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Research Article

Dual crosslinking of κ-carrageenan with glutaraldehyde and N’N’-methylenebisacrylamide (MBA) for high-efficiency methyl orange removal

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Abstract

The contamination of water sources by synthetic dyes such as methyl orange (MO) poses serious ecological and health hazards due to their persistence and toxicity. This study aims to develop a novel biopolymer adsorbent based on dual-crosslinked κ-carrageenan for the effective removal of MO from aqueous solutions. The adsorbent was synthesized using acrylic acid as the monomer, ammonium persulfate as the initiator, and a dual crosslinker system comprising N’N’-methylenebisacrylamide (MBA) and glutaraldehyde. Batch adsorption experiments were performed to evaluate the effects of pH, contact time, adsorbent dosage, initial dye concentration, and temperature. The material was characterized using SEM, FTIR, and EDX to assess surface morphology and functional group changes. The modified beads exhibited enhanced porosity and nitrogen incorporation, confirming successful crosslinking. Maximum MO percent removal of 95.26% was achieved at 5 ppm, pH 6–8, and 35 °C within 150 minutes. Isotherm analysis revealed excellent correlation with both Langmuir (R^2=0.9999) and Freundlich (R^2=1.000) models, indicating monolayer adsorption on a homogeneous surface. The Langmuir maximum adsorption capacity was 5.00 mg/g. These findings suggest that dual-crosslinked κ-carrageenan is a promising, biodegradable, and cost-effective adsorbent for environmental remediation of dye-contaminated wastewater.

Keywords: methyl orange adsorption, adsorption isotherm, biopolymer adsorbent, crosslinked κ-Carrageenan, dye removal

Introduction

The discharge of synthetic dyes into aquatic environments has become a significant environmental issue, especially in areas with active textile, dyeing, paper, and leather industries. Dyes are not only visually unappealing but also chemically stable, which makes them resistant to biodegradation and ineffective for removal through conventional wastewater treatment processes [1]. Methyl orange (MO) is an anionic azo dye that is commonly used as a pH indicator and in industrial coloring processes. However, it poses significant environmental risks due to its carcinogenic degradation products and its potential to disrupt aquatic ecosystems. Even trace amounts of MO can severely impact water quality by obstructing light penetration and reducing oxygen transfer, which in turn can harm aquatic plants and animals [2].

Various treatment technologies have been investigated for removing dyes from wastewater, including coagulation-flocculation, advanced oxidation processes, membrane filtration, and electrochemical treatment. These methods often have limitations, including high operational costs, energy intensity, incomplete dye degradation, and sludge generation. In contrast, adsorption has emerged as a cost-effective, straightforward, and efficient technique for dye removal. It provides high percent removal, operational flexibility, and the potential for adsorbent regeneration. While activated carbon is well-known as a standard adsorbent, its high production costs and regeneration difficulties have led to the exploration of low-cost and sustainable alternatives [3].

Numerous studies have reported the use of inexpensive materials such as graphene oxide, bentonite, chitosan-crosslinked κ-carrageenan, magnetic graphene combined with calcium alginate, magnetic carboxymethyl starch, and pineapple peel cellulose for the removal of methyl orange dye. Several of these adsorbents have shown adsorption capacities that approach or even rival those of activated carbon, although others still exhibit relatively modest performance [4]. Lately, there has been growing interest in using natural biopolymers as sustainable adsorbents. They stand out because they are readily available, biodegradable, and have functional groups that really help in binding pollutants. This makes them a great option for environmentally friendly applications [5].

Building upon this growing interest, numerous studies have explored various polysaccharide-based materials for adsorption applications, highlighting their structural versatility and tunable surface chemistry. Polysaccharides such as chitosan, alginate, cellulose, and carrageenan have shown considerable potential in this area [6]. κ-Carrageenan is a sulfated galactan derived from red seaweeds, known for its hydrophilicity, gel-forming ability, and the abundance of functional groups (–OH, $–SO_3^-$) that enhance interactions with dye molecules. Native κ-carrageenan has structural limitations, such as low mechanical strength, limited surface area, and a lack of active binding sites, which restrict its practical applications in adsorption processes [7].

To address these limitations, chemical crosslinking has become a promising strategy for enhancing the physicochemical properties of biopolymer-based adsorbents. Crosslinking agents such as glutaraldehyde, acrylic acid (AA), and N’N'-methylenebisacrylamide (MBA) have been widely used to improve the mechanical stability, porosity, and functionality of natural polymers [8]. For instance, it was reported that glutaraldehyde-crosslinked chitosan beads showed enhanced rigidity and increased adsorption capacity for reactive dyes. Similarly, the use of AA has introduced carboxylic groups, which enhance the surface reactivity of polysaccharides. The incorporation of MBA, a bifunctional crosslinker with amide groups, has been shown to create three-dimensional polymeric networks that enhance dye binding through hydrogen bonding and electrostatic interactions [9].

Although there have been advancements, few studies have explored the synergistic effects of various crosslinkers on κ-carrageenan, particularly concerning the effective removal of methyl orange adsorption [10]. Additionally, it is essential to thoroughly assess the structural, chemical, and elemental changes resulting from these modifications and to determine their relationship with adsorption performance across various environmental conditions [11].

This study aims to address existing gaps by synthesizing crosslinked κ-carrageenan beads using acrylic acid (AA) as a monomer and ammonium persulfate (APS) as an initiator. The dual crosslinking system includes glutaraldehyde and N’N'-methylenebisacrylamide (MBA). The goal of this modification is to enhance the structural integrity, surface functionality, and adsorption capacity of κ-carrageenan for the effective removal of methyl orange dye from aqueous solutions. The materials were characterized using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Energy Dispersive X-ray Spectroscopy (EDX). These techniques were employed to examine morphological changes, analyze the integration of functional groups, and determine the elemental composition. The adsorption behavior was systematically investigated under various operational parameters, including pH, contact time, adsorbent dosage, initial dye concentration, and temperature. The equilibrium data were analyzed using Langmuir and Freundlich isotherms to clarify the adsorption mechanism.

The findings of this study add to the expanding knowledge surrounding green adsorbents. They present a cost-effective, biodegradable, and high-performance solution for removing hazardous dyes from wastewater. This supports Sustainable Development Goals (SDG) 6, which focuses on Clean Water and Sanitation.

Materials and Methods

Materials

κ-Carrageenan (CAS No. 11114-20-8, Sigma-Aldrich) was used as the base material. Acrylic acid (AA, CAS No. 79-10-7, Merck), ammonium persulfate (APS, CAS No. 7727-54-0, Sigma-Aldrich), N,N’-methylenebisacrylamide (MBA, CAS No. 110-26-9, Sigma-Aldrich), and glutaraldehyde solution (25 wt%, CAS No. 111-30-8, Merck) were employed as polymerization and crosslinking agents. Potassium chloride (KCl, CAS No. 7447-40-7, Sigma-Aldrich) was used as the hardening agent. Methyl Orange (MO, CAS No. 547-58-0, Sigma-Aldrich) served as the model anionic dye for adsorption experiments. All reagents were of analytical grade and used without further purification.

