# Toward Mechanically Robust and Highly Recyclable Adsorbents Using 3D Printed Scaffolds: A Case Study of Encapsulated Carrageenan Hydrogel

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#### Abstract

Biopolymeric hydrogels have emerged as promising materials for water treatment; however, they exhibit limitations in terms of mechanical robustness and durability. To address these shortcomings, we implemented several strategies, such as (i) incorporation of graphene oxide (GO) to expand the range of molecular interactions within the hydrogels, (ii) increasing the degree of carrageenan biopolymer crosslinking by elevating the temperature of the ionic crosslinking bath, thereby enhancing the mechanical robustness of the hydrogels, and lastly, (iii) encapsulation of the nanocomposite hydrogels within 3D printed scaffolds to enhance the hydrogel durability. This study introduces the first adsorbent based on encapsulated hydrogels for water treatment, demonstrating a remarkable increase in its reusability, surpassing previous reports by at least 400%. Through the optimization of the 3D printed scaffold design, we achieved a 140% increase in the mass of encapsulated hydrogel, and engineered the available surface area to enhance both the durability and the environmental performance of the hydrogels. The addition of GO increased the adsorption capacity to 166.1 mg/g and the storage modulus at 10 Hz to 12.48 kPa, representing a 55% and 305% enhancement compared to the neat hydrogel, respectively. Moreover, the higher degree of ionic crosslinking further increased the storage modulus of the hydrogel by 261%. Increasing the degree of crosslinking resulted in a lower hydrogel swelling ratio, improved chemical stability, and increased the reusability of the hydrogel beads. Hydrogel encapsulation significantly increased the chemical stability and reusability of the adsorbents. More than 90% of the initial mass of the encapsulated hydrogel remained intact after 20 regeneration cycles. The reported results present a promising avenue toward the industrial-scale application of sustainable and green hydrogels for water treatment.

Keywords: Water treatment, Adsorption, Biopolymeric hydrogel, 3D printing, Graphene oxide

#### 1. Introduction

Polysaccharides, also referred to as biopolymers, are a broad class of naturally occurring carbohydrate polymers linked by glycosidic bonds. Polysaccharides have received considerable attention due to their

unique properties, including their natural and widespread abundance, low cost, renewability, stability, hydrophilicity, multifunctionality, and high chemical reactivity [1]. Like many bio-inspired materials, biopolymers also offer sustainable biological properties such as non-toxicity, biocompatibility, and biodegradability. The use of biopolymers as adsorbents in water treatment offers a sustainable alternative to traditional sorbents and has the potential to contribute to improved water quality and environmental protection. However, their low mechanical stability, compared to synthetic polymers, has limited their application in water treatment as hydrogel adsorbent [2]. Carrageenan is a biopolymer extracted from red algae, that can form a hydrogel in the presence of cationic ions, making it useful in a variety of applications, such as drug delivery and water treatment [3]. It has demonstrated the ability to effectively remove pollutants such as heavy metals and organic dyes from water [4]. To address the low mechanical properties of carrageenan, it has been studied mostly as a co-polymer with other polymeric compounds [5–8]. However, the durability assessment outcome, primarily quantified by the number of reusability cycles, indicates limited success, as the maximum reported number of regeneration and reuse cycles was six. [9–15].

The addition of nanomaterials improves the mechanical properties of biopolymers through the formation of physiochemical bonds, such as hydrogen bonding with polymer chains [16–19]. Among the nanomaterials investigated, graphene oxide (GO) has received significant attention in the context of water treatment. GO stands out due to its large surface area, presence of functional groups such as carboxyls and hydroxyls, and its capacity to form  $\pi$ - $\pi$  interactions as it is comprised of sp<sup>2</sup> carbons. This characteristic suggests the potential of GO as a promising material for improving the mechanical properties of biopolymers and, simultaneously, an effective adsorbent for water pollutants [20]. GO nanosheets exhibit significant affinity towards a diverse range of water contaminants [21–23]. Researchers have enhanced the mechanical properties of GO-containing hydrogels and strengthened the physical bond by subjecting the hydrogels to high temperatures in a thermal post-treatment step after their formation [24]. It has been proven that this post-treatment step not only increases the mechanical properties of the hydrogel but also improves its surface area [25].

Incorporation of the hydrogels inside porous scaffolds is another prominent strategy to enhance the mechanical properties of biopolymers. There are several reports of incorporating various hydrogels inside porous polymers for biomedical applications [26–28]. The effectiveness of this approach relies on the careful design of the porous scaffold, aiming to achieve a delicate balance between maximizing the available surface area and ensuring robust mechanical properties [29,30]. In recent years, the field of environmental remediation, including CO<sub>2</sub> capturing and water treatment, has witnessed significant interest in 3D printing techniques [31–38]. The interest in 3D printing stems from their versatility in design and material selection, as well as their exceptional ability to achieve a favorable balance between porosity and mechanical properties [39]. These factors have traditionally posed challenges in using conventional fabrication methods in environmental applications because they often exhibit adverse effects. Higher porosity and surface area drastically decrease the mechanical properties, and vice versa [40]. The advent of various 3D printing techniques offers new possibilities to overcome these limitations and improves efficiency in environmental applications. Nevertheless, the available related literature on the application of 3D printing in this field barely explores the design parameters of the scaffolds and their effect on structural performance and durability. Basic geometric structures such as cylinders and cubes are designs that have been frequently used [41,42]. The environmental remediation literature has not given enough attention to important 3D printing parameters such as infill pattern (pore shape) and infill density (porosity). The traditional woodpile infill pattern is frequently used, and infill density is often not reported. [33]. These two parameters have a significant impact on the mechanical properties of the final structure and its available surface area, offering a distinctive opportunity to achieve the desirable balance between them [43].

