SYNTHESIS AND CHARACTERIZATION OF MODIFIED κ-CARRAGEENAN POLY(ACRYLIC ACID) HYDROGEL BEADS

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ABSTRACT

Textile wastewater contains synthetic fabric dyes that pose leading threat to human health and the environment. As standard water treatment methods are unable to remove persistent pollutants from the environment, researchers are turning to better adsorption methods to treat synthetic dyes. The aim of this study is to create a modified hydrogel of κ-carrageenan/poly(acrylic acid) as adsorbent for water treatment. The hydrogel beads were produced by crosslinking N'N-methylene bisacrylamide (MBA) and glutaraldehyde using coating and mixing techniques. Each method generates three samples, A, B, and C, with different compositions of N'Nmethylene bisacrylamide (MBA) crosslinking agent. The swelling and Fourier Transform Infrared Spectroscopy (FTIR) tests were carried out to determine the physicochemical properties of the κ-carrageenan hydrogel beads. The outcomes of the FTIR test have demonstrated that there is a crosslinking agent present on κ-carrageenan hydrogel beads. Functional groups include the hydroxyl group (O-H) found in alcohol and phenol, the aliphatic saturated hydrocarbon chain (C-H), the carbonyl and amide group (C=O) and (C-N), the sulfonyl and sulfate groups (O=S=O) and (S-O), along with the ester, ether, carboxylic acid, and anhydrides (C-O) presence in each sample ensured that crosslinking agents were successfully present on k-carrageenan beads for both methods. The swelling of κ-carrageenan poly(acrylic acid) hydrogel beads provides an effective technique for designing and modifying polysaccharide-based beads for wastewater treatment.

Keywords: κ-carrageenan, N'N methylene bisacrylamide, Textile wastewater, hydrogel beads and crosslinking agent

1.0 INTRODUCTION

Water pollution from industrial effluents is a global environmental issue since water is the most reliable source of life for humans, animals, and plants. Our physical survival depends on water, but it's also essential for several domestic and industrial processes. However, water resources are currently dealing with some never-before-seen problems. Wastewater contains industrial effluent due to the modern synthetic fabrics' dyes. The health of people and aquatic life is seriously threatened when wastewater from the textile industry is discharged into rivers and areas where people live.

Not only dyes poisonous due to their colors, but they also produce toxic substances when they decompose [1]. The look and quality of water are greatly affected by even very small amounts of color [2]. It raises the BOD level and has an impact on sunlight transmission [3]. Because of the dye color's visibility in the recipient water, dye removal has been a source of concern. Dyes are one of the main hazardous compounds typically found in industrial effluents, and their presence raises serious concerns. Dyes are used extensively in various industries, including the

tannery, plastic, paper, cosmetic, leather, and textile sectors. Due to their mutagenic and carcinogenic properties, dyes disposed of in water harm the ecosystem and biological creatures [4].

As such, it is deemed a limited technique to remove colors from wastewater prior to its release into the environment. Conventional methods of wastewater treatment have struggled to effectively remove methylene blue dye due to its low biodegradability. In the past few decades, distinct methods have been devised to eliminate dyes, such as ion exchange, microbial degradation, photochemical, chemical coagulation, membrane separation, and adsorption [4]. However, adsorption is significantly the most often used purification technology due to its ease of use, low cost, and efficacy.

Adsorption is a type of physicochemical mass transfer in which an adsorbate, or material present in the fluid phase, adsorbates, or accumulates, on the surface of an adsorbent, the solid phase. The substance that dissolves may be adsorbed on the innermost layer of the adsorbent or transferred by diffusion into its pores [3]. Typically, hydrogel films are very useful adsorbents for the removal of dyes.

As current water treatment processes fail to remove persistent pollutants from the environment, researchers are turning more and more toward the use of polysaccharide-based adsorbents for the adsorptive removal of environmental contaminants due to it moderately cost and easily accessible. κ-carrageenan represents one of the natural polysaccharides and is the primary focus of this study. The sulfonic group (SO^{3-}) in carrageenan's linear chain makes it a promising material for film formation [5]. Because of its many sulphated pendants, which are very efficient in warding off certain cations, this natural polymer can be ionically crosslinked [6]. The likelihood of excess potassium ions being present in the kappa-carrageenan samples exists since industrial carrageenan is extracted from the red seaweed using hot alkali solutions, including potassium hydroxide (KOH) solutions [5].