Preparation of unmodified κ-carrageenan beads

To prepare unmodified κ-carrageenan beads, 2 g of κ-carrageenan were dissolved in 90 mL of distilled water at a temperature of 60°C. The solution was then allowed to cool to 50-55°C to form a gel. This gel solution was dripped into 50 mL of 0.3 M potassium chloride (KCl) solution, forming spherical beads. The beads were left in the KCl solution for one hour to harden. After hardening, the beads were rinsed with KCl solution and distilled water before being dried at room temperature. A summary of the preparation of the unmodified κ-carrageenan beads is illustrated in **Figure 1**.

Preparation of modified κ-carrageenan beads

To prepare coated κ-carrageenan beads, 2 g of κ-carrageenan was dissolved in 90 mL of distilled water at 60°C. After cooling the solution to 50-55°C, it was dripped into a biphasic system consisting of palm olein oil and 0.3 M potassium chloride (KCl) solution. This process formed spherical beads left in the KCl solution for 1 hour to harden. The beads were then rinsed with 0.3 M KCl solution and distilled water before being dried at room temperature. To prepare the coated beads, the dried beads were then mixed overnight with a solution containing 10 mL of acrylic acid, 0.2 g of N’N'-methylenebisacrylamide (MBA), 2 mL of 0.5% ammonium persulfate (APS), 5 mL of 12.5% glutaraldehyde, and 5 mL of 3 M KCl. After the coating process, the beads were rinsed with distilled water and left to dry at room temperature. A summary of the preparation of the coated κ-carrageenan beads is illustrated in **Figure 2**.

Physicochemical characterization

The structural functionality of the fabricated beads was analyzed using a Fourier transform infrared spectroscope (FTIR) in attenuated total reflectance (ATR) mode (Perkin Elmer, Frontier). The morphology of the hydrogel beads was examined with a scanning electron microscope (SEM). Additionally, the elemental composition of the beads was determined using energy-dispersive X-ray spectroscopy (EDX).

Adsorption study for removal of methyl orange dye

The synthesized κ-carrageenan beads were evaluated for their effectiveness in adsorbing methyl orange dye from aqueous solutions. Batch adsorption experiments were performed using 2 g of κ-carrageenan beads in 25 mL of dye solutions with varying concentrations. The mixtures were agitated at a constant temperature and stirring speed to ensure uniform contact between the adsorbent and the dye molecules. The initial and final dye concentrations were measured using UV-Vis spectrophotometry at a wavelength of 668 nm, and the percent removal (%) was calculated using Equation (1).

$$\text{Removal Efficiency (\%)} = \frac{\text{C initial} - \text{C final}}{\text{C initial}} \text{ x } 100 \tag{1}$$

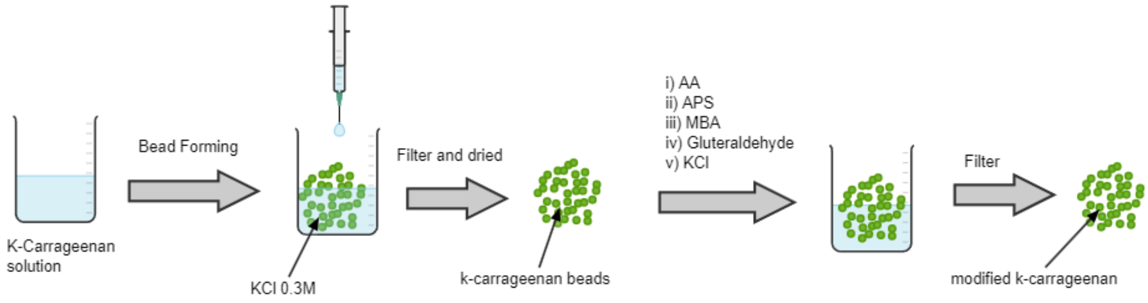


Figure 1. A summary of the preparation of the unmodified κ-carrageenan beads

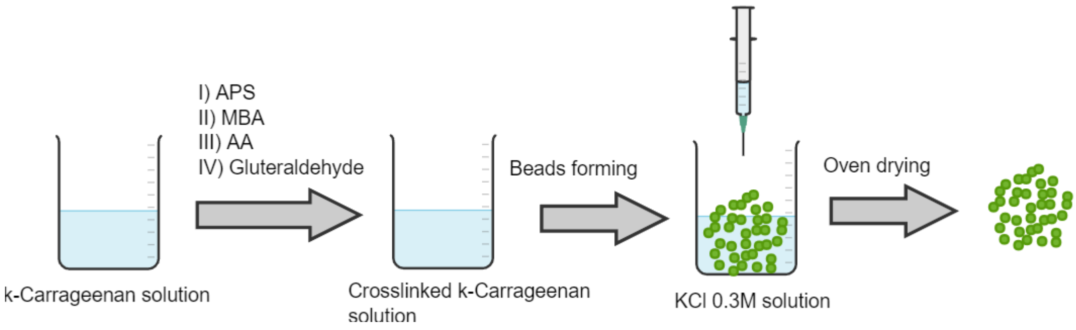


Figure 2. A summary of the preparation of the coated κ-carrageenan beads

Results and Discussion

Physical characterisation: SEM analysis

The structural, chemical, and elemental modifications of κ-carrageenan before and after crosslinking were thoroughly characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and energy dispersive X-ray (EDX) spectroscopy. The surface morphology of both unmodified and modified κ-carrageenan was analyzed using Scanning Electron Microscopy (SEM) to assess the structural changes resulting from chemical modification. In **Figure 3(a)**, the unmodified κ-carrageenan is shown to have a relatively compact and smooth surface with few visible pores or voids. This dense structure indicates a lower surface area, which may limit the availability of active sites required for efficient dye adsorption [12].

In contrast, the SEM image of the modified κ-carrageenan, shown in **Figure 3(b)**, synthesized through crosslinking with acrylic acid (AA), ammonium persulfate (APS), N'N'-methylenebisacrylamide (MBA), and glutaraldehyde, revealed a considerably rougher surface with numerous pores and interconnected microchannels. The porous structure observed in the material suggests that successful crosslinking and network formation have taken place. This enhancement increases the adsorbent's surface area and improves the accessibility of binding sites. The structural differences noted strongly indicate that the modified κ-carrageenan has better adsorption performance. The increased porosity allows for greater interaction with methyl orange molecules during the adsorption process [13]. This morphological transition is consistent with observations by Hassan et al. [14] and Hassanzadeh et al. [15], who reported that chemical crosslinking in polysaccharide-based adsorbents increases surface porosity and facilitates greater dye adsorption through improved diffusion and accessibility of active sites.

