

Preparation and characterization of poly(vinyl alcohol)/sodium alginate/TEMPO-oxidized cellulose nanofiber hydrogel for dye removal

Wing Shan Chan ¹⁾, Yuichi Shibata ¹⁾, Kento Nishi ¹⁾, Tatsushi Matsuyama ²⁾, Junichi Ida ^{2)*}

1) *Graduate School of Science and Engineering, Soka University, 1-236, Tangi-cho, Hachioji, Tokyo, 192-8577, Japan*

2) *Faculty of Science and Engineering, Soka University, 1-236, Tangi-cho, Hachioji, Tokyo, 192-8577, Japan*

* *Corresponding author: ida@soka.ac.jp*

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Abstract The composite hydrogel of poly(vinyl alcohol) (PVA)/sodium alginate (SA)/TEMPO-oxidized cellulose nanofiber (CNF) was prepared and employed as an effective adsorbent for dye removal. The effect of the weight ratio of incorporated SA and CNF components on the mechanical and dye removal properties of the hydrogel was examined in detail. While the PVA concentration and the SA + CNF concentration were maintained as constant (7.5 and 1.0 wt%, respectively), the weight ratios of SA:CNF were changed from 10:0 to 7:3. Cross-linking of PVA, SA, and CNF were carried out by using boric acid/borax and calcium chloride. The mechanical properties of prepared hydrogels were investigated by a compressive stress test and a durability test under severe agitation in a solution.

The PVA/SA hydrogel with no CNF addition (the 10:0 hydrogel) showed the highest compressive strength, and the elastic modulus is approximately 40 times greater than the highest reported value of the conventional PVA hydrogel cross-linked by glutaraldehyde (GA). The hydrogel prepared with SA:CNF ratio of 9:1 (the 9:1 hydrogel) showed the second-highest elastic modulus. In terms of durability, the 9:1 hydrogel was the highest. While the breakage ratio of the 9:1 hydrogel under very severe agitation condition of 2750 rpm was essentially negligible, it was reported that the conventional PVA hydrogel crosslinked with sodium sulfate was completely broken. Even under 3000 rpm, only 12% of the beads were broken for the 9:1 hydrogel.

Dye removal experiment was carried out by using methylene blue (MB) as a model dye. The result shows that the highest MB adsorption capacity of 243.9 mg g⁻¹ was obtained for the 9:1 hydrogel. The value was 1.4 times higher than that of the highest reported value for the conventional PVA-based adsorbent. With superior mechanical and dye adsorption properties, the developed PVA/SA/CNF hydrogel can be considered as a potential alternative for dye removal.

Keywords: cellulose nanofibers, composite hydrogel, dye removal, methylene blue, poly(vinyl alcohol)

1. Introduction

Synthetic dyes are generally used in various industries due to their easy application and inexpensive properties. However, dye effluents have become a growing concern due to their hazards to the environment and living things. Approximately 100 tones of dye effluent per year are discharged from the textile industry alone (Katheresan et al. 2018). Ingestion of dyes can cause serious health problems. For example, since cationic dyes (e.g. methylene blue) can interact with negatively charged cell membrane surfaces, these can enter cells easily, leading to long-lasting influences on the human organism (Li 2010). The adsorption dye removal method offers various advantages, such as the ability to treat a wide variety of dyes, easy operation, no formation of toxic by-products and secondary wastes (Katheresan et al. 2018). Therefore, it is one of the preferred techniques of dye removal.

