Impact of Counter Ions of Cationic Monomers on the Production and Characteristics of Chitosan-Based Hydrogel

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ABSTRACT: Chitosan-based hydrogel has received considerable interests because of its appealing properties and applications in many areas. The primary objective of this work was to produce novel cationic chitosan-based hydrogels via polymerizing chitosan with two cationic monomers of the same structure but with different counter ions [2-(methacryloyloxy)ethyltrimethylammonium methyl sulfate (METMS) and 2-(methacryloyloxy)ethyltrimethylammonium chloride (METAC)]. Polymerization of chitosan with the cationic monomers performed under the conditions of 50 °C, 5 h, 7 pH, and 2/1 mol/mol monomer/chitosan led to chitosan—METMS and —METAC with the cationic charge densities of 3.22 and 2.88 mequiv/g, respectively. Elemental analysis, gel permeation chromatography, Fourier transform infrared, X-ray diffraction, and differential scanning calorimetry analyses were used to confirm the impact of counter ions of cationic monomers (i.e., polarizability of monomers) on their polymerization performance and the characteristics of induced chitosan-based hydrogels. Also, the results of this work postulated that the counter ions associated with the monomers could dramatically impact the water uptake and swelling properties of the generated chitosan-based hydrogels as well as their performance in adsorbing an anionic dye from a simulated solution.

INTRODUCTION

Hydrogels are defined as a class of macromolecular and hydrophilic networks that can contain a large fraction of liquid within their structure. The hydrophilicity of hydrogels stems from the presence of hydrophilic groups, such as amine (—NH₂), carboxylic acid (—COOH), and hydroxyl (—OH) groups in the hydrogel networks.¹,² The main favorable properties of hydrogels are their ability to imbibe large amount of liquid when they expose to compatible solvents and their great adsorption performance.³–⁵ Hydrogels have received attentions for their wide range of applications, such as heavy metal remediation,³–⁵ wastewater treatment,⁶ pharmaceutical industry,⁷ drug delivery systems,⁸ and wound dressing.⁹,¹⁰

There is a broad variety of hydrogels produced from different natural polymers (e.g., polysaccharides) and synthetic polymers (e.g., poly(ethylene glycol)).¹⁵,¹⁶ Conventional synthetic polymer-based hydrogels have limited uses because of the difficulties in their production (e.g., side reactions and low coupling efficiency).¹⁷ Over past decades, hydrogels made from renewable and biodegradable resources have been the focus of studies. Natural-based hydrogels, especially polysaccharide-based ones, have obtained substantial interests because of their nontoxicity, biocompatibility, low production price, and structural versatility.¹⁸–²⁰ Starch,²¹ cellulose,²² hemicellulose,²³ lignin,²⁴,²⁵ alginic acid,²⁶ hyaluronic acid,²⁷ and chitosan-based hydrogels are the most studied polysaccharide-based hydrogels. Chitosan is composed of randomly distributed β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine units that is accessible, renewable, biocompatible, bioactive, and nontoxic.²⁸,²⁹ Despite the generation of chitosan-based hydrogels, their water swelling and adsorption characteristics have not been great, and the new generation of chitosan-based hydrogels can be produced with superior properties.³⁰

In recent studies, chitosan have been modified to produce hydrogel with improved properties in aqueous fluids.³¹–³⁵ One possibility for inducing high-performance chitosan-based hydrogel is to chemically crosslink it with other chemicals, such as ethylene glycol diglycidyl ether,³⁶ polyaniline,³⁷ glutaraldehyde,³⁸,³⁹ and epichlorohydrine.⁴⁰ The polymerization of chitosan with monomers, such as 2-acrylamido-2-methyl propane sulfonic acid,⁴¹ is another modification method. Although these results provide information on the influence of monomer’s structure and type on producing hydrogel with different properties, they do not discuss the impact of monomer’s counter ions on their reaction performance with chitosan for hydrogel generation.