Physical characterization: FTIR analysis

In addition to the morphological findings, the FTIR analysis depicted in **Figure 4** further confirmed the chemical modification of κ-carrageenan. The spectrum of unmodified κ-carrageenan (represented by the green line) displayed relatively weak and broad peaks. This pattern indicates the presence of basic functional groups, such as hydroxyl (–OH) and sulfate (S=O) moieties, which are characteristic of native carrageenan [16]. A weak O–H stretching vibration was observed around 3400 cm^{-1}. Additionally, characteristic bands appeared in the ranges of 1220–1260 cm^{-1} and 1000–1050 cm^{-1}, corresponding to sulfate esters and C–O–C glycosidic linkages, respectively. However, these bands were less intense, suggesting a simpler chemical structure and limited functional diversity [17].

In contrast, the FTIR spectrum of the modified κ-carrageenan (represented by the blue line) exhibited a broad and intense O–H stretching band at 3358 cm^{-1} and a C–H stretching vibration at 2923 cm^{-1}, indicating an increased presence of hydroxyl and alkyl groups resulting from polymerization and crosslinking. A distinct absorption peak at 1634 cm^{-1}, assigned to C=O stretching, confirms the successful incorporation of carbonyl functionalities introduced by acrylic acid and glutaraldehyde. The pronounced band at 1373 cm^{-1}, associated with S=O stretching, reflects the preservation and enhancement of the sulfate ester groups inherent to κ-carrageenan. Furthermore, the peaks at 1066 cm^{-1} (C–H bending), 1000 cm^{-1} (S–O stretching), and 602 cm^{-1} (O=C–N bending) indicate the formation of amide and sulfonated linkages due to the crosslinking reactions involving N,N′-methylenebisacrylamide (MBA) and glutaraldehyde. The appearance of C–N vibrations further support the introduction of nitrogen-containing functionalities, confirming successful structural modification of the polymer backbone.

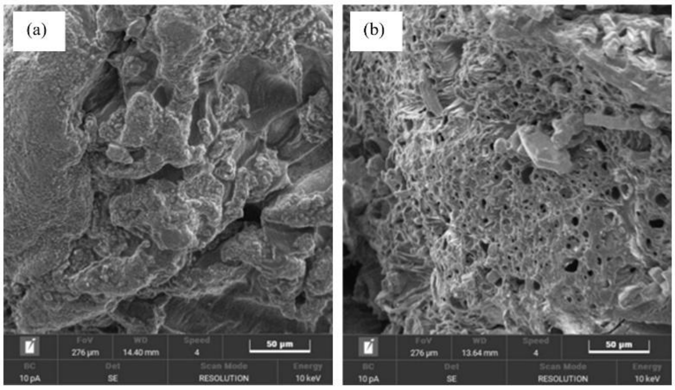


Figure 3. SEM images depicting the surface morphology of (a) unmodified κ-carrageenan, and (b) modified κ-carrageenan

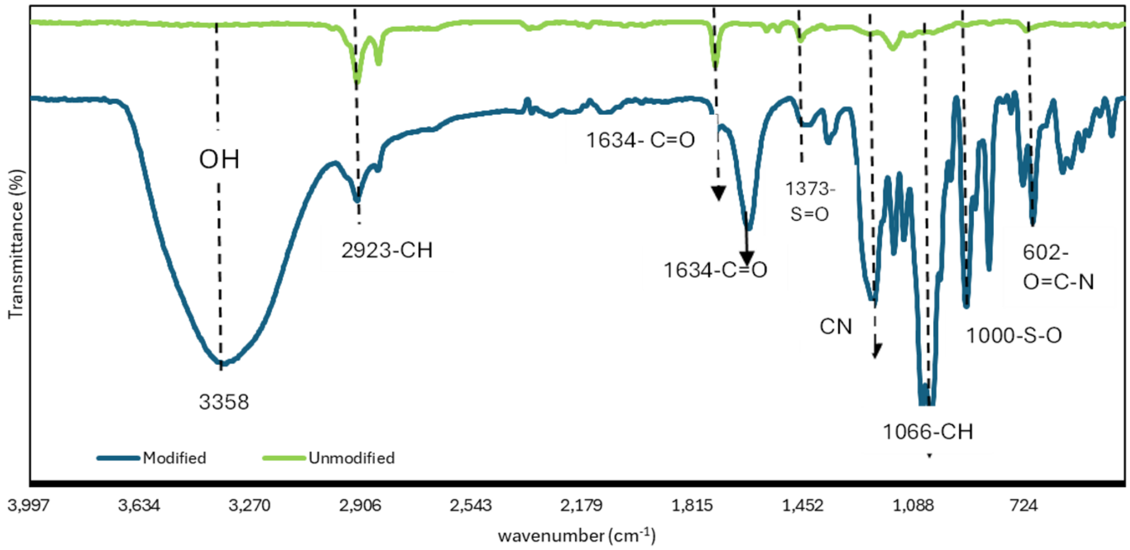


Figure 4. FTIR spectrum of unmodified κ-carrageenan and modified κ-carrageenan

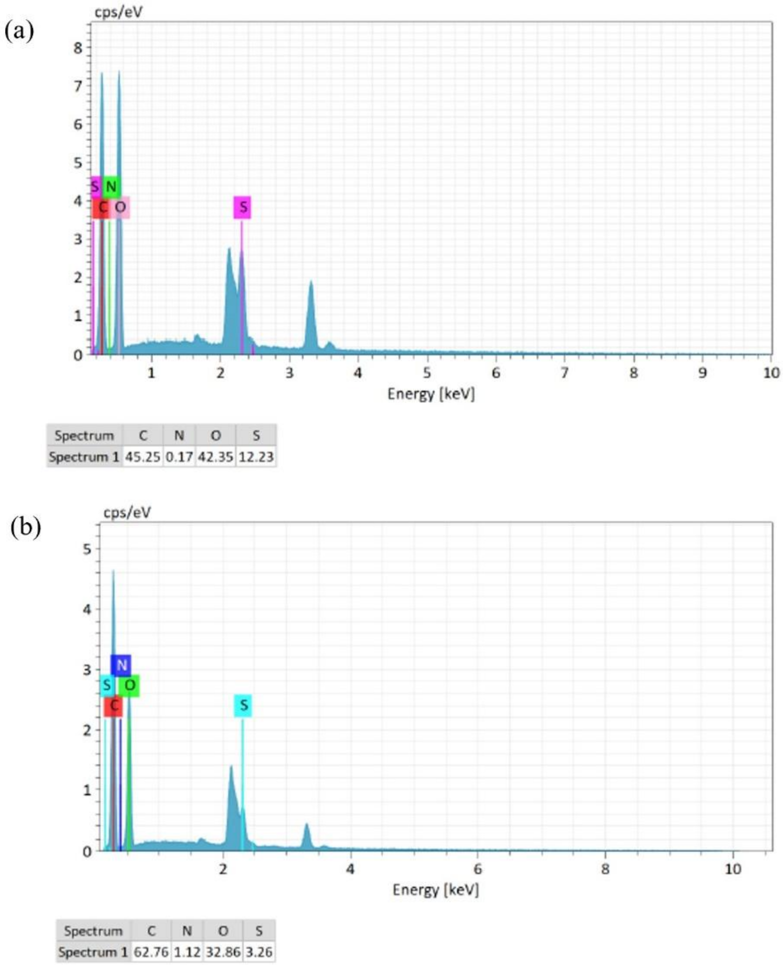
These spectral changes are consistent with previous reports by Hussain et al.,2020 [18] and Hussain et al., 2021 [19], who observed similar band shifts after chemically modifying κ-carrageenan and chitosan matrices for dye adsorption. Likewise, Ihsanullah et al. [20] reported that the emergence of new C=O and C–N peaks is a reliable indicator of amide bond formation, which enhances electrostatic and hydrogen bonding interactions with anionic dye molecules. The strengthened O–H and C=O absorptions observed in this study therefore validate the successful chemical crosslinking of κ-carrageenan, improving its surface reactivity and adsorption capacity for Methyl Orange removal.