Poly(vinyl alcohol) (PVA) hydrogels have been studied as dye adsorbents by many researchers due to their low cost, non-toxic, high chemical stability, and porous characteristics (Sinha & Chakma 2019). However, their poor mechanical strength and tendency to agglomerate are the main drawbacks in dye removal applications (Wu & Wisecarver 1991). Various modification methodologies have been tried to improve the physicochemical characteristics of PVA hydrogels. Dinh & Bach (2014) tried to change the surface properties of PVA hydrogel by incorporating sodium alginate (SA) and successfully suppressed the agglomeration of gel particles (Dinh & Bach 2014). To improve the mechanical strength of PVA hydrogel, nanocellulose is often used to synthesize composite hydrogels. Cellulose nanofiber (CNF) is a nanocellulose obtained from a plant cell wall in a form of filamentous fragments. It contains both amorphous and crystalline domains with dimensions of 5-30 nm

in width and an aspect ratio of over 50 (Nascimento et al. 2018). Moreover, oxidation of CNF using 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) radical converts C6 primary hydroxyl groups into carboxylate groups, which introduces negative charges to the cellulose surface (Saito & Isogai 2006). Due to its high stiffness, high aspect ratio, and surface carboxylate groups, TEMPO-oxidized CNF can be a good candidate to be used as a reinforcing agent to improve the weak mechanical properties of the PVA hydrogel. Zhang et al. (2018) have prepared SA/CNF hydrogel using calcium chloride as a crosslinking agent and improved the mechanical stability of the hydrogel. Han et al. (2013) synthesized borax cross-linked PVA hydrogels with CNF and examined the effects of particle size, aspect ratio, crystal structure, and crystallinity of CNFs on the compression property of the hydrogels. The results showed that the compressive strength of CNF reinforced hydrogel was 21 times greater than that of the pure PVA hydrogel (Han et al. 2013). However, synthesis and application for dye removal of the composite hydrogel consisting of PVA, SA, and TEMPO-oxidized CNF have not been reported yet.

In this study, by incorporating both SA and TEMPO-oxidized CNF, the PVA/SA/CNF hydrogels were prepared and the effects of weight ratios of SA and CNF on the mechanical properties and dye adsorption performance were examined. The mechanical properties of prepared hydrogels were investigated by a compressive stress test and a durability test. Also, a dye adsorption experiment was performed by using methylene blue (MB) as a model dye.

2. Materials and Methods

2.1 Materials

Sodium alginate (SA) powder, boric acid, and calcium chloride were purchased from FUJIFILM Wako Pure

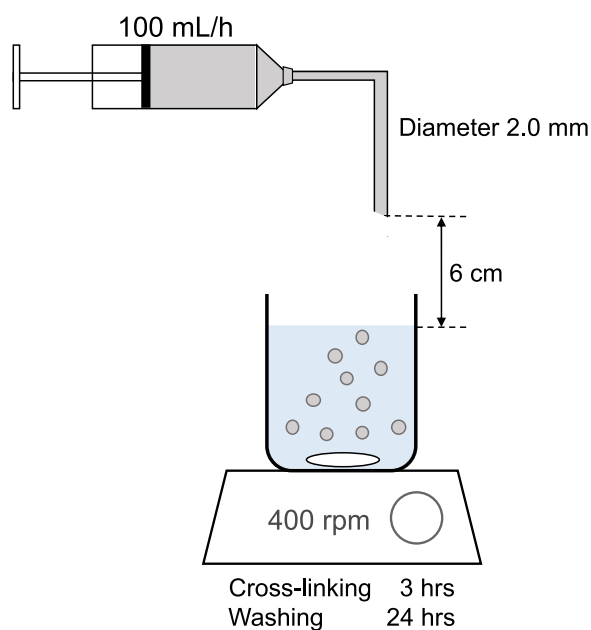


Fig. 1. Experimental set up for the preparation of PVA/SA/CNF hydrogels.

Chemical Corporation. Poly(vinyl alcohol) (PVA) (Kuraray, Japan), TEMPO-oxidized CNF dispersion (Nippon Paper Group, Japan), and borax (KENEI Pharmaceutical Co., Ltd.) were also used in the experiments.