However, polysaccharides, such as κ-carrageenan, must be blended with other materials to boost their adsorption capability. Polymer-based carrageenan hydrogels' low mechanical strength and adsorption capability hindered their implementation in the biomedical and adsorption sectors [7]. In line with study done by [4] discuss that even with all of its benefits, κ-carrageenan's utilization is still restricted due to its low environmental stability and weak gel strength. κ-carrageenan can be combined with other functional polymers to create a new adsorbent that has better adsorption capabilities [4]. Chemical crosslinking by adding N'N-methylene bisacrylamide and glutaraldehyde to carrageenan hydrogel will improve its strength as well as several other crucial properties, ranging from swelling, adsorption behavior, thermal stability, and reusability. Thus, the preparation of adsorbent from crosslinked hydrogel beads with varying composition ratios of N'N-methylene bisacrylamide and glutaraldehyde (as crosslinked agent) were carried out in this study. The characterization of modified κ-carrageenan hydrogel beads and their swelling behavior were also investigated.

2.0 RESEARCH METHODOLOGY

2.1 Materials

Acrylic acid is used as a monomer to provide samples. As cross-linking agents, N'N- methylene bisacrylamide and glutaraldehyde 12.5% are utilized, while ammonium persulfate $(NH_4)_2SO_4$ is used as a reaction starting material. A potassium chloride (KCl) 3M solution is also used to harden the beads.

2.2 Methods

2.2.1 Preparation Coated κ-Carrageenan Poly(Acrylic Acid) Hydrogel Beads

κ-carrageenan powder was dissolved into 90 mL of distilled water. The solution was heated to a temperature of 60°C. After that, the solution was left to cool to between 50 and 55°C. The sample was then dropped into a beaker consisting of a solution made up of a single thin layer of palm olein oil phase and salt solution aqueous phase (50 mL of 0.3M potassium chloride solution, KCl). When dripped, a sphere-shaped bead was formed and immersed in a 0.3M KCl solution for 1 hour. The beads were then rinsed three times with distilled water and 0.3 M KCl solution. The beads were dried at room temperature.

The κ-carrageenan beads were combined with 10 mL of acrylic acid, N'Nmethylene bisacrylamide (MBA), 0.2g of 2 mL ammonium persulfate $(NH_4)_2SO_4$, 5 mL of 12.5% glutaraldehyde, and 5 mL of 3M KCl. This mixture is shaken for 15 to 30 minutes before being washed with distilled water and dried at 50°C for 12 hours. The resultant κ-carrageenan hydrogel bead was then analyzed usingnalyzed using FTIR analysis for physical characterization. Table 2.1 outlines the compositions and crosslinking techniques used in producing κ-carrageenan hydrogel beads.

2.2.2 Preparation Mixed κ-Carrageenan Poly(Acrylic Acid) Hydrogel Beads

κ-carrageenan was mixed with 10 mL of acrylic acid and N'Nmethylene bisacrylamide (MBA) and thoroughly dissolved by heating to a temperature of 60°C. Then, 0.2g of 2mL ammonium persulfate $(NH_4)_2SO_4$, 5 mL of 12.5% glutaraldehyde, and 5 mL of 3M KCl were added to the mixture. Then, the solution was left to cool to between 50 and 55°C. The solution will form a gel solution at this temperature. The sample was then dropped into a beaker consisting of a solution made up of a single thin layer of palm olein oil phase and salt solution aqueous phase (50 mL of 0.3M potassium chloride solution, KCl). A sphere-shaped bead was formed. The compositions and crosslinking techniques used in the production of mixed κ- carrageenan beads are the same as the coated method as indicated in Table 2.1 below.