Charged monomers are generally available in solutions from different natural polymers (e.g., polysaccharides) and synthetic polymers (e.g., poly(ethylene glycol)).¹⁵,¹⁶ Conventional synthetic polymer-based hydrogels have limited uses because of the difficulties in their production (e.g., side reactions and low coupling efficiency).¹⁷ Over past decades, hydrogels made from renewable and biodegradable resources have been the focus of studies. Natural-based hydrogels, especially polysaccharide-based ones, have obtained substantial interests because of their nontoxicity, biocompatibility, low production price, and structural versatility.¹⁸–²⁰ Starch,²¹ cellulose,²² hemicellulose,²³ lignin,²⁴,²⁵ alginic acid,²⁶ hyaluronic acid,²⁷ and chitosan-based hydrogels are the most studied polysaccharide-based hydrogels. Chitosan is composed of randomly distributed β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine units that is accessible, renewable, biocompatible, bioactive, and nontoxic.²⁸,²⁹ Despite the generation of chitosan-based hydrogels, their water swelling and adsorption characteristics have not been great, and the new generation of chitosan-based hydrogels can be produced with superior properties.³⁰

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Charged monomers are generally available in solutions along with their oppositely charged counter ions, which are correlated together by Coulombic attraction.⁴²–⁴⁴ Binding efficiency of counter ions can be verified by considering the Hofmeister (lyotropic) series, which are defined as the classification of ionic materials according to their influence on these macroscopic properties.⁵⁵ Different counter ions...
with altered polarizabilities affect their polyions, which may severely impact the overall electron density of monomers and thus their reaction tendency in polymerization. In aqueous media, the penetration of water molecules in polyelectrolyte’s interlayer space reduces the attractive forces between the polyions and the counter ions.\(^{47,48}\) hence, polyions with different binding efficiencies may polymerize differently. The first objective of this work was to investigate the generation of chitosan-based hydrogel via polymerizing it with two similar polyelectrolyte agents, whose counter ions are different, \([2-\text{methylacryloyloxy} \text{ethyl}]-\text{trimethylammonium methyl sulfate (METMS)}\) and \([2-\text{methylacryloyloxy} \text{ethyl}]-\text{trimethylammonium chloride (METAC)}\).

Synthetic dyes are widely used in various industries, such as pulp and paper, textile, and food industries. The complex aromatic structure of dyes causes their degradation and retardation challenging, which has ecological and environmental footprints.\(^{49}\) Adsorption has been known as an effective technique for the dye removal from solutions because of its high efficiency, simplicity in operation, and the reusability of the adsorbent.\(^{50}\) Hydrogels have also been reported as effective adsorbents for dye segments.\(^{51,52}\) In one study, chitosan-based hydrogels were applied for the removal of different anionic dyes (Acid Red 18, Acid Orange 7, Methyl Orange and Basic Violet 14) from aqueous solutions.\(^{53}\) In another study, a surfactant-chitosan based hydrogel was utilized for removing Congo red dyes.\(^{56}\) The second objective of this work was to evaluate the performance of chitosan—METMS- and —METAC-based hydrogels in removing reactive yellow 50 dye from solutions. The main novelty of present work was the study on the impact of counter ions of cationic monomers on their polymerization efficiency with chitosan for hydrogel production and on the characteristics and performance of induced hydrogels.

## RESULTS AND DISCUSSION

**Reaction Mechanism.** The reaction scheme for the polymerization of chitosan and METMS or METAC is depicted in Figure 1. Briefly, free radicals on the NH\(_2\) of deacetylated part of chitosan would be initiated with the help of the initiator (H\(_2\)N\(_2\)CeO\(_4\)). The radicals would then attack the alkenyl group of cationic monomers, METMS or METAC, generating chitosan—METMS or chitosan—METAC polymers, respectively. In this case, the electron density of the carbon double bond of the cationic monomers would likely be affected by the binding affinity of the counter ions and the quaternary amine group, which may affect the polymerization efficiency of chitosan and the cationic monomer and properties of the induced hydrogels. Coincidentally, as shown in Figure 1b, METMS or METAC could participate in a side reaction generating the homopolymers of polyMETMS \([\text{P(METMS)}]\) or polyMETAC \([\text{P(METAC)}]\), respectively.\(^{57}\)

The charge density of deacetylated chitosan was reported to be +0.88 mmol/g, which is mainly due to the existence of the NH\(_2\) group on chitosan after dissolving in acidic solution.\(^{58}\) The polymerization of chitosan with METMS and METAC was carried out according to the research performed on methacryloyloxyethyl trimethyl ammonium chloride at temperature of 50 °C for 5 h at natural pH.\(^{59}\) However, to understand the polymerization performance of the cationic monomer and chitosan, the impact of the monomer/chitosan ratio on the charge density of the product was attested.

