-linking efficiency, hence on the radiation dose. The relationship between the swelling ratio and the gel fraction obtained at 60% w/v CMC is shown in Figure 2. The R^2 for the correlation was 0.7868 for the SCB hydrogel and 0.6511 for the OPF hydrogel. The hydrogels from both sources were cross-linked at 60% w/v carboxymethyl cellulose (CMC), and comparisons were made between hydrogels with and without acrylamide (AA) as copolymer.

In general, the gel fraction increases at favourable radiation doses, resulting in higher cross-linking density. Consequently, hydrogels became more packed, which restricted chain motion.[9] A more rigid gel layer, which is tightly packed, means lower relaxation of polymer chains, and this would lessen the ability of the hydrogel to absorb water. As a result, the rigid structure cannot be expanded, which increases the mechanical strength of the hydrogel. This phenomenon agrees with Suo *et al.*,[17] where the water absorbency of CMC hydrogel copolymer decreases considerably with an increase in the cross-linker concentration.

Upon electron beam irradiation, CMC hydrogels create a denser cross-linking bond, which reduces swelling. This dependence is in accordance with the afore-mentioned study by Pekel *et al.*[18] on hydroxypropylmethyl cellulose. Similar research work by Ibrahim *et al.*[9] showed that good swelling behaviour was accompanied by a lower gel fraction, due to a relatively low number of intermolecular bonds between CMC chains, which allowed the polymer to absorb water and various ions bound to the polymer chain, causing the hydrogel to swell.

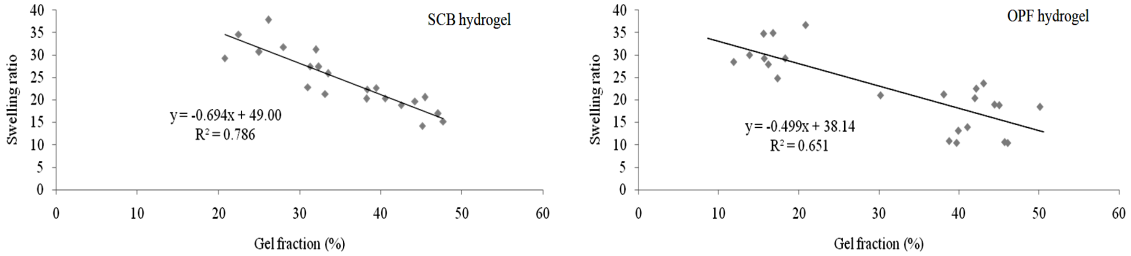

Figure 2: Scatter-plot showing the correlation between swelling ratio and gel fraction of sugarcane bagasse (SCB) hydrogel and oil palm fibre (OPF) hydrogel

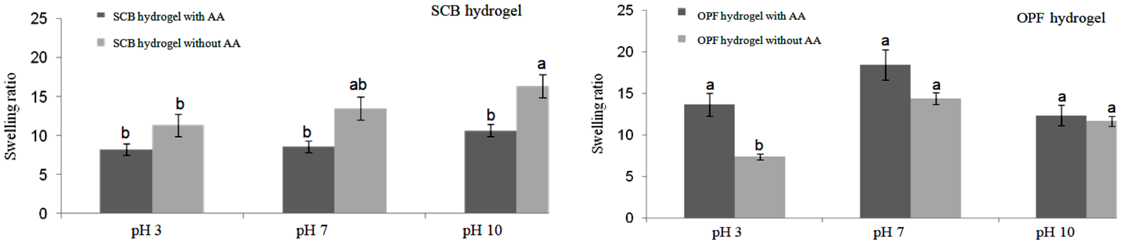

Figure 3: Swelling at different pH of sugarcane bagasse (SCB) hydrogel and oil palm fibre (OPF) hydrogel (significant differences at $P < 0.05$ as measured by the Tukey HSD test between SCB and OPF hydrogels at different pH were indicated with different letters (a–b))

In summary, an increase in gel fraction causes a reduction in swelling. Swelling is affected by the inclusion of acrylamide as copolymer. The inclusion acrylamide in the gel matrix increases the number of cationic groups, which bind with the anionic group of CMC, reducing the swelling. Furthermore, the hydrophobic nature of acrylamide increases the mechanical strength of the hydrogel. This observation is in agreement with the study done by Wang *et al.*,[19] who concluded that the addition of acrylamide resulted in a reduction in ionic hydrophilic groups because of electrostatic repulsion in the network, which eventually decreases the swelling ratio.