To evaluate the environmental performance of the hydrogel adsorbents, we used methylene blue (MB) as a model cationic contaminant and organic dye. The widespread use of organic contaminants such as dyes in various industries, for example, textile, printing, and food processing has been a growing environmental

concern [44]. Organic dyes can pose significant health and ecological risks by affecting water quality and altering aquatic ecosystems [45]. Additionally, we selected MB as the target contaminant due to previous reports on the formation of ionic metachromatic complexes with sulfated polymers like carrageenan [46]. This phenomenon manifests in the alteration of MB color from blue (with an absorption peak at 664 nm) to purple (with an absorption peak at 610 nm) in the presence of unbound carrageenan. Leveraging this distinctive feature, we could detect hydrogel disintegration and the leaching of un-crosslinked (free) carrageenan polymer via a straightforward UV-Vis spectroscopy technique.

In this study, we fabricated a novel encapsulated hydrogel adsorbent, aiming to enhance its mechanical properties and durability. We fabricated 3D printed scaffolds with rationally designed architecture to enhance the available surface area and to maximize the reusability of the hydrogels. Our unique adsorbents benefitted from three distinct strategies, namely, (i) incorporation of GO nanosheets into the carrageenan hydrogels, (ii) formation of hydrogels in high-temperature coagulation baths, and (iii) encapsulation of the nanocomposite hydrogels in 3D printed porous polylactic acid (PLA) scaffolds. All of these contributed to the improvement of the overall performance, mechanical properties, and durability of the biopolymeric hydrogels. While the biopolymeric-GO nanocomposite hydrogel beads were studied before for the adsorption of water contaminants [9,17,47], in this study, we investigate them from a new perspective, by focusing on their reusability to advance the application of these materials one step closer to large scale industrial implementation. Herein, we propose using *in-situ* thermal treatment to enhance the mechanical properties by increasing the degree of crosslinking in the hydrogels, simplifying the fabrication process by eliminating the need for post-treatment. Predominantly, the novelty of this work lies in the design and fabrication of efficient 3D printed scaffolds for hydrogel encapsulation, achieving a desirable balance between the adsorption performance of the hydrogels and their reusability.

Our investigation involved exploring the effect of GO content, coagulation bath temperature, infill pattern and density of the 3D printed scaffolds, alongside an examination of the adsorption capacity and reusability potential of the hydrogels. We systematically studied these parameters using beads (spherical hydrogels), as well as our novel encapsulated hydrogels in 3D printed scaffolds.

#### 2. Materials and Methods

#### 2.1 Chemicals

The following chemicals were used as received without further purification: κ-carrageenan (Carg, TCI), potassium chloride (Sigma-Aldrich, > 99.0%), polylactic acid (PLA, NatureWork, 4043D), methylene blue (MB, Sigma-Aldrich, > 97%), methyl violet (MV, Sigma-Aldrich), rhodamine B (RhB, Sigma-Aldrich, >95%), malachite green chloride (MG, Sigma-Aldrich, analytical standard), expandable graphite (Asbury carbon), sulfuric acid (Fisher, ACS plus), potassium permanganate (Sigma-Aldrich, ACS reagent), and hydrogen peroxide (VWR, 30%).

#### 2.2 GO Synthesis

GO was prepared using a modified Hummer's method [48]. In summary, graphite was expanded at 1000  $^{\circ}$ C, and 0.5 grams of the expanded graphite was mixed with 100 ml sulfuric acid and 5 grams of potassium permanganate in a round bottom flask. The mixture was stirred for 24 hours in a 45  $^{\circ}$ C water bath. For the next step, the flask was put in an ice bath to cool down, and 125 ml H<sub>2</sub>O<sub>2</sub> solution with 1:5 volume ratio of H<sub>2</sub>O<sub>2</sub>:deionized (DI) water was added slowly. After half an hour, the pale brown mixture was centrifuged several times using 1M HCl solution and DI water as washing solution. In each washing step, the supernatant was discharged, and the cake was dissolved in the solution. After 8 rounds of washing (3 times with acid and 5 times with DI water), the resulting cake was dispersed in the appropriate volume of DI water to reach 2 mg/ml concentration. The final pH of the GO suspension was 3.5.

## 2.3 Formation of Hydrogel Beads

The hydrogel bead formation method is schematically shown in Figure 1a. Carrageenan powder was dissolved in DI water at a concentration of 1 wt% using a magnetic stirrer, until a homogenous solution was obtained. In this study, different amounts of GO was added to the biopolymeric matrix due to its high

available surface area, compatibility with carrageenan chemistry, and the capability of forming  $\pi$ - $\pi$  and electrostatic bonds with it [49]. To reduce the cost of the adsorbents, and to minimize the potential of leaching nanomaterials in water, the concentration of the GO was kept to less than 2.5 wt%. Different amounts of GO (0, 0.25, 0.5, 1, and 2.5 wt%) were added to the solution. Then, the mixture was added dropwise to a coagulation bath containing 1M potassium chloride as an ionic crosslinker to form hydrogel beads. After 24 hours of resting in the coagulation bath, the beads were then washed several times with DI water to remove the excess crosslinker.

To improve the durability and reusability of the beads, they were formed in the coagulation baths heated to 30, 40, and 50 °C. For simplicity, the coagulation bath at room temperature was named cold coagulation bath (CCB) and the one heated to 50 °C was named hot coagulation bath (HCB). Higher temperature bath results in increasing the beads' degree of crosslinking by taking advantage of the increased activity of potassium and makes the synthesis process simpler by eliminating any required post treatment [50].