2.2 Preparation of PVA/SA/CNF Hydrogel

Four different 50 mL of polymers solutions containing PVA, SA, and CNF were prepared by changing each component concentration as shown in Table 1. In this study, while the PVA concentration and the (SA + CNF) concentration were maintained as constant (7.5 and 1.0 wt%, respectively), the weight ratio of SA:CNF was changed from 10:0 to 7:3. Different amounts of SA powder (0.5, 0.45, 0.4, and 0.35 g) were dissolved in deionized water. After 0.75 g of PVA was added into the solution, the mixture was transferred to an autoclave (TOMY, SX-500). It was heated at 121°C for 20 min, followed by stirring at 80°C in a water bath for 50 min. Different amounts of 1 wt% CNF dispersion (0, 5, 10, and 15 g) were

Table 1. Compositions of PVA/SA/CNF hydrogels used in this study.

Sample name (SA:CNF)	PVA (wt%)	SA (wt%)	CNF (wt%)
10:0	7.5	1	0
9:1	7.5	0.9	0.1
8:2	7.5	0.8	0.2
7:3	7.5	0.7	0.3

added into the solution and stirred at 80°C for 10 min. Then, the suspension was mixed using a homogenizer (Ika T 25, Germany) for 3 min to obtain a homogeneous suspension. Air bubbles that remained in the suspension were removed using a centrifuge (HITACHI SCT 5B, Japan) at 3000 rpm for 10 min. By dripping the obtained PVA/SA/CNF mixture into 500 mL of cross-linking agent solution containing 5 wt% boric acid/borax and 3 wt% calcium chloride at a dripping rate of 100 mL h⁻¹, hydrogel beads were obtained. The beads were washed with 400 mL of deionized water for 24 h with stirring and stored in 3 wt% calcium chloride solution. The prepared PVA/SA/CNF hydrogel samples are referred to as “SA weight ratio”:“CNF weight ratio”. For example, the sample prepared with the weight ratio of SA:CNF of 9:1 is referred to as the 9:1 hydrogel.

2.3 Mechanical Strength

2.3.1 Elastic modulus

The mechanical property of hydrogels was analyzed with a tabletop testing machine (A&D STB-1225S, Japan) using a 50 N load cell. The compressive strength tests were performed with a crosshead speed of 10 mm min⁻¹. The elastic modulus was determined based on the data within 0-20% of the

strain range by using the following equation from the Hertz model:

$$F = \frac{4}{3}ED^{0.5}\Delta D^{1.5} \quad (1)$$

where F is the compressive load (N), E is the elastic modulus (MPa), D is the diameter of the hydrogel bead, and ΔD is the displacement (mm). 5 specimens were tested for each sample and the average data was used.

2.3.2 Durability

The durability of the hydrogels was examined using a Tornado overhead stirring system (As One SM-101, Japan). 100 hydrogel beads were dispersed in 1.0 L of deionized water and stirred strongly at an agitating speed of 2250 to 3500 rpm for 5 min. Then, the number of hydrogel beads without any damage (unbroken hydrogel beads) was counted. The breakage ratio was calculated by the following equation:

$$\text{Breakage ratio} = \frac{N_a - N_u}{N_a} \times 100\% \quad (2)$$

where N_a is the number of hydrogel beads added and N_u is the number of unbroken hydrogel beads.

2.4 Dye Adsorption Experiment

Dye adsorption isotherms on the hydrogels were examined by using MB as a model synthetic dye in batch processes. MB is a cationic dye widely used in textile industries.

Twenty hydrogel beads were added into 40 mL of MB solutions with a concentration range of 100 to 1000 ppm. The MB concentration at adsorption equilibrium was measured after 6 days. The data were analyzed by the Langmuir isotherm model to investigate the adsorption mechanism.