Physical characterization: EDX analysis

Energy dispersive X-ray (EDX) spectroscopy was used to assess the elemental composition and confirm the incorporation of new functional groups in κ-carrageenan after chemical modification. The EDX spectrum of unmodified κ-carrageenan (**Figure 5(a)**) shows that the material primarily consists of carbon (45.25%) and oxygen (42.35%), with sulfur present at 12.23%. This sulfur content is attributed to the natural sulfate ester groups found in native carrageenan. A very low nitrogen content (0.17%) was detected, which is consistent with the absence of nitrogen-based functional groups in the unmodified structure. This composition reflects the native polysaccharide backbone of κ-carrageenan, which is made up of repeating galactose units and sulfate groups [21].

In contrast, the EDX spectrum of the modified κ-carrageenan (**Figure 5(b)**) reveals notable changes in elemental composition compared to the unmodified form. The carbon content increased substantially to 62.76%, attributable to the incorporation of carbon-rich monomers such as acrylic acid (AA) and the crosslinking agent glutaraldehyde, which expanded the hydrocarbon framework within the polymeric matrix. A marked rise in nitrogen content from 0.17% to 1.12% confirms the successful introduction of nitrogen-bearing crosslinkers, primarily N,N′-methylenebisacrylamide (MBA). The appearance and intensification of nitrogen peaks provide direct evidence of amide bond formation between the κ-carrageenan backbone and the introduced crosslinking agents. Similar nitrogen enrichment following chemical modification has been reported by Kalaiselvi et al. [22] and Khir et al. [23] in carrageenan–chitosan and polysaccharide–acrylate composites, supporting the establishment of covalent linkages that contribute to improved chemical stability and functional diversity.

The oxygen content slightly decreased to 32.86%, which may be due to a relative dilution effect caused by the higher incorporation of carbon and nitrogen atoms within the network. Meanwhile, the sulfur content decreased markedly from 12.23% to 3.26%, suggesting partial masking or substitution of native sulfate groups during the grafting and crosslinking reactions. This phenomenon has also been observed by Kulal et al. [24] who attributed similar reductions in sulfur signals to the structural rearrangement of sulfate domains following chemical modification in polysaccharide-based adsorbents. Such changes indicate the successful replacement of some sulfate sites by newly introduced carbonyl and amide functionalities, thereby reorganizing the polysaccharide framework.



(a)

Spectrum	C	N	O	S
Spectrum 1	45.25	0.17	42.35	12.23

(b)

Spectrum	C	N	O	S
Spectrum 1	62.76	1.12	32.86	3.26

Figure 5. EDX spectra of (a) unmodified κ-carrageenan, and (b) modified κ-carrageenan

Overall, the EDX findings corroborate the FTIR results, confirming the successful incorporation of monomers and crosslinkers into the κ-carrageenan matrix. The increased carbon and nitrogen content validates the occurrence of crosslinking and grafting reactions, while the altered sulfur distribution signifies structural reconfiguration at the elemental level [25]. These compositional changes are consistent with earlier reports on modified biopolymer adsorbents and are expected to enhance adsorption performance by providing additional active binding sites and promoting stronger electrostatic and hydrogen bonding interactions with anionic dye molecules such as methyl orange.

Adsorption study: Methyl orange adsorption

The adsorption of methyl orange using modified κ-carrageenan was assessed at various concentrations ranging from 5 ppm to 25 ppm using an adsorbent dosage of 0.1 g, maintained at room temperature (≈25 °C) and a solution pH of 6. The results were compared between modified and unmodified κ-carrageenan, as illustrated in **Figure 6**. The absorbance values obtained for each concentration were utilized to determine the final concentration of methyl orange after the adsorption process. The percentage of methyl orange removal was calculated by comparing the initial and final concentrations. The modified κ-carrageenan samples exhibited a percent removal ranging from 92.22% to 95.26%, with the highest removal rate observed at the lowest concentration of 5 ppm. In comparison, the unmodified κ-carrageenan showed slightly lower removal efficiencies, ranging from 91.54% to 94.54%. Both materials demonstrated relatively stable removal efficiencies, indicating their effectiveness in removing methyl orange at various concentrations.

The results indicate that κ-carrageenan crosslinked with N’N'-methylene bisacrylamide and glutaraldehyde demonstrates improved percent removal for methyl orange compared to its unmodified version. The increase in percent removal

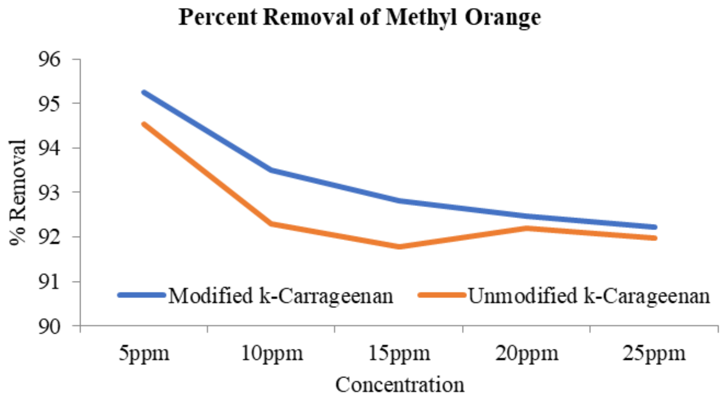


Figure 6. Percent removal of methyl orange dye

at lower concentrations, particularly at 5 ppm, suggests that crosslinking has significantly enhanced the adsorbent's structural integrity and the availability of binding sites. The crosslinked structure likely provides more binding sites for methyl orange molecules due to the enhanced polymeric networks [26]. N'N'-methylenebisacrylamide and glutaraldehyde enhance the stability and rigidity of κ-carrageenan chains, which increases their surface area and affinity for dye molecules. This may also account for the higher adsorption observed at low concentrations, where the available binding sites are not saturated and can effectively attract the dye [27].