**Figure 1**. Preparation method of the beads and encapsulated hydrogels showing, (a) the procedure for the formation of nanocomposite beads, and (b) the procedure for 3D printing of the PLA-based porous scaffolds and the encapsulation of nanocomposite hydrogels inside the scaffolds, where (c) SEM image and digital photographs of the typical hydrogels encapsulated in 3D printed scaffolds are represented in top and cross-section view.

#### 2.4 3D Printing of Porous Scaffolds

Porous scaffolds with various designs were fabricated using a fused deposition modeling (FDM) 3D printer (Prusa i3 MK2S) using PLA feedstock. The scaffolds were specifically designed using CATIA software to provide efficient models that offer high specific surface area. Fabrication of the scaffold included pellet extrusion and filament preparation, and FDM 3D printing of the models. Briefly, PLA pellets were first

extruded at 205°C using a single screw extruder (FilaFab PRO 350 EX Extruder) to obtain a 1.75±0.05 mm filament. The diameter of the filament was continuously monitored through a control system using a high-speed, high-precision micrometer measurement instrument (Keyence L9000). Then, the filament was loaded to the 3D printer and extruded through a heated nozzle which heats the filament to its melting point. The model was printed layer by layer according to the G-code from the slicer, Simplify3D. The printing parameters have been summarized in Table S1.

In this study, four patterns of scaffolds with the dimensions of 2 cm×2 cm×2 cm were printed (Figure 2). One pattern follows woodpile (WP) design, which is typically used in literature for various fields of application. In the WP design, each layer comprises of a series of parallel lines, with any adjacent layer rotated 90° with respect to their neighboring layer. The other three patterns, having complex customized (CC) architecture, were engineered by combining different infill patterns to improve the interactive surface area of the encapsulated hydrogel with contaminated water. CC design is comprised of 14 layers, where the first (bottom) and 14<sup>th</sup> (top) layers are rotated 45° with respect to their neighboring layer. The other neighboring layer. The rest of the layers are rotated 90° with respect to their neighboring layer (Video S1). The distance between the parallel lines determines the pore size and infill density of the 3D printed structures.



Figure 2. Scaffold design specifications and digital photographs of the 3D printed scaffolds from the top and cross section view.

#### 2.5 Formation of Nanocomposite Hydrogels inside the Scaffold

Fabrication of the encapsulated nanocomposite hydrogel in 3D printed scaffolds follows the same method of bead fabrication with some modifications (Figure 1b). Firstly, the Carg-GO nanocomposite dispersion was prepared following the procedure described in section 2.3. Then, the 3D printed scaffold was immersed in the suspension for 30 minutes to allow the suspension to infuse into the scaffold and completely fill its pores. After that, the scaffold was slowly pulled out of the suspension and immersed in the cold or hot coagulation baths. After resting for 24 hours in the coagulation bath, the hydrogel that formed outside of the scaffold was carefully wiped off, and the trapped hydrogel in the 3D printed structure was washed several times with DI water to remove excess cross-linkers. Figure 1c shows an SEM image of the resulting

3D-printed encapsulated hydrogel (3DPEH). This image highlights the porous nature of the encapsulated hydrogel and confirms its adhesion to pore (infill) surfaces of the 3D-printed scaffold.

### 2.6 Adsorption Experiment

The removal of several organic dyes (MB, MV, RhB and MG) with beads and 3DPEH were studied. If not specifically mentioned, the initial concentration of the organic dyes was kept at 50 ppm. In these experiments, the weight of the beads and the weight of trapped hydrogel in 3DPEH were equal, and the experiment conditions for both adsorbents were kept the same. It is worth mentioning that the pH of the solutions was monitored before and after the adsorption experiments and determined to remain constant. Removal efficiency has been chosen as the main parameter to evaluate the removal performance of the adsorbents, which defines as:

$$Removal efficiency = \frac{C_0 - C_t}{C_0} \times 100$$
(1)

Where  $C_0$  and  $C_t$  are the concentration (ppm) of the dye at the beginning of the experiment and at time *t*, respectively [5,41]. Except for the kinetic studies where concentration was measured at several time points,  $C_t$  was measured after 24 hours, when the adsorption reached equilibrium.

The kinetics of dye adsorption onto hydrogel beads was studied. Typically, 100 mg of hydrogel beads (dry weight) was added to MB solution (100 ml, 50 ppm). Samples were collected at fixed time intervals for 24 hours. The adsorption capacity ( $Q_t$ ) was calculated using Equation 2 and plotted with respect to time (hours) for obtaining the adsorption kinetics graphs. The adsorption kinetics data were fitted to the pseudo-first order (Equation 3) and pseudo-second order (Equation 4) models.

$$Q_t = (C_0 - C_t) \times \frac{V}{m}$$
<sup>(2)</sup>

$$\ln(Q_e - Q_t) = \ln Q_{e,cal} - k_1 t \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_{e,cal}} \tag{4}$$

Where V and m are solution volume and the adsorbent dry mass, respectively. Moreover, the predicted equilibrium adsorption capacity ( $Q_{e,cal}$ ) and rate constants ( $k_1$  and  $k_2$ ) have been calculated and reported.

The equilibrium isotherms of hydrogel beads were obtained by immersing 100 mg of adsorbents (dry weight) into 100 ml of MB solution with different concentrations (50, 100, 200, 300, 500, 800, and 1500 ppm). The isotherm experimental data were fitted to Langmuir (Equation 5) and Freundlich (Equation 6) isotherm models and models' constant were reported in Table S2.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \left(\frac{1}{Q_m \times k_l}\right) \tag{5}$$

$$\ln(Q_e) = \ln(k_F) + \frac{1}{n} * \ln C_e$$
(6)

In Eq.5,  $k_1$  is the Langmuir constant related to the affinity of the binding sites,  $Q_m$  is the maximum adsorption capacity, representing the monolayer coverage of the adsorbent. Additionally in Eq. 6, *n* is the heterogeneity factor, indicating the intensity of the adsorption process.