Table 2.1: Compositions and crosslinking techniques for the production of κ- carrageenan hydrogel beads

Beads	**κ-Carrageenan (g)**	**Acrylic acid (mL)**	**Ammonium persulfate, 0.6g (mL)**	**3M KCl (mL)**	**Crosslink agents**	
					MBA (g)	**Glutaraldehyde (mL)**
Coated A	0.5	10	2	5	0.05	5
Coated B	0.5	10	2	5	0.1	5
Coated C	0.5	10	2	5	0.2	5
Mixed A	0.5	10	2	5	0.05	5
Mixed B	0.5	10	2	5	0.1	5
Mixed C	0.5	10	2	5	0.2	5

2.2.3 To Study physical characteristics of κ-Carrageenan Poly(Acrylic Acid) Hydrogel - Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The structural functionality of the fabricated beads were characterized using Fourier-transformed infrared spectroscopy (Brucker platinum ATR, Invenio S) for the identification of the functional groups. All the κ-carrageenan beads that were prepared from the coated and mixed method have been sent to Fourier Transform Infrared Spectroscopy (FTIR) Analysis to determine whether the coating substance is present. Before conducting the FTIR analysis, the bead samples were collected and labeled each of the ratios. Through the identification of changes in functional groups, the Fourier transform infrared (FTIR) method of spectroscopy can identify modifications in the overall composition of biomolecules [8]. FTIR is used to quantify how molecules vibrate and rotate in response to infrared radiation at a specific wavelength [8]. A material's Infrared spectroscopy (IR) spectrum is influenced by its chemical composition, isomorphic substitution, layer stacking order, and structural alterations [9]. As a result, FTIR is the most informative technology for identifying not only functional groups but also other interactions between components [9]. An adsorbent's surface functional groups are crucial to the adsorption process because they provide target adsorbates with contact sites for fixation.

2.2.4 To Study physical characteristics of κ-Carrageenan Poly(Acrylic Acid) Hydrogel- Swelling Test

The hydrogel beads' swelling behavior was ascertained by immersing the samples in room-temperature distilled water. The enlarged hydrogel beads were removed, cleaned with filter paper, and weighed after the necessary amount of time had passed. The equation utilized to calculate the swelling ratio (%) was:

$$\text{Swelling Ratio (\%)} = \frac{(W_s - W_o)}{W_o} \times 100 \qquad \text{Equation 1}$$

Where,
W_O = the weights of samples before (g)
W_S = the weights of samples after being taken out from water (g)

3.0 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR analysis of mixed and coated κ-carrageenan hydrogel beads has been observed. Figures 3.1 and 3.2, indicate the analysis results obtained for each modified preparation techniques of κ-carrageenan hydrogel bead.

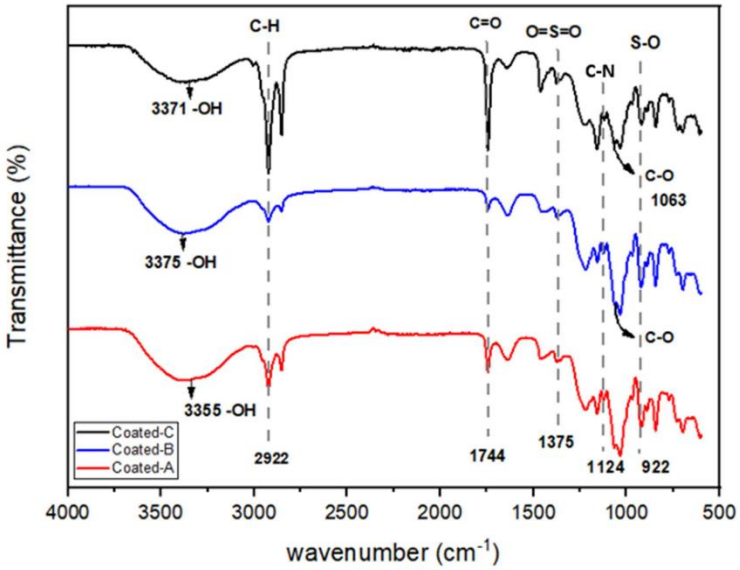

Figure 3.1: Combination of 3 waves in FTIR Analysis for Sample Coated A, B, and C.