At higher concentrations, both modified and unmodified κ-carrageenan exhibit similar removal efficiencies, suggesting that saturation of adsorption sites may restrict further enhancements in adsorption capacity. However, the modified κ-carrageenan still shows superior performance, indicating it could be more effective in environments with lower dye concentrations, such as in post-treatment wastewater applications [28]. The strong adsorption performance of modified κ-carrageenan across all concentrations indicates that crosslinking κ-carrageenan is an effective method for improving the adsorption of methyl orange from aqueous solutions [29].

Effect of contact time on methyl orange adsorption

The impact of contact time on the adsorption of Methyl Orange using modified κ-carrageenan was analyzed over a duration of 15 to 240 minutes, employing an adsorbent dosage of 0.1 g, at room temperature (≈25 °C), pH 6, and an initial dye concentration of 5 ppm. As shown in **Figure 7**, the percent removal remained consistently stable throughout the experiment, with percent removal values ranging from 94.5% to 94.8%.

At the initial contact time of 15 minutes, the percentage removal was recorded at 94.76%, with an absorbance value of 0.446. This indicates that the modified κ-carrageenan adsorbent is highly efficient, as it is able to achieve significant levels of adsorption in a short amount of time. Additionally, the adsorption performance remained relatively stable as the contact time increased, suggesting that equilibrium was reached quickly. After 150 minutes, the system reached a near-equilibrium state, as evidenced by a consistent percent removal value of 94.76%, which remained stable until the 240-minute mark. The data indicate that equilibrium for the adsorption of methyl orange was achieved at around 150 minutes. After this point, the percentage of removal remained constant, indicating that further increases in contact time did not lead to significant improvements. This suggests that most of the adsorption sites on the κ-carrageenan adsorbent were occupied by methyl orange molecules, and the adsorption process had reached its maximum capacity under the given conditions [30].

The quick attainment of high adsorption levels (94.76% within 15 minutes) suggests that the adsorption process is likely governed by surface adsorption at the initial stages, where the available active sites on the adsorbent quickly capture the dye molecules [31]. As time passes, the active sites on the adsorbent become saturated, causing the adsorption rate to decrease. This leads to an observed equilibrium after about 150 minutes. The data indicate that extending the contact time beyond 150 minutes does not significantly improve the adsorption capacity, which is likely due to the saturation of the adsorbent's surface area [32]. The results indicate that modified κ-carrageenan is an effective adsorbent for methyl orange. Adsorption occurs rapidly within the first 15 to 30 minutes, and equilibrium is reached by 150 minutes. This finding is promising for practical applications, as it suggests that the adsorption process can be completed relatively quickly, making it efficient for potential industrial applications or wastewater treatment methods.

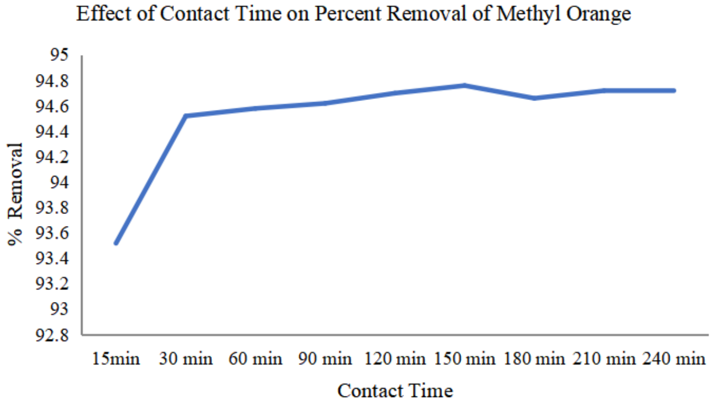


Figure 7. Effect of contact time on percent removal of methyl orange dye

Effect of pH on methyl orange adsorption

The study investigated the adsorption of Methyl Orange using modified κ-carrageenan across a pH range of 2 to 10, with an adsorbent dosage of 0.1 g, at room temperature (≈25 °C) and an initial dye concentration of 5 ppm. The goal is to determine how solution pH affects the percent removal, as shown in **Figure 8**. The results indicated that the percentage removal of methyl orange increased with increasing pH, reaching maximum adsorption at a neutral to slightly basic pH. At a highly acidic pH of 2, the percent removal was the lowest at 88.90%. The higher absorbance value of 0.739 and the final concentration of 0.555 ppm indicate that the adsorption capacity of modified κ-carrageenan is less effective in strongly acidic conditions. As the pH increases to 4, the percent removal improves significantly to 93.32%, suggesting that the adsorbent performs better in less acidic environments [33].

The percent removal reaches its highest point at a pH of 6 and above, achieving percent removal values between 94.20% and 94.24%. The data indicates that the adsorption process is most effective at a pH range of 6 to 8, where the absorbance is at its lowest, signifying the highest adsorption capacity. Notably, at pH 10, the percent removal remains stable, showing only a slight decrease to 94.18%. This indicates that modified κ-carrageenan retains high percent removal over a wide range of pH levels [25]. The variation in percent removal with pH can be attributed to the ionization state of the methyl orange dye molecules and the surface charge of the adsorbent. At low pH (pH 2), the high concentration of hydrogen ions (H^+) in the solution can compete with the positively charged methyl orange molecules for the active sites on the adsorbent's surface [34]. This competition likely decreases the number of available binding sites, leading to reduced percent removal [16].