In order to compare the reusability of the adsorbents, they were immersed in an MB solution ( $C_0$ =50 ppm) for 24 hours. Then, they were removed from the feed and immersed in a regeneration solution (mixture of ethanol and 1M potassium chloride solution at 1:1volumetric ratio) for 5 hours. The regeneration and reuse cycles continued until all the hydrogel beads disintegrated in the feed solution. In the case of 3DPEH, since the disintegration rate was significantly slower, the regeneration and reuse were continued for 20 cycles, and the weight of the remaining hydrogel inside the scaffold was reported as the indicator of the rate of the 3DPEH disintegration after several reuse cycles.

#### 2.7 Measurement of the Hydrogel Swelling Ratio and Gel Fraction

Swelling equilibrium and kinetic measurements are standard parameters to determine the degree of crosslinking, where hydrogels with lower degrees of crosslinking tend to absorb more water and swell more in comparison with those with higher degrees of crosslinking. For this measurement, the initial weight of the freeze-dried beads ( $M_0$ ) was measured. Then, the beads were transferred into a metal mesh container

and immersed in DI water. The weight of beads ( $M_t$ ) was measured for up to 24 hours until it reached an equilibrium amount. The swelling ratio was calculated using Eq. (7).

$$Swelling \ ratio = \frac{M_t - M_0}{M_0} \tag{7}$$

The chemical stability of the hydrogels was assessed using the gel fraction test, as described in the literature [51,52]. For this test, hydrogels with the initial polymeric composite mass  $M_p$  were immersed in DI water. The hydrogels were removed from water at fixed time intervals up to 24 hours. While immersed, the uncrosslinked portion of the hydrogels gradually dissolve in water, whereas the cross-linked fraction remains intact. The hydrogels were then freeze-dried, and their gel fraction, corresponding to the cross-linked portion of the hydrogels, was calculated using Eq. 8.

$$Gel \ Fraction = \frac{M_d}{M_p} \times 100 \tag{8}$$

where  $M_d$  is the mass of the freeze-dried hydrogel, and  $M_p$  is the mass of the initial polymeric composite.

#### 2.8 Mechanical Compression Tests

Uniaxial compression test was performed on different 3D-printed scaffolds and encapsulated hydrogels to determine the effect of infill density, customization of the design, and hydrogel encapsulation on scaffold mechanical properties. The force was applied to the scaffolds perpendicular to the 3D-printed layers using a UTS STM-50 testing machine (United Testing Systems, Concord, Canada) with a 50 kN load cell for WP-25 and CC-50 and a 2.2 kN for the rest of the samples, at a constant crosshead speed of 1 mm/min. Engineering compressive stress and compressive displacement were calculated using recorded force and crosshead displacement, respectively. All tests were conducted in triplicates.

#### 2.9 Characterization Techniques

The concentration of dyes was measured using an Agilent Cary 60 UV-Vis Spectrophotometer, operating in the visible light range or at the respective absorption peaks of the dyes, namely 665 nm for MB, 584 nm for MV, 615 nm for MG, and 550 nm for RhB. Rheological evaluations were carried out using an Anton Paar SmartPave 102 rheometer. For storage modulus measurements, a parallel plate geometry with a

diameter of 25 mm was used. The gap size for all tests was set at 2 mm, and a frequency sweep was conducted within the range of 0.1-100 Hz, while maintaining a constant strain of 1%. To analyze the functional groups at a molecular level, Fourier transform infrared spectroscopy (FTIR) spectroscopy was performed using an Agilent Cary 630 FTIR Spectrometer, spanning the range of 400 to 4000 cm<sup>-1</sup>. The pore architecture and surface morphology of the hydrogel beads were examined using scanning electron microscopy (SEM, JEOL JSM-6380LV) using secondary electrons accelerated at 20 kV. The samples were gold coated using a sputter coater prior to SEM imaging. The Brunauer-Emmett-Teller (BET) surface area of the hydrogel beads was determined using nitrogen at 77 K using a Micromeritics Tristar 3000 instrument, following overnight degassing of the samples at 90 °C. The water contact angle was measured using a contact angle goniometer (DataPhysics Instruments OCA 15EC).

#### 2.10 Statistical Analysis

In this study, all tests were performed in triplicates, and the significance of the difference between datasets was analyzed using the Origin software (v.10.0, OriginLab Corporation, USA). Depending on the number of sample sets, *t*-test or one-way ANOVA, including Tukey's test, was used to analyze the significance of the difference between the results. The *p*-value for each analysis was set to  $P \le 0.05$ .