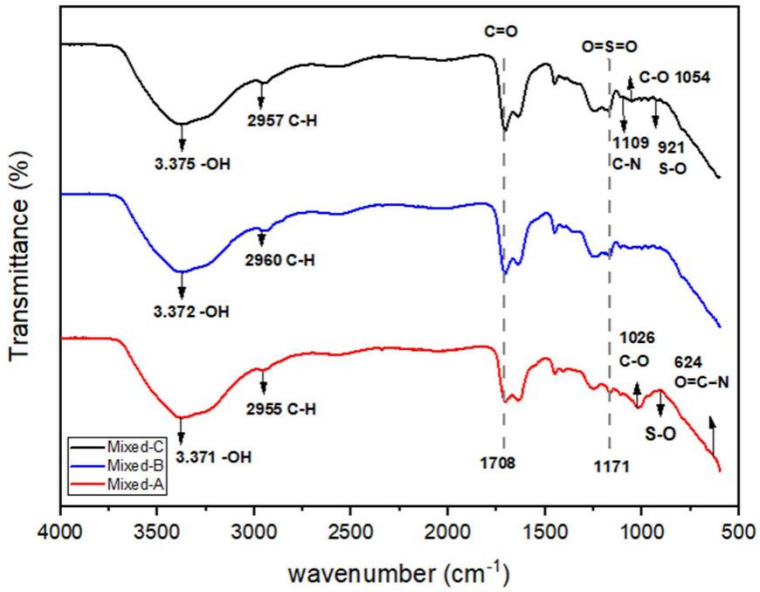

Figure 3.2: Combination of 3 waves in FTIR Analysis for Sample Mixed A, B, and C

The results presented in Table 3.1 are self explanatory. For all 3 coated samples, there are strong infrared band in range 3355.4 - 3371.77 cm^{-1} which assigned to O-H stretching vibration. On the other hand, all mixed samples also have O-H stretching vibration which are at 3371.53 cm^{-1}, 3372.4 cm^{-1}, and 3375.63 cm^{-1}.This indicates that polymeric materials, such as alcohol and phenols, have both free and hydroxyl groups with hydrogen bonds [10].

Table 3.1: Wavelength range FTIR analysis of sample coated-A, B, C and sample mixed-A, B, C

Wavelength Range (cm^{-1})	Wavenumber						Bands
	Coated-A	Coated-B	Coated-C	Mixed-A	Mixed-B	Mixed-C	
3400-3200	3355.4	3375.22	3371.77	3371.53	3372.4	3375.63	The hydroxyl group in alcohol and phenols (O-H)
3000-2840	2922.93	2922.99	2922.58	2955.46	2960.12	2957.83	Aliphatic saturated hydrocarbon chain (C-H)
2540-1000	1744.53	1744	1744.64	1708.12	1706	1707.21	Carbonyl group (C=O)
1350-1140	1375.76	1374.91	1225.67	1234.1	None	1171.42	Sulfonyl group (O=S=O)
1300-1000	1064.17	1064.15	1064.85	1026.44	1025.07	1054.2	Carbonyl group (C=O)
1350-1000	1191.87	1157.55	1159.55	1168.74	1166.25	1109.44	Amine group (C-N)
1000-750	969.69	969.97	970.01	969.39	None	968.61	Sulfate (S-O)
630	645.81	664.84	646.73	624.04	618.53	614.38	Amide IV (O=C-N)

The strong infrared band near 1700 cm^{-1} for all 6 coated and mixed samples is assigned to carbonyl group (C=O) stretching mode. This carbonyl group indicates for vibrations of both crosslinking agent used in modified techniques which are N'N methylene bisacrylamide and gluteraldehyde. This is in line with a study done by Venkatram et al, 2008 [11] where they observed infrared band for C=O near 1650 cm^{-1}. The aliphatic saturated hydrocarbon chain (C-H) is present in all samples, with a range of 3000-2840 $cm^{-1.}$ The S-O stretching vibration are calculated between 750 -1000 cm^{-1} for all samples except for mixed B sample where there is no wavelength detected in FTIR analysis. The infrared band near 1140 and 1350 cm-1 has been assigned to sulfonyl group (O=S=O) stretching vibrations. The strong absorption in infrared near 1234.1cm^{-1}, 1253.02 cm^{-1} and 1171.42 cm^{-1} are assigned to sample coated A,B and C respectively.