As the pH increases, the concentration of H^+ ions decrease, which reduces competition for active sites on the adsorbent. This allows more methyl orange molecules to be adsorbed. Between pH levels 6 and 8, the surface of the adsorbent becomes more negatively charged, enhancing the electrostatic attraction between the adsorbent and the dye molecules. This leads to higher percentage removal. At pH 10, the percent removal remains high, indicating that the structure of the adsorbent is stable in mildly basic conditions. The slight decrease in percent removal

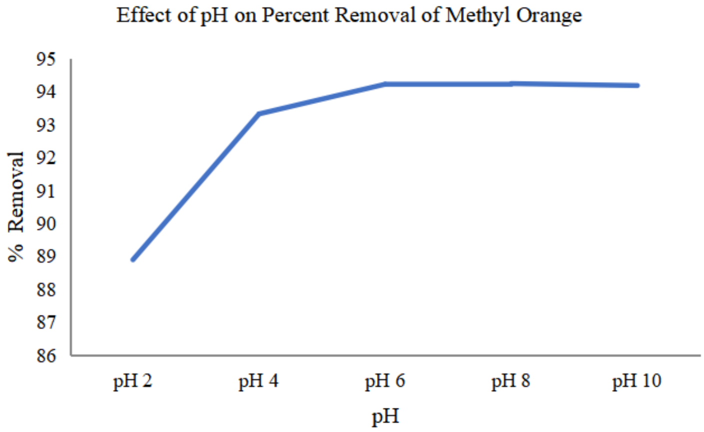


Figure 8. Effect of pH on percent removal of methyl orange dye

may be attributed to deprotonation effects, which could slightly change the interaction between the dye and the adsorbent [35]. Data indicates that modified κ-carrageenan effectively adsorbs dyes across various pH levels, making it a versatile solution for dye removal in different environments [36]. The results indicate that modified κ-carrageenan effectively adsorbs methyl orange across a wide pH range, with optimal performance observed in neutral to slightly basic conditions (pH 6 to 8).

Effect of adsorbent dosage on methyl orange adsorption

Figure 9 illustrates how varying dosages of adsorbent (from 0.05 g to 0.5 g) affect the percent removal of Methyl Orange when using modified κ-carrageenan, under conditions of 0.1 g adsorbent dosage, room temperature (≈25 °C), pH 6, an initial dye concentration of 5 ppm, and a contact time of 150 minutes. The percentage of methyl orange removed increases slightly with higher adsorbent doses, peaking at 0.1 g. Beyond this point, the percent removal either stabilizes or experiences a slight decrease.

At the lowest adsorbent dosage of 0.05 g, the percentage removal of methyl orange was 94.44%. When the adsorbent dosage increased to 0.1 g, the percent removal peaked at 94.82%. However, further increases in the adsorbent dosage led to either a slight decrease or stabilization in the percentage removal, with values ranging from 94.74% to 94.38% for dosages between 0.2 g and 0.5 g. The highest percent removal was noted at an adsorbent dosage of 0.1 g, indicating that this dosage offers adequate surface area and active sites for the adsorption of methyl orange molecules [37]. At this optimal dosage, the dye concentration was reduced more effectively, indicating that the adsorbent operates at its maximum capacity to capture dye molecules from the solution. Increasing the adsorbent dosage beyond 0.1 g did not significantly enhance the percent removal. A slight decrease in the percent removal was observed at higher dosages of 0.3 g and 0.5 g. This decline may be attributed to the overlap of adsorption sites or the formation of agglomerates among the adsorbent particles. Such phenomena reduce the effective surface area available for adsorption, leading to a minor decrease in overall efficiency [38]. At higher dosages, the solution may become saturated with adsorbent, resulting in little to no improvement in dye removal, as the available dye molecules are already adsorbed onto the adsorbent's surface [23]. The data indicate that 0.1 g of modified κ-carrageenan is the optimal dosage for adsorbing methyl orange, as it achieves the highest percent removal.

Although the effect of dosage appears less pronounced under the tested conditions, this result confirms that dual-crosslinked κ-carrageenan exhibits strong adsorption affinity, requiring only small amounts of material to achieve high percent removal. The researcher acknowledges that testing at higher initial dye concentrations would provide clearer differentiation in dosage effect, as greater competition for adsorption sites could reveal a more noticeable dosage-dependent trend. This has now been noted as a limitation of the present study, with a recommendation for future work to explore performance under higher concentration ranges to further validate the adsorbent's efficiency.

Effect of initial methyl orange concentration on adsorption

Figure 10 illustrates how varying the initial concentrations of methyl orange (ranging from 5 to 25 ppm) affects the percent removal when using modified κ-carrageenan, with an adsorbent dosage of 0.1 g, at room temperature (≈25 °C), pH 6, and a contact time of 150 minutes.

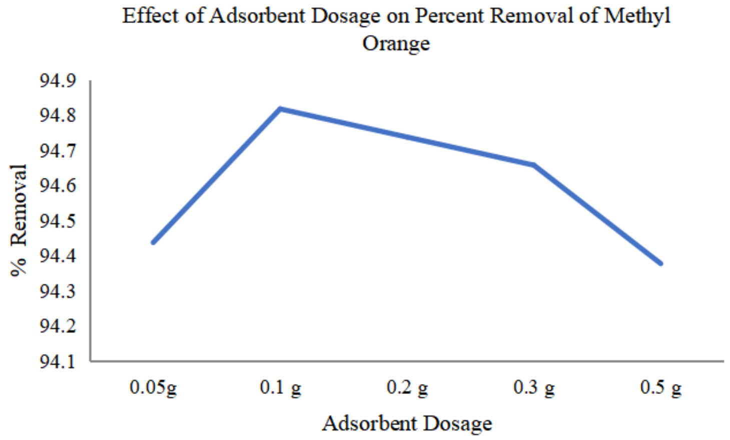


Figure 9. Effect of adsorbent dosage on percent removal of methyl orange dye

As the initial concentration of methyl orange increases, the percentage of dye removal decreases, indicating that there is a limit to the adsorption capacity of the adsorbent at higher dye concentrations.

At the lowest initial concentration of 5 ppm, the adsorbent demonstrated the highest percent removal, achieving 95.26% and resulting in a final concentration of 0.237 ppm. This suggests that the modified κ-carrageenan adsorbent has enough active sites to effectively bind the majority of dye molecules at low concentrations. However, as the concentration of methyl orange increases, the percent removal declines. At a concentration of 10 ppm, the percent removal decreased to 93.49%. This decline continued with further increases in concentration: it dropped to 92.81% at 15 ppm, 92.46% at 20 ppm, and 92.22% at 25 ppm. This gradual reduction in percent removal with increasing dye concentration indicates that the active sites of the adsorbent become saturated as the dye concentration rises, resulting in a decreased adsorption capacity at higher concentrations [39].

At higher concentrations of 20 ppm and 25 ppm, the performance of the adsorbent levels off, yielding similar percent removal values of 92.46% and 92.22%, respectively. This suggests that the adsorbent has reached its saturation point, where all available adsorption sites are filled, and any additional dye molecules remain in the solution [40] . At higher concentrations, the increase in methyl orange exceeds the available binding sites, leading to reduced percent removal. The data show that modified κ-carrageenan exhibits a highly effective percent removal for methyl orange at low initial concentrations, as it achieves over 95% removal at a concentration of 5 ppm. However, as the initial concentration increases, the percent removal gradually declines due to the saturation of active sites on the adsorbent [41]. This behavior is typical of adsorption systems, where the limited availability of adsorption sites restricts the overall capacity of the adsorbent.