#### 3. Results and Discussions

#### 3.1 Characterization and Performance Evaluation of the Nanocomposite Beads

#### 3.1.1 Effect of GO Concentration

Although the abundance of functional groups on the backbone of carrageenan makes it a desirable adsorbent for a wide range of contaminants, the moderate overall adsorption capacity and low mechanical properties are the main drawbacks in the application of this biopolymer in water treatment [53]. While the primary objective of this investigation is to enhance the durability of the carrageenan hydrogel, a major priority is to enhance its environmental performance as a sustainable adsorbent. This ensures that the hydrogel is not only robust but also an efficient adsorbent of high performance. Graphene oxide, with high surface area and the ability to form various physical interactions such as hydrogen bonding and  $\pi$ - $\pi$  interaction, was chosen to achieve the mentioned objectives. Moreover, based on previous reports on the incorporation of nanomaterials in the biopolymeric matrix, the addition of GO nanosheets significantly improves the adsorption capacity [5–7,9]. Figure 3a demonstrates the effect of various GO concentrations on the MB adsorption performance of the nanocomposite beads in comparison with the neat Carg beads. MB is a model organic contaminant, and its adsorption capacity using different sorbents is widely reported in the literature [54,55]. In this experiment, the initial concentration of MB solution was set at a relatively high amount of 250 ppm to highlight the effect of GO concentration on the removal capacity. As shown, the adsorption capacity of the beads increases with the addition of GO and reaches its optimum amount in the GO content range of 0.5 to 2.5 wt% (Figure 3a). Statistical analysis indicates that the measured adsorption capacities of the different GO-containing hydrogel beads are comparable, and the observed variations are not significant. However, there was a statistically significant difference between neat Carg hydrogel beads and all GO-containing hydrogel beads. Since one of the important objectives of this study was the economic viability of the adsorbents, the formulation containing only 0.5wt% GO (Carg-0.5GO) was selected as the optimum GO concentration for the rest of the study.





enhancement might stem from changes in hydrogel morphology as well as the establishment of stronger physical interaction between contaminants and the GO-containing hydrogel. The experimental kinetics data were fitted using the pseudo-first order and pseudo-second order kinetic adsorption models, as given by Eqs. (3) and (4), respectively. The calculated parameters suggest an increase in the rate constants and calculated  $Q_e$  as the result of GO addition to the biopolymeric beads (Table S2).

Equilibrium isotherms offer valuable insight into the theoretical maximum adsorption capacity of an adsorbent and the underlying interactions between the adsorbate and the adsorbent in equilibrium conditions. Based on the equilibrium isotherm study and model fitting of the hydrogel beads, the Langmuir model better explains the adsorption process compared to the Freundlich model for all the studied formulations. This demonstrates that the adsorption mechanism is a monolayer physical adsorption. The values of isotherm parameters are presented in Table S2.

Figure 4 compares the surface and cross-sectional morphology of the hydrogel beads at different GO concentrations. The addition of GO to the biopolymeric beads led to the appearance of wrinkles on the surface compared to the pure Carg hydrogel bead (Figure 4a-d), and consequently, the active surface area increased. The change in the BET surface area was quantified using nitrogen adsorption measurement which is summarized in Table S2. In addition, GO-containing beads tend to have smaller pore sizes with thicker walls (Figure 4 e-h).



**Figure 4.** The effect of GO concentration on the morphology of the hydrogel beads. Surface and cross-sectional views of (a and e) neat Carg bead, (b and f) Carg-0.5GO, (c and g) Carg-1GO, and (d and h) Carg-2.5GO beads.

Moreover, adding GO to carrageenan improves the nanocomposite's physical properties, resulting in more stable structures in terms of mechanical and thermal stability and durability. We used dynamic rheometry to measure the storage modulus of the hydrogels (Figure 5a). The storage modulus of the Carg-0.5GO hydrogel at 10 Hz increased from  $3.4 \pm 0.1$  kPa for neat Carg to  $12.4 \pm 0.4$  kPa, confirming the reinforcing effect of GO even at a small amount. The significant enhancement (more than three times) of this mechanical property originates from the increased interactions between biopolymeric chains and GO nanosheets, and the possible formation of secondary physical interactions inside the nanocomposite hydrogel[18]. The main objective of this work was to improve the relatively low mechanical properties of carrageenan, which was achieved by using GO nanosheets.

FTIR spectroscopy was performed to analyze the effect of GO addition on functional groups (Figure 5b). The bands at 3315 and 1648 cm<sup>-1</sup> are attributed to O–H and aromatic C=C bonds, respectively. The bands at 1213, 1067, and 925 cm<sup>-1</sup> correspond to C–O stretching and vibrations including in glycosidic linkage and polyhydroxy groups of carrageenan. The band at 843 cm<sup>-1</sup> corresponds to the stretching vibration of the C–O–SO<sub>3</sub> carrageenan group. In the case of nanocomposite hydrogels, the intensity of all normalized bands increased, suggesting the formation of physical interaction between carrageenan and GO nanosheets. According to the molecular structure and functional groups of the bead components, we hypothesize that hydrogen bonding, van der Waals, and electrostatic interactions are among the intermolecular forces between GO nanosheets and carrageenan chains. Additionally, the C–O–SO<sub>3</sub> group shifts to a slightly lower wavenumber (835 cm<sup>-1</sup>), suggesting the specific participation of this functional group in the physical interactions[56].



Figure 5. (a) Storage moduli and (b) FTIR spectra of the neat Carg and Carg-0.5GO nanocomposite hydrogels.

## 3.1.2 Effect of the Coagulation Bath Temperature

Apart from adding GO nanosheets, one strategy to improve the mechanical properties of carrageenan hydrogels is to increase the degree of ionic cross-linking. In addition to the room temperature coagulation bath (CCB), we formed carrageenan-based beads in coagulation baths with elevated temperatures at 30, 40, and 50°C (HCB). The elevated temperature increases the activity of the ionic cross-linking process, and it can result in beads with higher degrees of crosslinking. To measure the effect of temperature on the degree of crosslinking, swelling tests, dynamic rheometry, and reusability tests were performed on the beads.