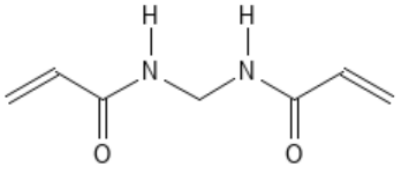

Figure 3.3: Structure of N'N-Methylene bisacrylamide

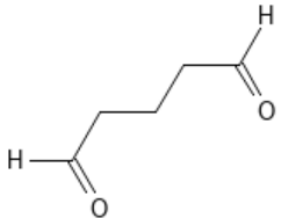

Figure 3.4: Structure of Gluteraldehyde

The presence of asymmetric O=S=O stretching can be due to the κ-carrageenan while C-N stretching of amines might be due to the N'N-methylene bisacrylamide (MBA) components. The existence of the O=S=O and S=O stretching could be due to the ioniccrosslinking. Peak form and intensity are greatly influenced by hydrogen bonding (O- H), which typically results in peak broadening and shifts in absorption to lower frequencies [12]. All bands' presence in each sample ensured that crosslinking agents were successfully present on κ-carrageenan beads for both methods. This is in line with a study reported by [4], observed various distinct peaks at 3350, 1239, 1061, 927 and 843 cm^{-1} which were attributed to -OH stretching, O=S=O asymmetric stretching of sulfate ester, S-O stretching, C-O-C stretching in 3, 6- anhydro galactose and C-O-S stretching, respectively.

C-N stretching vibration is observed between 1109-1191 cm^{-1}. Both coated and mixed samples have the amine group (C-N), which has a range of 1350–1000 cm^{-1}. Sample coated-A exhibits its presence at 1191.87 cm^{-1}, followed by sample coated-B at 1157.55 cm^{-1}, sample coated-C at 1159.55 cm^{-1}, and sample mixed-A at 1168.74 cm^{-1}. The amine group (C-N) also observed at 1166.25 cm^{-1} for sample mixed-B and 1109.44 cm^{-1} for sample mixed-C. Venkatram et al, 2008 [11] also observed C-N stretching mode near 1301 cm^{-1}. The amide IV band (O=C-N) is identified near 630 cm^{-1} in infrared spectrum which can increase entanglement and aggregation, resulting in a strong crosslinked structure [13]. The infrared spectrum reveals absorptions near 645.81 cm^{-1} for sample coated A, 664.84 cm^{-1} for sample coated B and 646.73 cm^{-1} for sample coated C. While for mixed sample A,B and C have strong absorption in infrared near 624.04 cm^{-1}, 618.53 cm-1 and 614.38 cm^{-1} respectively.

3.2 Swelling Test Analysis

In this study, N'N methylene bisacrylamide and gluteraldehyde were used as crosslinking agent of κ-carrageenan hydrogel beads to improves the physical characteristics by crosslink. Chemical crosslinking is a direct reaction between linear polymer or branches and at least a bifunctional component, small molecular weight and called as crosslinker which link the polymer chains with its functional groups. Crosslinking is important because the unreacted κ-carrageenan is still easily soluble in water. Thus crosslinking will improve the stability of hdrogel beads in aqueous medium [14]. All six samples of the κ-carrageenan hydrogel beads' stability in distilled water are determined in this study. N'N-methylene bisacrylamide (MBA) solutions at threedifferent concentrations are used as ionic crosslink medium to produce the κ- carrageenan hydrogel beads, as shown in Table 2.1. Figures 3.5 and 3.6 show percentages of κ- carrageenan beads expanding over 15 to 90 minutes at room temperature.