**RESULT AND DISCUSSION**

![Figure 1](image)

**Figure 1.** (a) Polymerization reaction of chitosan with METMS/METAC in the presence of initiator and (b) generation of METMS/METAC homopolymers.

**Effect of Monomer/Chitosan Molar Ratio.** Figure 2 presents the effect of METMS and METAC dosage on the charge density of chitosan—METMS and chitosan—METAC polymer.

![Figure 2](image)

**Figure 2.** Effect of the monomer/chitosan molar ratio on the charge density of chitosan—METMS and chitosan—METAC polymer. As depicted in Figure 2, increasing the molar ratio mimics chitosan—METMS and chitosan—METAC polymer with a higher charge density, which is basically due to the attachment of more METMS/METAC group to chitosan. Chitosan—METMS and chitosan—METAC polymers exhibit the maximum charge densities of +3.22 and +2.88 mmol/g at 1 mol/mol monomer/chitosan ratio, respectively. The drop in the charge density at a higher reagent/chitosan ratio could be due to the progress in the formation of homopolymers of PMETMS and PMETAC (Figure 1b).\(^{60,61}\) A similar trend was reported for the polymerization of xylan and METMS.\(^{62}\)

**Fourier Transform Infrared Analysis.** Figure 3 displays the Fourier transform infrared (FTIR) spectra for unmodified and modified chitosan. The broad and strong peak ranging 3200—3600 cm\(^{-1}\) attributes to different vibrations, namely, O–
reveals a strong peak at 2\(\theta\) shown in Figure 4. The XRD pattern for chitosan powder stretching vibration of C\(\equiv\)O at 3360 cm\(^{-1}\). The bands indicated at 2929 cm\(^{-1}\) contributed to sp\(^3\) C–H stretching vibration of chitosan backbone and C–N stretching, bands indicated at 2870 cm\(^{-1}\) belonged to the stretching of (–C\(\equiv\)O) of the amid group (CONHR) of chitosan, bands indicated at 1605 cm\(^{-1}\) are attributed to –NH\(_2\) bending, and bands indicated at 1647 cm\(^{-1}\) are associated with carbonyl (C=O) stretching of secondary amid. The adsorption bands at 1566 cm\(^{-1}\) are assigned to N–H bending and N–H angular deformation in the CO NH plane.

Furthermore, in both unmodified and modified chitosan polymers, adsorption bands at 893, 942, and 1109 cm\(^{-1}\) are attributed to C–O ring stretching, CH\(_2\) bending vibration, and C–O–C stretching, respectively. Two sharp peaks at 1488 and 1724 cm\(^{-1}\) in chitosan–METMS and chitosan–METAC polymers are assigned to asymmetric angular bending of methyl groups of quaternary hydrogen, and carbonyl stretching vibration of C=O groups existed in both METMS and METAC, which confirms the polymerization of chitosan and METMS and METAC monomers.

**X-ray Diffraction Analysis.** The structural properties of chitosan before and after dissolution in acetic acid for hydrogel formation as well as chitosan–METAC and chitosan–METMS polymers after hydrogel formation were analyzed using an X-ray diffraction (XRD) technique, and the results are shown in Figure 4. The XRD pattern for chitosan powder reveals a strong peak at 2\(\theta\) of 20\(^\circ\) and one weak peak at 2\(\theta\) of 10\(^\circ\), which are the indicators of the existence of crystalline and amorphous regions, respectively. The crystallinity of chitosan is because of arranged saccharide backbone and the ordered regions formed by amino groups on saccharide units.

The crystallinity peaks were decreased by converting chitosan powder to hydrogel and after polymerization with METMS or METAC. These changes are due to the significant change in chitosan’s functional groups and decreasing the crystallinity of chitosan by converting it into hydrogel via polymerization.

**Properties of Chitosan before and after Modification.** Elemental compositions, molecular weight, and charge density of the samples were investigated, and the results are shown in Table 1. Chitosan–METMS and chitosan–METAC hydrogels had 4.57 and 4.4 wt % nitrogen contents, respectively, which were higher than that of unmodified chitosan-based hydrogel (1.07 wt %). The increase in the nitrogen content of hydrogel stems from the nitrogen part of METMS or METAC monomer attached to the chitosan–METAC or –METMS polymers. On the other hand, chitosan–METMS and chitosan–METAC hydrogels contained more hydrogen and less oxygen compared to unmodified chitosan hydrogel, which is attributed to the higher proportion of hydrogen and lower proportion of oxygen in METAC and METMS monomers attached to the polymer.