Figure 6a shows a comparison between the swelling kinetics of Carg-0.5GO beads that have been formed in coagulation baths with different temperatures. There is an inverse correlation between the coagulation bath temperature and the swelling ratio of the beads, confirming the hypothesis that coagulation temperature impacts the degree of crosslinking of the beads. The swelling ratio of the beads formed at 50°C reaches equilibrium within the first 30 minutes in water at the maximum swelling ratio of 4.3, while the bead formed at 25°C reaches a swelling ratio of 8 and then starts to disintegrate after 5 hours due to poor mechanical properties. While disintegration is not observed for beads formed at 30 and 40 °C after 24 hours, their high swelling ratios significantly reduce the mechanical properties of the beads, resulting in fragile beads. The ANOVA analysis was conducted on the dataset at the fifth hour of sampling before the hydrogels started to disintegrate, confirming a significant difference in swelling ratio across all four temperatures.

The observations on the swelling ratio of the beads were further confirmed using dynamic rheometry. As shown in Figure 4a, the storage modulus of the nanocomposite hydrogel formed in HCB (50 °C) is approximately three times higher than that of the nanocomposite hydrogel formed in CCB (25 °C). At 10 Hz, the storage modulus increased from  $12.4 \pm 0.4$  to  $32.5 \pm 0.6$  kPa. These observations indicate that the formation of beads at elevated temperatures leads to an overall stiffer structure with a higher degree of crosslinking and reduces the rate of bead disintegration.

Figure 6b exhibits the impact of coagulation bath temperature on the chemical stability of the hydrogel beads. The gel fraction of the hydrogels formed in a lower-temperature coagulation bath drastically decreased within 24 hours. The hydrogels formed at 50 °C had the least decrease in gel fraction over time, confirming their higher density of cross-linking in comparison with those hydrogels that were formed at lower temperatures. This result was in agreement with our observation from the swelling ratio test, confirming our hypothesis that a higher coagulation bath temperature leads to a higher degree of cross-linking.

As mentioned in the introduction, we used the ionic metachromatic complexes between MB and leached carrageenan as an indicator of carrageenan hydrogel disintegration which was assessed using colorimetric methods. This phenomenon was observed during the adsorption of MB by both neat and GO-containing carrageenan beads (Figure S1). This approach provides a unique opportunity to study the stability of hydrogel beads without changing the adsorption conditions. Thus, to evaluate the stability of the beads during dye adsorption, we regenerated and reused the beads for the adsorption of MB for several cycles. As shown in Figure 6c, HCB beads could be reused for 6 cycles, after which the MB solution color shifted from blue to purple, indicating the release of free carrageenan molecules into the solution. CCB beads disintegrated after one regeneration cycle, resulting in the MB solution color shift. Our findings are different from the previous report on the effect of temperature on ionic crosslinking, which found this parameter

insignificant [50]. This discrepancy originates from different methodologies that have been utilized to monitor the stability of the hydrogel. Jóźwiak et al. [50] evaluated the effectiveness of temperature on ionic crosslinking by the exposure of the biopolymeric hydrogel to acidic conditions and compared the adsorption capacity after the acid treatment. They visually examined the damage and swelling as a tool to probe, while we followed tests such as hydrogel swelling, gel fraction, and reusability coupled with the colorimetric method for detection of hydrogel disintegration. One potential explanation for drawing different conclusions on the effect of temperature is the harsh conditions of acid exposure for inherently mechanically weak polymers and the absence of a proper probe to evaluate the stability of the hydrogels.



**Figure 6.** Effect of coagulation bath temperature on the properties of the Carg-0.5GO beads. (a) Comparison between the swelling ratios of CCB and HCB beads, (b) Comparison between the gel fraction of CCB and HCB beads, and (c) MB removal efficiency of the beads after several cycles of regeneration and reuse.

We also investigated the effect of the coagulation bath temperature on the kinetics of MB adsorption by the Carg-0.5GO nanocomposite beads (Figure 5c). We conducted a *t*-test to determine if there was a significant difference in adsorption capacity of the beads at various time intervals (*p*-value  $\leq 0.05$ ). The removal efficiency of MB after 24 hours was comparable for both CCB and HCB beads (95% for HCB compared to 93% for CCB). However, there was a significant difference in the adsorption kinetics, with HCB beads showing faster kinetics in the first 3 hours compared to their CCB counterpart. On average, the HCB beads exhibit a smaller diameter (3–4 mm) compared to CCB beads (4–5 mm). SEM images of the HCB beads (Figure 7b) illustrate finer surface features than those observed in CCB beads (Figure 7c), contributing to

a higher surface area. The BET surface area of the Carg-0.5GO beads formed in HCB ( $147.2m^2/g$ ) was 47% higher than the same beads formed in CCB ( $100.1 m^2/g$ ). The increase in the specific surface of the HCB beads leads to faster MB adsorption kinetics in comparison with CCB beads.



**Figure 7.** Effect of coagulation bath temperature on the properties of the Carg-0.5GO beads. (a) the MB adsorption kinetics of the beads formed in HCB and CCB, and (b-c) the SEM micrograph showing the external morphology of Carg-0.5GO formed in HCB and CCB, respectively.

# 3.2 Characterization and Performance Evaluation of Nanocomposite Hydrogels Encapsulated in 3D Printed Polymeric Scaffolds

Although the formation of beads in HCB has a significant effect on their overall stability, the nanocomposites need further improvement in durability before they can be applied in industrial-scale water treatment. One strategy to improve the mechanical properties and the reusability of hydrogels is to embed them in proper scaffolds with good mechanical properties. In this work, we use 3D printed porous scaffolds with rationally designed pore architecture for embedding the nanocomposite hydrogels for water treatment. PLA has been chosen for 3D printing the scaffolds due to its green nature and low cost [57]. The water contact angle of PLA was measured to be  $72.3 \pm 4^{\circ}$  (Figure S2), which is higher than the contact angle of Carg-0.5GO hydrogel ( $53.2 \pm 2^{\circ}$ ). The porous 3D printed PLA scaffold provides external support for the nanocomposite hydrogels, thus lowering the rate of disintegration. Furthermore, the scaffolds provide a platform to incorporate the hydrogels in any desired geometry, such as impellers, which would not be

possible with crosslinked beads. The flexibility of 3D printing and CAD provides the opportunity to design multifunctional structures that not only participate in water treatment but also improve the rate of mixing of contaminants in water by effectively lowering the diffusion barriers. The interaction between the PLA scaffold and the embedded hydrogel is physical in nature. The main physical interaction is the van der Waals force between the PLA scaffold and biopolymeric-GO dispersions. Furthermore, the macroporous structure of the scaffolds results in capillary action between pore walls and nanocomposite solution before the ionic crosslinking of the hydrogels.