3. Results

3.1 Elastic modulus

The elastic modulus of hydrogels determined based on the results of compressive stress tests was shown in Fig. 2. The compressive strength of hydrogels was high in the order of 10:0 > 9:1 > 8:2 > 7:3. The 10:0 hydrogel shows the highest elastic modulus of 1.0 MPa, and the value is approximately 1.8 times larger than that of the 7:3 hydrogel, showing the lowest value. The results indicate that the PVA/SA hydrogel with no CNF addition shows the greatest compressive strength, and the addition of CNF decreased the strength. It should be noted here that compared to the conventional PVA hydrogel cross-linked by glutaraldehyde (GA), the elastic modulus of the 10:0 hydrogel is approximately 40 times greater and even the lowest elastic modulus for the 7:2 hydrogel is approximately 22 times greater than that for the PVA hydrogel.

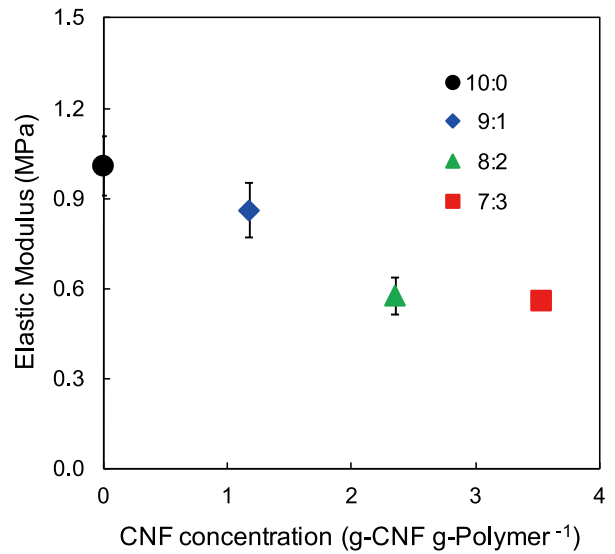


Fig. 2. Elastic modulus of the 7:3, 8:2, 9:1 and 10:0 hydrogels determined by a compressive stress test.

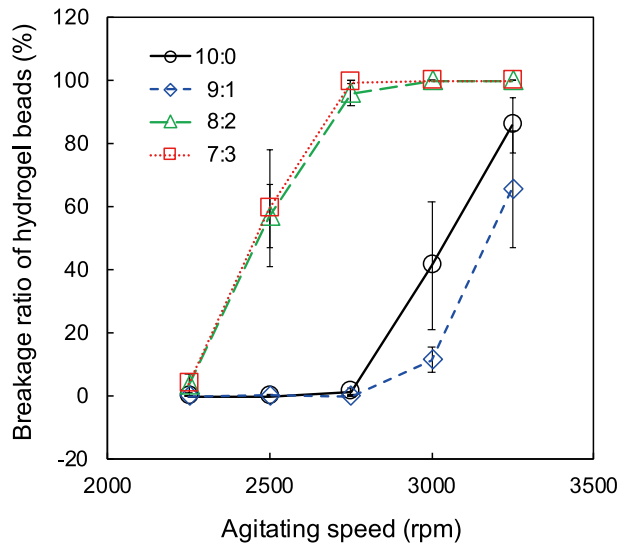


Fig. 3. Breakage ratio of hydrogel beads for the 7:3, 8:2, 9:1 and 10:0 hydrogels under severe agitation conditions of 2250-3250 rpm in a solution.

3.2 Durability

The breakage ratios of the hydrogels under severe agitation from 2250 to 3250 rpm in solution are shown in Fig. 3. According to the results at the maximum agitating speed of 3250 rpm, the durability of hydrogels is high in the order of 9:1 > 10:0 > 8:2 = 7:3. For the 8:2 and 7:3 hydrogels, all the hydrogel beads were broken after being agitated at 3000 rpm for 5 min. Under the same condition, approximately 42% of the beads were broken for the 10:0 hydrogel. On the other hand, only 12% of the beads were broken for the 9:1 hydrogel. The results indicate that to improve the durability of the PVA hydrogel for agitation, the addition of an appropriate ratio of SA and CNF is necessary and that is 9:1 under the condition used in this study.

For the later dye adsorption experiments, the 10:0 and the 9:1 hydrogels were selected since they exhibited high mechanical strength and durability.