**Differential Scanning Calorimetry Analysis.** The differential scanning calorimetry (DSC) curves of chitosan, chitosan–METMS, and chitosan–METAC hydrogels are presented in Figure 5. The endothermic humps in DSC curves
for all of the samples at the temperature higher than 160 °C are attributed to the transition of the samples from solid state to soft and rubbery states, that is, glass transition temperature \( T_g \) of the materials, which were specifically 167, 169, and 178 °C for chitosan, chitosan−METMS, and chitosan−METAC hydrogels, respectively.\(^{72}\) The increase in the chitosan−METMS and chitosan−METAC hydrogel glass transition temperatures can confirm the improvement in the thermal stability of the hydrogel.\(^{72}\) In one study, a similar DSC trend was reported for glutaraldehyde cross-linked chitosan, and the endothermic peaks were observed in the range of 130 and 155 °C.\(^{29}\)

### WATER UPTAKE BEHAVIOR OF UNMODIFIED AND MODIFIED CHITOSAN HYDROGELS

Figure 6a shows the water uptake (WU) of the samples as a function of time in neutral pH. It can be seen that the rate of WU was fast in the first minute of the test and then slowed down. As depicted, unmodified chitosan hydrogel’s WU increased from 239% in 1 min to 517% in 1300 min. On the other hand, chitosan−METMS absorbed 404 and 1286% and chitosan−METAC absorbed 175 and 678% water in 1 and 1300 min, respectively. During swelling, the hydrophilic groups of hydrogel start to absorb water and expand within the structure by forming primary bound water.\(^{75}\) By completing polar groups’ hydration, hydrophobic groups in hydrogel interact with water, forming secondary-bound water. After saturation of hydrophilic and hydrophobic groups, the osmotic driving force of the network chain causes the absorption of more water.\(^{75}\)

It was also observed that acidic (pH 3) and alkaline (pH 11) environments had pronounced effects on the WU profiles of hydrogels (Figure 6). In fact, the WU was more profound in acidic environment than other media. Also, the rate of WU was significantly lower in alkaline pH than other pH. During the swelling of unmodified and modified chitosan hydrogels, the amino groups located on the surface of hydrogel are ionized first. Then, water will penetrate into the hydrogel, and this penetration is facilitated via electrostatic repulsion created between adjacent ionized amino groups.\(^{76}\) Low pH (i.e., acidic medium) favors the protonation of amino groups in the hydrogels leading to high repulsion and hence higher WU.\(^{76,78}\) On the other hand, the slower and less amount of WU in basic environment was attributed to the presence of the OH− group in the medium that would suppress the protonation of amino groups and thus hinder the electrostatic repulsion development. Similar behavior was reported for chitosan-based hydrogels in the past.\(^{77,78}\)

Figure 7 presents the water swelling of unmodified chitosan, chitosan−METMS, and chitosan−METAC hydrogels as a function of time. The water swelling results confirm the trend similar to those of Figure 6 for WU. However, the swelling amount was 1.43−2 times as large as the WU after 420 min. In opposition to the WU that occurs only in an axial direction, the water swelling results (Figure 7) provide evidence that the hydrogels had a tendency to absorb water in radical and tangential directions in addition to the axial direction (Figure 6).\(^{79}\)

Both WU and swelling results exhibited the following order of chitosan−METMS > chitosan−METAC > chitosan (Figures 6 and 7) in absorbing water. The difference in their performance could be related to their altered structures. The morphologies of hydrogel samples after swelling are shown in Figure 8. It can be seen that the structure and surface pattern of the unmodified and modified hydrogels were completely different. The surface structure of chitosan hydrogel (Figure 8a) was smooth and uniform, whereas chitosan−METAC and chitosan−METMS hydrogels had rougher and more porous
structure (Figure 2b,c), which probably increased the surface area and porosity of the hydrogels facilitating their higher WU and swelling affinity.