We embedded the best-performing nanocomposite bead formulation (Carg-0.5GO) in 3D printed PLA scaffolds with different pore design parameters. Figure 8a shows that the MB removal kinetics of the 3D printed encapsulated hydrogels (3DPEH) with CC design is slower than beads. The available surface area in the case of the beads is the sum of each bead's surface area, while in 3DPEH, it is limited to the outer area of the structure that is exposed to the feed solution. However, both types of adsorbents have statistically comparable equilibrium removal efficiencies for different organic dyes, including MB (Figure 8b). Among the studied dyes, MB, MV, and MG show the highest removal efficiencies, as they not only interact with the hydrogel through electrostatic forces between the cationic dyes and the anionic hydrogels but also benefit from metachromatic interactions with carrageenan.

The reusability study highlights a significant improvement in the durability of the 3DPEH. The 3DPEH that were formed in HCB and CCB were regenerated and reused ten times without significant change in their removal efficiencies (Figure 8c). The disintegration mechanism of the 3DPEH is different from beads, as the surface to volume ratio of 3DPEH is smaller than the hydrogel beads, resulting in a larger diffusion path for leaching un-crosslinked carrageenan polymeric chains. Consequently, the disintegration of 3DPEH is significantly slower and their reusability is improved. In this study, the remaining amount of the hydrogel inside the scaffolds after regeneration and reuse was measured as an indicator of the 3DPEH stability. After 10 regeneration and reuse cycles, 93% of the 3DPEH that was formed in HCB remained intact, while only 33% of the hydrogels remained in the scaffold when it was formed in CCB. It is evident that the formation

of biopolymeric hydrogels in HCB coupled with using a 3D printed scaffold enhances the mechanical properties and reusability of these sustainable and green nanocomposite adsorbents for practical water treatment applications.



Figure 8. Comparison between the Carg-0.5GO beads and encapsulated hydrogels (3DPEH): (a) MB removal kinetics, (b) overall efficiency in removing various organic dyes, and (c) the reusability of 3DPEH formed in CCB and HCB using CC-25 scaffold.

#### **3.3 Effect of Infill Pattern and Density on the Environmental Performance of 3DPEHs**

Modifying the infill pattern and density impacts the mass of PLA utilized for printing the scaffold. We designed porous scaffolds in a WP, as well as a more complex CC pattern, which allows more hydrogel to penetrate inside the scaffold and potentially increases the adsorption capacity of the resulting 3D printed structure. To compare the effect of the infill pattern, the amount of encapsulated hydrogel in the WP and CC scaffolds was measured while keeping the infill density at 25%. The CC scaffold encapsulated 144% more nanocomposite hydrogel in comparison with the WP pattern (Table 1), which demonstrates that the CC pattern provides more porous volume for hydrogel encapsulation.

More porous volume does not always guarantee better performance, as it results in fewer contact points between the PLA support and the encapsulated hydrogel, which directly affects its disintegration rate and reusability. Accordingly, infill density was the second 3D printing design parameter that we studied. Scaffolds with CC patterns having three different infill densities (10%, 25%, and 50%) were printed and encapsulated with hydrogels. We measured the amount of hydrogel encapsulated in the scaffold and their

reusability. The amount of encapsulated hydrogel varies by changing the infill density; however, a higher infill density does not necessarily result in a lower amount of encapsulated hydrogel. For instance, despite providing more free space, the amount of hydrogel encapsulated in structures with 10% and 25% infill density are comparable. The lack of sufficient contact points between the PLA scaffold and the carrageenan-GO dispersion, coupled with its low viscosity, results in losing part of the dispersion during the transfer of the structure to the coagulation bath. Consequently, there is a balance between the available free space in the CC scaffold and adequate contact points for obtaining the optimum scaffold design.

Scaffold Design	Infill Density	Empty Scaffold	Encapsulated	Compressive
(Structure Name)	(%)	Mass (g)	Hydrogel Mass (g)	Strength (MPa)
Woodpile (WP-25)	25	3.22	2.46	34.3
Customized (CC-10)	10	1.47	5.97	17.9
Customized (CC-25)	25	3.41	6.00	20.7
Customized (CC-50)	50	6.81	1.02	31.1

Table 1. Effect of scaffold design on the mass of encapsulated hydrogel and mechanical compressive properties.

To investigate the effect of infill design and density on the scaffold's mechanical properties, the mechanical compression test was performed. The compressive stress-displacement curves of different scaffold designs are shown in Figure 9a. The compression test results indicate a higher compressive strength for the WP-25 design compared to the CC-25 design at the same infill density. The WP pattern is a 2D standard infill pattern that demonstrated high compressive strength when force was applied perpendicular to the 3D-printed layer [58]. The aim of customizing the infill design in this study was to increase the porous fraction and engineer the hydrogel's exposed surface area to enhance the scaffold's adsorption rate, thereby increasing the mass of the encapsulated hydrogel. We also examined the effect of infill density on the compressive strength. The results show that higher infill density led to an increase in compressive strength. Higher infill density provides better support for the structure resulting in higher plastic deformation before structural failure [59]. In our customized infill design, we hypothesize that higher maximum displacement

results from collapsing different infill layers onto each other. Since the mechanical properties of the fluid (in this case, air) filling the porous volume is much lower than that of PLA, and there is no significant hydraulic resistance, the scaffolds exhibit a higher maximum displacement before failure. A summary of the measured mechanical properties of the designs is presented in Table 1.