3.3 Adsorption Isotherm Model

The adsorption isotherms of MB on the 10:0 and the

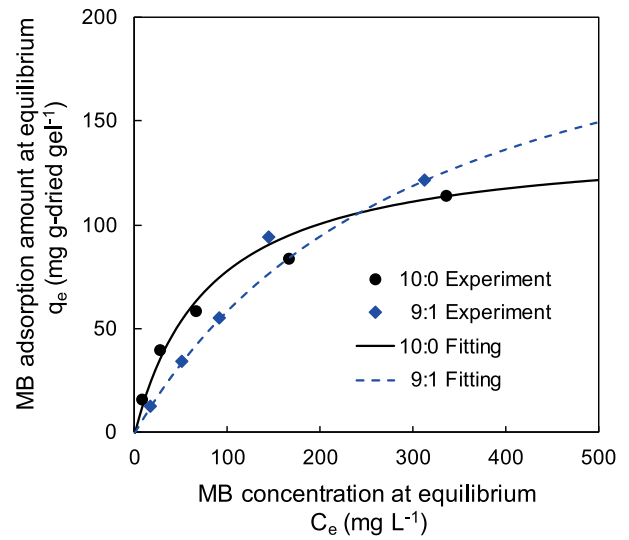


Fig. 4. Methylene blue adsorption isotherm on the 10:0 and the 9:1 hydrogel adsorbent at 25°C.

9:1 hydrogels were determined at 25°C and shown in

Fig. 4. The results were analyzed by the Langmuir Eq. (3).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_e and C_e are the amount of MB adsorbed (mg g^{-1}) and the MB concentration (mg L^{-1}) at equilibrium, q_m is the saturated adsorption capacity for MB adsorption (mg g^{-1}), K_L is Langmuir isotherm constant (L mg^{-1}).

Parameters obtained by each adsorption isotherm equation are shown in Table 3. The coefficients of determination for the Langmuir equation, R^2 were > 0.996 for both samples, indicating the MB adsorption results are in good agreement with the Langmuir model. Therefore, the adsorption process can be described as monolayer adsorption on the surface of adsorbents with relatively homogeneous sites. The saturated adsorption capacity for the 9:1 hydrogel is 243.9 mg g^{-1} , which is approximately 1.7 times higher than that for the 10:0 hydrogel. However, since the MB concentration range used in this study is limited to less than 350 mg L^{-1} at equilibrium, the maximum adsorption

Table 2. Parameters of Langmuir isotherm model for the 9:1 and 10:0 hydrogels.

Adsorbent	Langmuir isotherm model			
	$q_m(\text{exp.})$ (mg g^{-1})	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2 (-)
10:0	161.19	140.85	0.012	0.9963
9:1	167.18	243.90	0.003	0.9982

Table 3. Adsorption characteristics of PVA-based polymer composite adsorbents for dye removal.

Adsorbent	Dye	C_0 (mg L^{-1})	q_m (mg g^{-1})	Adsorption isotherm	Reference
PVA/SA/CNF hydrogel (9:1)	Methylene blue	1000	243.9	Langmuir	This study
Sodium alginate- polyacrylamide-(TEMPO)- oxidized cellulose nanofibers	Methylene blue	500	57.1	Langmuir	Yue et al. (2019)
Poly(vinyl alcohol)-sodium alginate-chitosan- montmorillonite	Methylene blue	70	137.2	Langmuir	Wang et al. (2018)
Poly(vinyl alcohol)/ carboxymethyl cellulose/ graphene oxide/bentonite	Methylene blue	250	172.4	Langmuir	Dai et al. (2018)
Poly(vinyl alcohol)	Methylene blue	25	13.8	Langmuir, Freundlich, Temkin	Umoren et al. (2013)

amounts observed for both hydrogels did not show a significant difference and were 161.19 mg g^{-1} and 167.18 mg g^{-1} for the 10:0 and the 9:1 hydrogels, respectively.