Swelling behaviour at different pH

CMC hydrogels are often expected to be pH sensitive as protonation and deprotonation of the hydroxyl groups alter the charge of the polymer strands.[12] Deprotonation endows the polymer strands with a negative charge, which would attract water and increase swelling. Swelling of SCB hydrogels with and without AA remained fairly constant, with only a small increase at pH 10 for the SCB hydrogel without AA (Fig. 3). The hydrogels from both sources were cross-linked at 60% w/v carboxymethyl cellulose (CMC), and comparisons were made between the hydrogels with and without acrylamide (AA) as copolymer. Some increase in swelling was observed pH 7 and pH 10 for OPF hydrogel without AA, but mostly the swelling ratios were similar across different pH. We therefore conclude that the radiation dose, which affects cross-linking density and gel fraction, has a much greater impact on swelling, compared to pH.

Absorption and retention of methylene blue

The cation exchange capacity of CMC hydrogels and the insoluble CMC from OPF, based on the absorption and retention of methylene blue, is shown in Table 2. The absorption ability varies according to the radiation dose used to cross-link the hydrogels, lower doses (20 and 30 kGy) leading to slightly higher absorption than higher doses (40 kGy). In terms of methylene blue retention, all the hydrogels and the insoluble CMC from OPF showed excellent retention. All the absorbents retained more than 98% of the absorbed methylene blue after 24 h immersion in distilled water.

In general, the bio-absorbents derived from OPF showed higher absorption of methylene blue than those from SCB. This also includes insoluble CMC from OPF. The inclusion of acrylamide as a copolymer did not improve methylene blue absorption, even though it is still desirable because it increases gel fraction and consequently hydrogel production.

Table 2
Cation exchange capacity of SCB and OPF hydrogels (with and without AA) and the insoluble CMC from OPF based on absorption and retention of methylene blue

Material	Dosage (kGy)	Absorption (mmol/g)	Release (mmol/g)	Retention (%)
SCB hydrogel without AA	20	0.791 ± 0.059^{ab}	0.006 ± 0.001^{b}	99.27
	30	0.827 ± 0.052^{a}	0.006 ± 0.001^{b}	99.28
	40	0.723 ± 0.032^{b}	0.007 ± 0.002^{a}	98.97
SCB hydrogel withAA	20	0.892 ± 0.037^{a}	0.005 ± 0.001^{b}	99.40
	30	0.797 ± 0.111^{ab}	0.005 ± 0.001^{b}	99.35
	40	0.722 ± 0.044^{b}	0.007 ± 0.001^{a}	99.01
OPF hydrogel without AA	20	0.954 ± 0.061^{a}	0.005 ± 0.001^{a}	99.48
	30	0.911 ± 0.082^{a}	0.002 ± 0.001^{b}	99.78
	40	0.771 ± 0.024^{b}	0.002 ± 0.001^{b}	99.74
OPF hydrogelwith AA	20	0.924 ± 0.020^{b}	0.009 ± 0.001^{ab}	99.03
	30	0.987 ± 0.026^{a}	0.011 ± 0.002^{a}	98.89
	40	0.869 ± 0.090^{b}	0.008 ± 0.001^{b}	99.08
Insoluble CMC from OPF	n.a.	0.924 ± 0.080	0.004 ± 0.001	99.55

Abbreviations: SCB = sugarcane bagasse, OPF = oil palm fibre, CMC = carboxymethyl cellulose, AA = acrylamide and n.a. = not applicable (significant differences at $P < 0.05$ as measured by the Tukey HSD test between different radiation dosages for the same material were indicated with different superscripts (a-b))

Methylene blue absorption is a function of cation-exchange, accessibility to the gel matrix and non-ionic attraction. Methylene blue is a cationic compound with aromatic organic groups.[20] It can bind to the COO− group of CMC by the electrostatic force and also interact non-ionically with −OH groups.