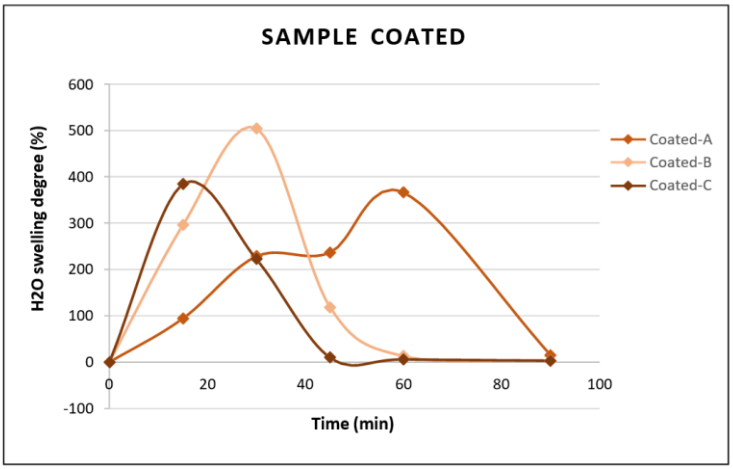

Figure 3.5: The swelling percentage of coated κ-carrageenan hydrogel beads

The significant water absorption of hydrogel adsorbents is a key feature for theapplication of dye removal. The materials should swell to allow water to diffuse throughthe crosslinked network, and the dye molecules dissolved in water can interact with functional groups in the hydrogel adsorbent's molecular chain. [15]. The graph above depictsthe results of a comparison between the two techniques. The graph for sample Coated A increases but then begins to drop after 60 minutes. This demonstrates that sampleCoated A's maximal absorption capability is limited to 60 minutes. However, for sample Coated B, the graph shows good swelling behavior for 30 minutes, with swelling percentages of 504%, before gradually decreasing. Sample Coated C, on the other side, has the lowest water absorption capacity. It only remains for 15 minutes andstarts to dissolve after that. As a result, after 15 minutes, the graph of sample Coated C started to decrease. In comparison to these three samples, Coated A, Coated B, and CoatedC, all exhibit poor swelling behavior and low absorption capacity, indicating that the coated approach is ineffective for developing an adsorbent for our environment.

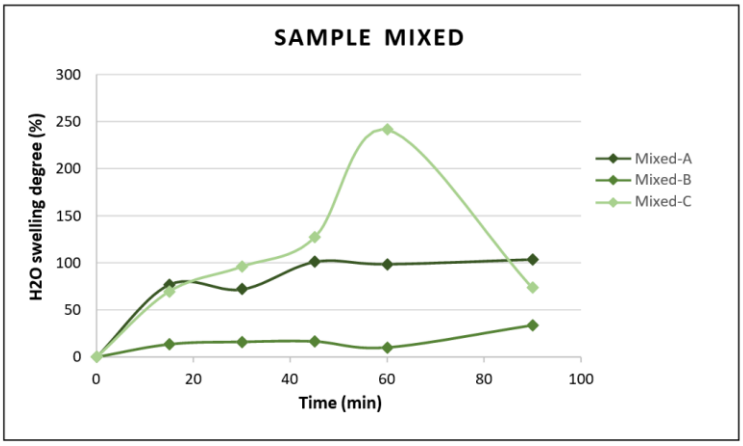

Figure 3.6: The swelling percentage of mixed κ-carrageenan hydrogel beads

The mixed sample exhibits superior graph behavior than the coated sample. Thegraph for sample mixed C decreases after 60 minutes, which is not excellent compared to samples mixed A and mixed B. Both samples mixed A and mixed B show an increasing and steady graph. However, sample mixed B had lower water uptake, absorbing just around 15% of the water compared to sample mixed A. Sample mixed A displays good swelling behavior with the increasing trend up to 76% for 15 minutes. Then, the graph begins to decrease after 15 minutes and remains constant after 30 minutes. Thus, the mixed A sample has a strong adsorption capacity and might be a potential material for developing a new adsorbent for our environment.

4.0 CONCLUSION AND RECOMMENDATION

Ultimately, a range of κ-carrageenan poly(acrylic acid) hydrogels beads were produced by crosslinking with N'N-methylene bisacrylamide (MBA) and glutaraldehyde and then formed into spherical beads using the ionic gelation technique in a potassium chloride (KCl) solution. The coated samples' functional groups that correspond to the mixed samples are O-H, C-H, C-N, O=S=O, S-O, C-O, and C=O. However, after six samples were evaluated, sample mixed-A with a low quantity of N'N-methylene bisacrylamide and a specific functional group, amide IV (O=C-N), demonstrated excellent swelling behavior. The amount of crosslinked agent N'N- methylene bisacrylamide is proved necessary to be low to the increased adsorption capacity of hydrogels κ-carrageenan beads. Thus, sample mixed-A beads show high adsorption ability and may be a promising material to create a new adsorbent.

Several analyses must be carried out following κ-carrageenan experiments to produce a suitable adsorbent with commercial potential. It recommends that numerous analyses be carried out to further the research on κ-carrageenan poly(acrylic acid). Firstly, the improvement of the production process is necessary since κ- carrageenan is quickly contaminated. Therefore, research on optimizing parameters like temperature, pH, and mixing time can reduce the chance of contamination and enhance the consistency of the beads. Second, thermogravimetric analysis (TGA). TGA calculates mass variations in response to temperature or time. It aims to investigate the composition, decomposition behavior, and thermal characteristics of materials. Hydrogels' moisture content may also be determined via TGA. Lastly, Variable Pressure Scanning Electron Microscopy (VPSEM). High-resolution imaging of hydrogel surface morphology is possible with VPSEM. It can be a useful method for describing hydrogels, offering an in-depth understanding of their structural and morphological characteristics.

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