Kinetics of Dye Removal. The adsorption of dye with adsorbents is important for eliminating it from effluent. The adsorption capacity of chitosan-METMS hydrogel for reactive Y50 dye is depicted in Figure 9. Unmodified chitosan hydrogel reached the highest performance in the dye removal after 60 min with equilibrium adsorption capacity of 60.5 mg/g dye/hydrogel. The adsorption capacity of chitosan-METMS hydrogel was 153.5 mg/g dye/hydrogel after 80 min and that of chitosan-METAC hydrogel reached the capacity of 147.5 mg/g dye/hydrogel after 360 min. An increase in the dye removal is attributed to the presence of more available quaternary amine groups in the hydrogel structures.

A similar trend was observed by Vakili and his colleagues reporting that chitosan hydrogel modified with 3-aminopropyl triethoxysilane removed reactive blue 4 (RB4). Also, chitosan-METMS hydrogel adsorbed dyes more quickly than other samples. The results confirmed that the equilibrium adsorption capacity of chitosan hydrogel on RB4 dye (500 mg/L concentration) increased 1.37 times by polymerizing with 3-aminopropyl triethoxysilane.

Comparison of Chitosan−METMS and Chitosan−METAC Hydrogels. During polymerization in aqueous media, water molecules penetrate into the interlayer space between the polyions and counter ions in polyelectrolytes. The electrostatic charge pattern within the colloidal system causes the adsorption of polyions to the opposite charged materials. The ionic effect of polyelectrolytes not only depends on the ionic groups of polyions but it also depends on the counter ions’ properties (i.e., charge, charge distribution, and polarizability). Therefore, the nature of counter ions in polyelectrolyte can considerably influence the properties of their polyions. Hence, two polymers with identical polyions but different counter ions could have different properties. Counter ions differ by their polarization affinity, that is, their binding affinity according to the sequence of Hofmeister series. Two used monomers in current study have identical polyions ([2-(methacryloyloxy)ethyl]trimethylammonium) and two different counter ions, methyl sulfate and chloride for METMS and METAC, respectively. Based on Hofmeister series, which describes the binding affinity of anionic as SO$_4^{2-}$ > HPO$_4^{2-}$ > CH$_3$COO$^-$ > Cl$^-$ > Br$^-$ > NO$_3^-$ > I$^-$ > SCN$^-$, methyl sulfate has a higher binding affinity than chloride. Thus, it neutralizes the charge of quaternary ammonium group of the monomer more effectively, affecting the polarizability of the monomer. This interaction will less significantly affect the electron clouds of the carbon double bonds of the monomers participating in the polymerization reaction. The stronger electron density of the carbon double bond of METMS than METAC most probably led to its more effective polymerization with chitosan, which generated a more effective hydrogel.
CONCLUSIONS

This work presented a process for polymerizing chitosan with monomers of the same structure but with different counter ions to produce hydrogels. The polymerization enhanced the charge density of chitosan from +0.88 to +3.22 and +2.88 for METMS and chitosan−METAC, respectively. The molecular weight of chitosan increased almost 2 times via polymerization. The polymerization of chitosan was confirmed by means of FTIR and XRD. DSC results showed the higher thermal and network stability for chitosan−METMS than chitosan−METAC due to its higher polymerization efficiency. Chitosan−METMS and chitosan−METAC hydrogels revealed 1.7 times WU as much as chitosan hydrogel. Polymerized chitosan hydrogel with METMS and METAC revealed much more adsorption for reactive Y50 dye than did chitosan hydrogel. In this case, chitosan−METMS hydrogel exhibited higher dye adsorption capacity (153.5 mg dye/g hydrogel) and shorter equilibrium time (80 min) than chitosan−METAC hydrogel with 146.5 mg/g of dye/hydrogel adsorption capacity and longer equilibrium time of 360 min. Generally, hydrogels behaved differently in altered pH, and they absorbed more water at acidic pH. Overall, the results confirmed that the counter ion’s binding affinity, which would impact the polarity of the cationic monomer, indeed influenced the performance of the cationic monomer in polymerizing with chitosan and the properties of chitosan-based hydrogels. Thus, the impact of counter ions of the cationic monomers on hydrogel production must be taken into account when cationic monomers are selected.