However, because of its size, the accessibility of the methylene blue ion to the gel matrix would also influence absorption. This would explain the difference in absorption observed at different radiation doses, as the radiation dose affects cross-linking density and gel fraction.

Hameed *et al.*[21] reported that bamboo-based activated carbon had a maximum methylene blue absorption capacity of 454.2 mg/g or 0.142 mmol/g. This is much lower than the values reached by the OPF and SCB hydrogels reported in this study, which ranged from 0.722-0.987 mmol/g. Activated carbon developed from other sources by Hameed *et al.*[21] achieved an absorption capacity of 0.002-0.147 mmol/g. The high absorption properties of these CMC hydrogels exceed by far those of activated carbon, suggesting that the hydrogels are suitable biomaterials for use as methylene blue absorbents for the removal of the dye from industrial wastewater.

The insoluble CMC from OPF (Table 2) is of particular interest. It showed high absorption capacity of methylene blue of 0.924 ± 0.080 mmol/g, accompanied by 99.55% retention after 24 h immersion. The fact that it is insoluble means that it can be applied directly as a bioabsorbent without cross-linking. Moreover, the insoluble CMC from OPF comprises approximately 70% of CMC produced after etherification of OPF cellulose. Besides absorption of methylene blue, the insoluble CMC from OPF also absorbs phosphate ions (1.736 mmol/g) and potassium ions (1.083 mmol/g).[20] In comparison, lower absorption capacity of methylene blue was recorded in palm kernel fibres (0.298 mmol/g) by El-Sayed[22] and in coconut coir dust (0.092 mmol/g) by Etim *et al.*[23]

Furthermore, because methylene blue is often used as a measure of cation exchange in soil science, these hydrogels may also be used as soil conditioners to prevent the leaching of fertiliser ions. Work on these ions is in progress and we intend to submit another manuscript on the topic in the near future.

CONCLUSION

Widely planted in Southeast Asia, oil palm and sugarcane are major crops that generate large amounts of waste biomass, which can be converted into CMC and cross-linked into hydrogels, using electron beam irradiation. The methylene blue absorption of all the hydrogels examined in this study exceeded by far that of activated carbon. This makes the absorbent hydrogels suitable for cationic dye removal from industrial wastewater. The insoluble CMC developed from OPF is of particular interest, as it showed high absorption and retention of methylene blue, coupled with the fact that it can be used as an absorbent without cross-linking. In the future, we would like to explore the possibility of applying the high cation exchange capacity of these absorbents to prevent leaching of fertiliser ions, which is a major problem in the tropics.

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REFERENCES

[1] DoA, Industrial Crops Statistics, Department of Agriculture, Peninsular Malaysia, 218 pp., (2018), http://www.doa.gov.my/index/resources/aktiviti_sumber/sumber_awam/maklumat_pertanian/perangkaan_tanaman/perangkaan_tnmn_industri_2018.pdf

[2] FAO, FAOSTAT, Food and Agriculture Organization (FAO) of the United Nations, (2017), http://www.fao.org/3/X0513E/x0513e22.htm

[3] D. Glew, L. C. Stringer and S. McQueen-Mason, *Waste Manag.*, **33**, 1499 (2013), https://doi.org/10.1016/j.wasman.2013.03.005

[4] P. X. Chia, L. J. Tan, C. M. Y. Huang, E. W. C. Chan and S. Y. W. Wong, *e-Polymers*, **15**, 411 (2015), https://doi.org/10.1515/epoly-2015-0133