Although the adsorption experiments in this study were conducted at initial Methyl Orange concentrations up to 25 ppm, this range was selected to ensure solution stability and avoid dye aggregation or precipitation observed at higher concentrations. Within this range, equilibrium adsorption behavior could be clearly established, allowing accurate modeling of the adsorption process. However, it is acknowledged that extending the concentration range beyond 25 ppm would provide deeper insight into the adsorbent's saturation capacity and site limitation behavior under higher pollutant loads. Future work will therefore consider testing at elevated concentrations to better evaluate the full adsorption potential and real-world applicability of the modified κ-carrageenan adsorbent.

Effect of temperature on methyl orange adsorption

Figure 11 examines how temperature affects the percent removal of Methyl Orange when using modified κ-carrageenan, with experiments conducted at 25 °C, 35 °C, and 45 °C, using an adsorbent dosage of 0.1 g, an initial dye concentration of 5 ppm, pH 6, and a contact time of 150 minutes. The results indicate that temperature significantly influences percent removal, with the best performance observed at 35°C.

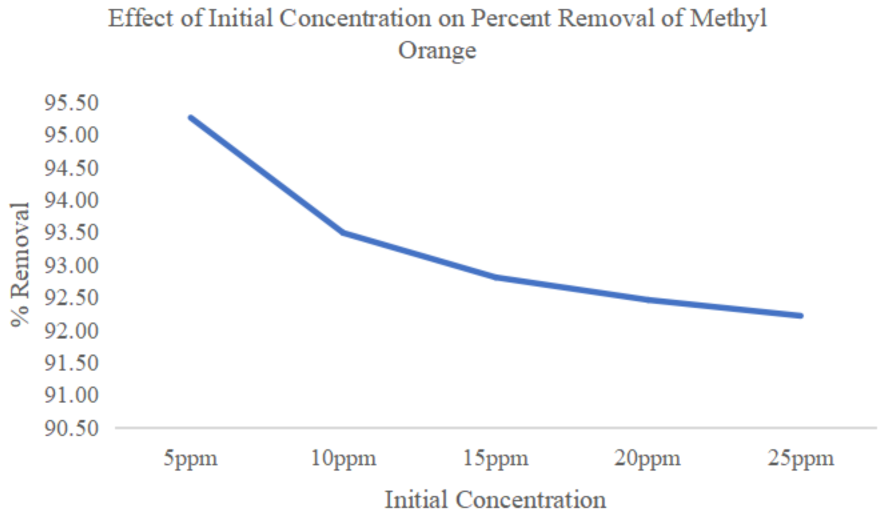


Figure 10. Effect of initial concentration on percent removal of methyl orange dye

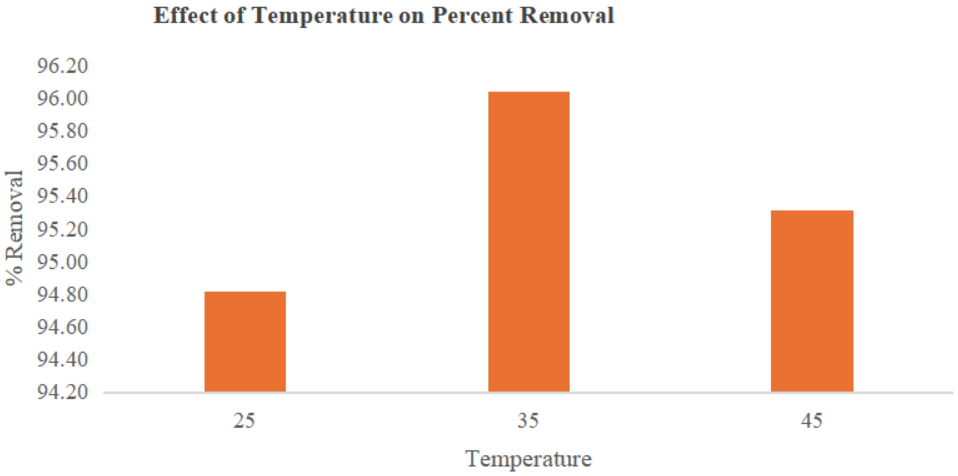


Figure 11. Effect of temperature on percent removal of methyl orange dye

At 25°C, the percent removal of methyl orange was 94.82%, indicated by an absorbance value of 0.443. When the temperature increased to 35°C, the percent removal improved, reaching a maximum percent removal of 96.04%. However, further increasing the temperature to 45°C led to a slight decrease in percent removal, which dropped to 95.32%. The highest percent removal was observed at 35°C, indicating that this temperature improves the interaction between methyl orange molecules and the modified κ-carrageenan adsorbent. The increased adsorption at 35°C may be attributed to the greater mobility of the dye molecules at elevated temperatures, allowing them to interact more easily with the active sites of the adsorbent [6]. Moreover, the slight increase in thermal energy at this temperature may enhance the diffusion rate of dye molecules into the adsorbent pores, leading to more efficient adsorption [13].

At 45°C, a slight decrease in percent removal was noted compared to 35°C. This decline could be due to the desorption effect, where increased thermal energy causes the adsorbed methyl orange molecules to detach from the adsorbent surface. Additionally, elevated temperatures can diminish the stability of the adsorbent material, impairing its ability to effectively retain dye molecules [42]. The data indicate that temperature significantly influences the adsorption of methyl orange onto modified κ-carrageenan. The optimal temperature for this process is 35°C, which strikes the best balance between the adsorption capacity and the mobility of dye molecules. Higher temperatures may decrease the percent removal due to desorption or structural changes in the adsorbent [43]. For practical applications, adsorption processes around 35°C are likely to achieve the highest percent removal.

Adsorption isotherm

The adsorption behavior of methyl orange onto modified κ-carrageenan was evaluated using two standard isotherm models namely Langmuir and Freundlich, to elucidate the interaction mechanism between the dye molecules and the adsorbent surface.

Langmuir isotherm

The Langmuir isotherm model assumes adsorption occurs at specific, homogeneous sites within the adsorbent. After a dye molecule occupies a site, no further adsorption can take place at that site [44]. This model suggests a monolayer adsorption mechanism without interaction between adsorbed species. It is commonly used to estimate the maximum adsorption capacity of an adsorbent under equilibrium conditions. The linearized Langmuir equation is:

$$\frac{1}{q_e} = \frac{1}{q_{max}K_L C_e} + \frac{1}{q_{max}} \qquad (2)$$

In this text, q_{max} represents the maximum monolayer adsorption capacity (mg/g), while K_L indicates the Langmuir constant associated with adsorption energy (L/mg). The adsorption behavior of Methyl Orange (MO) onto both the modified and unmodified κ-carrageenan adsorbents was analyzed using the Langmuir isotherm model. The linearized Langmuir plots of 1/qe against 1/Ce (**Figure 12(a)**) exhibited excellent linear correlation, with coefficients of determination (R^2) equal to 1.000 for the modified κ-carrageenan and 0.9999 for the unmodified κ-carrageenan. These high R^2 values confirm that the adsorption process fits well with the Langmuir model, suggesting that the dye molecules form a monolayer adsorption on a homogeneously distributed surface with energetically equivalent active sites.