EXPERIMENTAL SECTION

Materials. Chitosan powder (with 75–85% degree of deacetylation and 190 000–310 000 kg/mol molecular weight) was obtained from Sigma-Aldrich. Also, METMS, METAC, ceric ammonium nitrate (CAN), methanol, sodium hydroxide pellets, poly diallyldi methylammonium, acetic acid (90 vol %), HCl (37%), sulfuric acid (98 wt %), and direct yellow 50 (Y50) dye were purchased from Sigma-Aldrich company. Potassium polyvinyl sulfate (PVSK) (with molecular weight of 200–300 kg/mol, 98.4% esterified) was provided by Wako Pure Chemical Industries Ltd., Japan. Cellulose acetate dialysis membrane (molecular weight cut-off of 1000 g/mol) was purchased from Wako Chemicals, Japan. In this research work, no unexpected or unusually high safety hazards were encountered.

Preparation of Modified-Chitosan Hydrogel. In this set of experiments, a 2 g sample of chitosan powder was dissolved homogeneously in 40 mL of acetic acid (1 vol %) by stirring overnight. The gel-like sample was then mixed with certain amounts of METMS or METAC in plastic bags. The mixtures were stirred thoroughly prior to adding 0.03 g of CAN as the initiator. The mixtures were deoxygenated under nitrogen atmosphere and then kept at 50 °C for 5 h while mixing every 15 min. Then, they were cooled down and precipitated by ethanol (95%) to extract modified chitosan polymer from the reaction media. The rest of unreacted monomers were separated from the products by membrane dialysis, while changing water every 2 h for the first 6 h and then once a day for 2 days. Thereafter, the sample was dried using a freeze-dryer.

Afterward, unmodified and modified chitosan-based hydrogels were prepared by dissolving the samples in a 1% acetic acid solution via mixing overnight. Then, the solutions were added drop-wise into an alkaline solution containing deionized water, methanol, and sodium hydroxide with ratio of 4:5:1 (wt/wt/wt), respectively, to form hydrogels. The formed hydrogels were then filtered and washed thoroughly to neutral pH.

Charge Density Analysis. In this set of experiments, 0.2 g of freeze-dried chitosan, chitosan−METMS, and chitosan−METAC hydrogels were dissolved in 19.8 mL of deionized water. Then, they were incubated in a water bath shaker (Innova 3100, Brunswick Scientific, Edison, NJ) for 1 h at the revolution of 150 rpm and temperature of 30 °C. After incubation, the samples were centrifuged for 10 min at 1000 rpm. Then, the charge density of prepared samples was measured by a particle charge detector, Mutek, PCD 04 titrator (Herrsching, Germany) with PVSK solution (0.0052 M). All experiments were carried out in triplicates, and the average values were reported.

Elemental Analysis. The elemental analysis was carried out for unmodified and modified chitosan-based hydrogels to determine their carbon, hydrogen, oxygen, and nitrogen contents using an elemental analyzer, Elementar Vario EL (Germany). In preparing the sample for this analysis, they were first oven-dried at 60 °C, and about 0.02 g of the samples was transferred into the carousel chamber of the elemental analyzer. The combustion of the samples was performed at 1200 °C, and the gases were reduced to analyze the elemental content of the samples.

GR was calculated based on their nitrogen content, according to eq 1.

\[
GR = \frac{N_{14}}{100 - \frac{N_{14}}{100} \times MW_m} \times 100
\]

where N is the nitrogen content determined by the elemental analysis (wt %) and MW_m is the molecular weight of monomer.

Molecular Weight Analysis. The molecular weight of chitosan, chitosan−METMS and chitosan−METAC were assessed using a gel permeation chromatograph instrument (Malvern GPCmax VE2001 Module + Viscotek TDA305), which was equipped with RI and viscometer detectors at the flow rate of 0.7 mL/min and temperature of 30 °C. The samples were prepared by drying for 72 h using a freeze-dryer prior to use. Then, approximately 10 mg of each sample was dissolved in 20 mL of 5.0 wt % acetic acid by stirring at 600 rpm for 48 h. Thereafter, the solution was filtered with a nylon filter (pore size 0.2 μm) and used for the molecular weight analysis.

Fourier Transform Infrared. The FTIR analysis was conducted for determining the structure of chitosan and chitosan−METMS and chitosan−METAC hydrogels. The samples were dried in an oven at 60 °C overnight, and 0.1 g of the sample was used for the analysis using the FTIR instrument (Bruker Tensor 37, Germany, ATR accessory). The spectra were recorded in a transmittance mode in the range of 590–4000 cm⁻¹ with 32 scan and resolution of 4 cm⁻¹.