[5] C. M. Y. Huang, P. X. Chia, C. S. S. Lim, J. Q. Nai, D. Y. Ding *et al.*, *Cellulose Chem. Technol.*, **51**, 665 (2017), http://www.cellulosechemtechnol.ro/pdf/CCT7-8(2017)/p.665-672.pdf

[6] S. Hokkanen, A. Bhatnagar and M. Sillanpää, *Water Res.*, **91**, 156 (2016), https://doi.org/10.1016/j.watres.2016.01.008

[7] S. Utech and A. R. Boccaccini, *J. Mater. Sci.*, **51**, 271 (2016), https://dx.doi.org/10.1007/s10853-015-9382-5

[8] W. E. Hennink and C. F. van Nostrum, *Adv. Drug Deliv. Rev.*, **64**, 223 (2012), https://doi.org/10.1016/S0169-409X(01)00240-X

[9] S. Ibrahim, K. Salmawi and A. H. Zahran, *J. Appl. Polym. Sci.*, **104**, 2003 (2007), https://doi.org/10.1002/app.25916

[10] H. Dai, Y. Zhang, L. Ma, H. Zhang and H. Huang, *Carbohyd. Polym.*, **215**, 366 (2019), https://doi.org/10.1016/j.carbpol.2019.03.090

[11] R. H. Moghaddam, S. Dadfarnia, A. M. H. Shabani and M. Tavakol, *Carbohyd. Polym.*, **206**, 352 (2019), https://doi.org/10.1016/j.carbpol.2018.10.030

[12] V. Pushpamalar, S. J. Langford, M. Ahmad, K. Hashim and Y. Y. Lim, *J. Appl. Polym. Sci.*, **128**, 451 (2012), https://doi.org/10.1002/app.38192

[13] A. Shyichuk and G. Tokaryk, *Polimery*, **50**, 219 (2005), https://doi.org/10.14314/polimery.2005.219

[14] S. Sultana, M. Islam, N. Dafader, M. Haque, N. Nagasawa *et al.*, *Int. J. Chem. Sci.*, **10**, 627 (2012), https://www.tsijournals.com/articles/effect-of-mono-and-divalent-salts-on-the-properties-of-carboxymethyl-cellulose-hydrogel-under-irradiation-technique.pdf

[15] B. Fei, R. A. Wach, H. Mitomo, F. Yoshii and T. Kume, *J. Appl. Polym. Sci.*, **78**, 278 (2000), https://doi.org/10.1002/1097-4628(20001010)78:2%3C278::AID-APP60%3E3.0.CO;2-9

[16] T. Fekete, J. Borsa, E. Takács and L. Wojnárovits, *Cellulose*, **21**, 4157 (2014), https://doi.org/10.1007/s10570-014-0445-6

[17] A. Suo, J. Qian, Y. Yao and W. Zhang, *J. Appl. Polym. Sci.*, **103**, 1382 (2007), https://doi.org/10.1002/app.23948

[18] N. Pekel, F. Yoshii, T. Kume and O. Guven, *Carbohyd. Polym.*, **55**, 139 (2004), https://doi.org/10.1016/j.carbpol.2003.08.015

[19] H. Wang, Z. Wang and B. Zhu, *React. Funct. Polym.*, **67**, 225 (2007), https://doi.org/10.1016/j.reactfunctpolym.2006.11.004

[20] H. D. Utomo, R. Y. N. Phoon, Z. Shen, L. H. Ng and Z. B. Lim, *Nat. Resour.*, **6**, 209 (2015), https://doi.org/10.4236/nr.2015.64019

[21] B. H. Hameed, A. M. Din and A. L. Ahmad, *J. Hazard. Mater.*, **141**, 819 (2007), https://doi.org/10.1016/j.jhazmat.2006.07.049

[22] G. El-Sayed, *Desalination*, **272**, 225 (2011), https://doi.org/10.1016/j.desal.2011.01.025

[23] U. J. Etim, S. A. Umoren and U. M. Eduok, *J. Saudi Chem. Soc.*, **20**, 67 (2016), https://doi.org/10.1016/j.jscs.2012.09.014