**Figure 9.** The compressive stress-displacement curves of (a) different scaffold designs and (b) encapsulated hydrogel compared to the empty scaffold. (c) gel fraction as a function of time for different 3DPEH designs.

To investigate the impact of hydrogel encapsulation on the mechanical properties of the scaffold, we conducted compression tests on the encapsulated hydrogels in the CC-25 scaffold (3DPEH CC-25) and compared the results with those of the empty scaffold (figure 9b). We observed that the compressive strength increased to 24.5 MPa, while the maximum displacement significantly decreased. This might originate from the filling of porous volume with hydrogels that have higher compressive strength compared to air, as well as the hydraulic forces applied from the hydrogel to the scaffold.

Figure 9c demonstrates the effect of encapsulation on the chemical stability of the hydrogels. Generally, the cross-linked gel fraction in the encapsulated hydrogels proved to be higher than that of hydrogel beads. This result might stem from the increase in the diffusion pathway in encapsulated hydrogels from the core of the 3D printed structure to its surface, compared to the smaller diffusion pathway of the hydrogel beads. Moreover, higher infill density increases gel fraction by reducing water mobility into the encapsulated hydrogel, resulting in a lower rate of leaching of uncross-linked polymer to the solvent.

We also conducted reusability studies on the three CC designs with different infill densities and compared their overall performance and durability. The CC-50 structure shows the lowest MB removal efficiency (Figure 10a), as it contains the least amount of encapsulated hydrogel. Additionally, the high infill density of this scaffold results in a pronounced effect on water mobility inside of the 3DPEH and creates barriers for water-contaminant complex diffusion into the nanocomposite hydrogel. Although the CC-10 structure shows comparable MB removal efficiency for the first six cycles, its progressive disintegration leads to eventually lower MB removal efficiency in comparison with the CC-25 structure. Overall, after 20 regeneration and reuse cycles, only 10% of the total hydrogel mass of CC-25 structure was disintegrated in the process, whereas in the case of CC-10, the entire embedded hydrogel disintegrated by the 20th cycle. Based on our study, encapsulated GO-containing biopolymeric hydrogels in 3D printed CC design scaffolds with 25% infill density provide an excellent balance of properties for the removal of contaminants such as organic dyes from water. Figure 10b illustrates the superior performance of our design in comparison with the existing designs in the literature in terms of reusability. Such structures show great promise in the fast and simple manufacturing of the next generation of point-of-use water treatment systems by simultaneously leveraging the advantages of additive manufacturing and nanotechnology.



Figure 10. (a) The reusability of Carg-0.5GO hydrogels encapsulated in CC 3DP scaffolds with different infill densities. (b) Comparison between the reusability of our design in comparison with other carrageenan-based hydrogel studies.

#### 4. Conclusions

This study aimed to address the mechanical properties and reusability of biopolymeric hydrogels, which are major obstacles to their potential large-scale application as adsorbents. For this purpose, carrageenan was selected as a model biopolymer, and three approaches were explored to improve its adsorption performance, mechanical properties, and reusability. Although the primary purpose of incorporating GO nanosheets was to increase the adsorption rate and capacity of the hydrogel, the physical interaction between polymer chains and nanosheets also resulted in improved mechanical properties. The addition of only 0.5 wt% GO nanosheets resulted in a 305% enhancement in the storage modulus of the hydrogels and improved the overall MB removal efficiency by 36%. We proposed increasing the degree of ionic crosslinking by raising the temperature of the coagulation bath as a strategy to eliminate the need for thermal post-treatment. We investigated the effect of this strategy through a series of tests including dynamic rheometry, swelling and gel fraction tests, and reusability experiments. The findings indicated that this approach led to greater chemical stability (increasing from 33% for CCB to 60% for HCB) and reduced swelling ratio (decreasing from 8 for CCB to 4.3 for HCB), both indicating a higher degree of crosslinking. Additionally, the storage modulus of the hydrogel increased by 264%, and the reusability test demonstrated a significant improvement over CCB hydrogels by reducing the rate of hydrogel disintegration.

Most importantly, this study establishes a novel pathway for the fabrication of robust, durable, and sustainable adsorbents by encapsulating polymeric hydrogels within a 3D printed scaffold. We underscore the critical role of engineering the scaffold's pore design. The infill pattern (pore architecture) and infill density (porosity) were found to be crucial parameters impacting both the encapsulation process and the environmental performance of the 3DPEHs. The results indicated that a 3D printed scaffold with complex customized design and 25% infill density (CC-25) exhibited the highest MB removal efficiency and encapsulated 144% more hydrogel in comparison to the conventional woodpile design of the same infill density (WP-25). The applied strategies successfully increase the reusability of the encapsulated hydrogel

four times (20 cycles for 3DPEH CC-25) higher than previous reports without any significant weight loss of the hydrogel due to disintegration.

Declaration of competing interest: Authors declare no conflict of interest.

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# **Supporting information:**

<sup>1</sup> Video of layer-by-layer printing of woodpile design (MP4).

- <sup>2</sup> Video of layer-by-layer printing of complex customized design (MP4).
- <sup>3</sup> Additional experimental details including SEM and digital images, and reusability graphs (PDF).

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