X-ray Diffraction. The XRD analysis was conducted on chitosan powder, chitosan hydrogel, and chitosan−METAC and chitosan−METMS hydrogels. The freeze-dried samples were used in this analysis using an XRD (Panalytical X-pert Pro) with a high-resolution goniometer and a Pixel solid-state detector. The X-ray tube contained a copper anode and was set...
to 45 kV and 40 mA. The samples were set to analyze from 6° to 96° (2θ) with a step size of 0.026°.

**Differential Scanning Calorimetry.** The thermal behavior and glass transition temperature (Tg) of chitosan, chitosan–METMS, and chitosan–METAC hydrogels were analyzed using a DSC, TA instruments Q2000, in standard cell RC mode. In this set of experiments, the samples were oven-dried at 60 °C, and then, 2–5 mg of the dried samples was loaded into a Tzero aluminum pan and analyzed via heat/cool/heat methods in a temperature range of 50–210 °C at 50 mL/min in nitrogen.

**WU and Swelling.** The WU of chitosan, chitosan–METMS, and chitosan–METAC hydrogels from their axial surface was determined by capillary rise of water on a bed of freeze-dried hydrogel following the Washburn theory. The test was performed with 0.05 g of samples using a Sigma 700/701 optical tensiometer (Espoo, Finland) after conditioning its temperature at 20 °C. A vessel containing water (100 mL) was placed on the platform of the machine and moved until water touched the sample bed, after which capillary force caused water absorption by the sample. To study the effect of pH on the WU of hydrogels, the pH of water was adjusted to 3, 7, and 11 by using 0.1 M of HCl and NaOH solutions. The mass uptake by the hydrogel was subsequently recorded every 1 min for 1300 min. The WU of each sample at different time intervals was calculated according to eq 2

\[ \text{WU} \% = \frac{W_w - W_D}{W_D} \times 100 \]  

where \( W_D \) and \( W_w \) are the weight (g) of hydrogels before and after exposing to water at different time duration, respectively.

The swelling experiment of unmodified and chitosan–METMS and chitosan–METAC hydrogels was performed manually by immersing the freeze-dried samples in deionized water to swell. At different time intervals, the samples were removed and blotted by paper towel to extract excess water from their surface. The swelling ratio of hydrogel (Q) was determined following eq 3

\[ Q = \frac{W_s - W_o}{W_o} \times 100 \]  

where \( W_s \) and \( W_o \) are the weights of swollen hydrogel and dried hydrogel, respectively.

**Surface Morphology of Hydrogel.** The unmodified and modified hydrogels were swollen in water at pH 7 and room temperature for 24. Then, they were freeze-dried and coated on gold using an EFPA coater (Ernest F. Fullam, USA). The structures of the freeze-dried hydrogels were analyzed using a Hitachi SU-70 scanning electron microscope (SEM) at 10 kV under 10⁻⁷ to 10⁻³ Pa.

**Removal of Reactive Yellow 50 Dye.** Adsorption experiments were carried out to assess the capacity of the unmodified and chitosan–METMS and chitosan–METAC hydrogels for removing the reactive Y50 dye molecules from a simulated aqueous medium. Reactive Y50 dye solution, which is an anionic dye, was prepared by dissolving dye powder in deionized-distilled water (23 mg/L) at pH 2 while stirring at 300 rpm and 25 °C for 1 h. About 100 mg of unmodified/modeled chitosan hydrogels was mixed with 50 mL of the prepared dye solution. During the adsorption process, 5 mL of solution was drawn out at certain time intervals and its concentration was measured using a Genesy 10s UV–vis spectrophotometer at the wavelength 390 nm. The adsorption capacity of the hydrogels (q, mg/g) for Y50 dye was calculated based on the changes in dye concentrations before and after adsorption following eq 4.

\[ q = \frac{(C_0 - C_f)V}{W} \]  

where \( q \) (mg/g) represents the dye adsorption capacity and \( C_0 \) (mg/L) and \( C_f \) (mg/L) represent the dye concentration before and after adding the hydrogel samples, respectively. \( V \) represents volume (L) and \( W \) (wt) represents the dry weight of hydrogel samples. All experiments in this study were performed in triplicate under identical conditions to assure the accuracy of the results.

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