4. Discussion

4.1 Mechanical Strength

The results of the compressive strength tests show that the PVA/SA hydrogel with no CNF addition has the highest compressive strength, and the addition of CNF resulted in the decrease of the strength. The considered reason is that although the stiffness of CNF itself is remarkable, the interaction between CNF and calcium

ions is weaker than that between SA and calcium ions. For the PVA/SA, due to the “egg-box” structure formed by strong interaction between SA and calcium ions, the hydrogel matrix could exhibit very high stability for compression operation (Shivakumara et al. 2019). On the other hand, for the case of cross-linking between CNF and calcium ions, since a strong structure could not be formed, it leads to the low stability of the hydrogel for compression operation.

4.2 Durability

The results of durability tests under severe agitation showed the 9:1 hydrogel possessed the highest dura-

bility, different from the compressive strength results. The compressive strength defined by an elastic modulus represents the hardness of the hydrogel. Therefore, the increase of stronger crosslinking of SA and calcium ions simply resulted in the increase of the hardness. On the other hand, for the durability tests, to absorb collision energy during agitation, moderate softness is also required for the hydrogel beads while maintaining their shape with sufficient hardness. Therefore, a good balance between hardness and softness is important. Although the results need to be examined in more detail, the highest durability for the 9:1 hydrogel indicates that the addition of appropriate ratio of SA and CNF would contribute to afford the PVA hydrogel a balanced hardness and softness, and significantly improves both the compressive strength and the durability for PVA hydrogel. In addition, a comparison of our durability result with that of the highest reported value for the PVA/SA hydrogel cross-linked by sodium sulfate was made (Dinh & Bach 2014). Under the same experimental condition, although their hydrogels were completely broken at 2750 rpm, and the breakage ratios for 10:0 and 9:1 hydrogel were negligible. Since the higher durability under severe agitation conditions indicates the hydrogel could offer long-lasting usage for dye removal, the developed hydrogel can be considered as a potential alternative for dye adsorbent.

4.3 Dye Adsorption Performance

Table 3 shows the comparison of dye adsorption performance between the 9:1 hydrogel and other reported PVA-based adsorbents (Dai et al. 2018, Umoren et al. 2013, Wang et al. 2018, Yue et al. 2019). Compared to the highest adsorption capacity reported by Dai et al. (2018), the 9:1 hydrogel exhibits approximately 1.4 times higher adsorption capacity (243.9 mg g^{-1}). The reason for the large adsorption capacity is probably due to the

abundant carboxyl groups in SA and CNF which have a high affinity for cationic dyes due to electrostatic interaction. In particular, since the CNF component used in this study is the TEMPO-oxidized CNF, it possesses a high surface area and high density of surface carboxyl groups (Saito & Isogai 2006). Normally, it is known that only hydroxyl groups exist on the surface of CNF. However, since the hydroxyl groups on the TEMPO-oxidized CNF were transformed into carboxyl groups by the TEMPO catalytic oxidation method, the surface density of the carboxyl group is very high. This also contributed to the increase of negative charge on the CNF and resulted in repulsion of each fiber of cellulose, leading to high dispersion and high surface area of each CNF component. These could be the reason for the high adsorption capacity of the developed adsorbent.

5. Conclusion

In this study, the PVA/SA/CNF hydrogels were prepared by incorporating both SA and TEMPO-oxidized CNF and the effects of weight ratios of SA and CNF on the mechanical properties and dye adsorption performance were examined. The results showed that the addition of an appropriate ratio of SA and CNF is important to improve the durability of the PVA hydrogel for agitation and which is 9:1 under the condition used in this study. The 9:1 hydrogel also shows the highest saturated MB adsorption capacity of 243.9 mg g^{-1} , that is 1.4 times higher compared to the highest reported value for the conventional PVA-based adsorbent. These superior mechanical and dye adsorption properties indicate that the developed PVA/SA/CNF hydrogel can be considered as a potential alternative for dye removal adsorbent material.

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