According to the Langmuir theory, adsorption occurs at specific homogeneous sites within the adsorbent, and once a molecule occupies a site, no further adsorption can take place at that site. The linearity of the plots supports this assumption, implying that there is no significant interaction between adsorbed molecules and that the binding process is uniform across the surface [45]. The slope and intercept of the Langmuir plots were used to determine the Langmuir constants, K_L and q_{max}. The modified κ-carrageenan recorded a slope of 4.163 and an intercept of 0.0089, resulting in a monolayer adsorption capacity (q_{max}) of 112.36 mg g^{-1} and a Langmuir constant (K_L)of 0.00214 L mg^{-1}. In contrast, the unmodified κ-carrageenan yielded a slope of 4.1928 and an intercept of 0.0091, giving a q_{max} value of 111.11 mg g^{-1} and a K_L of 0.00215 L mg^{-1}. Although the difference is small, the slightly higher q_{max} value of the modified κ-carrageenan indicates improved surface characteristics and enhanced adsorption performance.

This improvement can be attributed to the dual crosslinking modification using glutaraldehyde and N,N′-methylenebisacrylamide (MBA), which strengthens the polymeric network, increases the available surface area, and introduces additional functional groups such as –OH, $–SO_3^-$, and –C=O that serve as active sites for MO binding [46]. The modification likely enhances electrostatic attraction between the anionic dye molecules and the positively charged sites on the adsorbent surface, facilitating greater dye uptake.

Freundlich isotherm

In contrast, the Freundlich isotherm model uses a more empirical approach, accommodating adsorption on heterogeneous surfaces characterized by a non-uniform distribution of adsorption heat and affinities across the surface [47]. Unlike the Langmuir model, the Freundlich model accommodates multilayer adsorption and is especially useful for characterizing adsorption on natural or structurally irregular materials, such as biopolymers. The Freundlich isotherm effectively describes adsorption on heterogeneous surfaces. The linear form is:

$$\log q_e = \log K_F + \frac{1}{n} \qquad (3)$$

In the Freundlich equation, K_F represents the constant indicating adsorption capacity, while n denotes the adsorption intensity. The linear Freundlich plot of log qe versus log Ce (**Figure 12(b)**) produced an ideal fit with an R^2 value of 1.000 for modified and R^2 value of 0.9897 for unmodified, indicating excellent applicability of the model. The Freundlich constants were derived from the slope and intercept: the adsorption intensity parameter n=1.78, and the adsorption capacity K_F=0.245. A value of n close to 1 indicates that the adsorption process is favorable and nearly linear. This suggests that the adsorption energy across the surface sites is relatively uniform, even if there is minor structural heterogeneity. The Freundlich model supports the idea that, while the adsorbent appears to have characteristics of a homogeneously functionalized surface (as indicated by the Langmuir model), it still retains some inherent heterogeneity that is typical of biopolymeric materials like carrageenan [17].

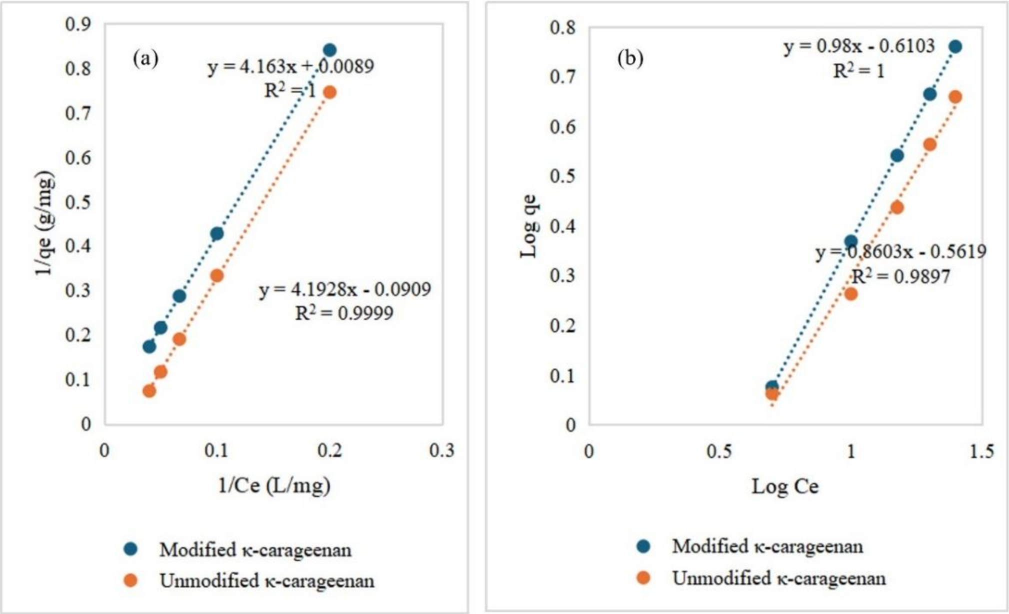


Figure 12. Adsorption isotherm: (a) Langmuir and (b) the Freundlich of methyl orange dye onto unmodified and modified κ-carrageenan adsorbents

Table 1. Summary of adsorption isotherm

Langmuir			Freundlich		
Parameters	**Unmodified**	**Modified**	**Parameters**	**Unmodified**	**Modified**
q_{max} (g/mg)	111.11	112.36	K_F	0.174	0.245
K_L (L/mg)	0.00215	0.00214	n	1.16	1.78
R^2	0.9999	1	R^2	0.9897	1

Table 1 presents the isotherm parameters for Methyl Orange adsorption on unmodified and modified κ-carrageenan. Both the Langmuir and the Freundlich models fit the data well, with R^2 values above 0.98, confirming good model applicability. According to the Langmuir model, the modified κ-carrageenan exhibited a slightly higher adsorption capacity (q_{max} =112.36 mg g^{-1}) than the unmodified sample (q_{max}=111.11 mg g^{-1}), indicating that dual crosslinking improved the surface uniformity and availability of active sites. The nearly identical K_L values (≈0.002 L mg^{-1}) suggest similar adsorption affinities for both materials, consistent with monolayer adsorption on homogeneous surfaces.

From the Freundlich model, the modified adsorbent also showed higher K_F (0.245) and n (1.78) values compared to the unmodified sample (K_F =0.174, n=1.16), reflecting stronger binding affinity and more heterogeneous adsorption sites after modification. Overall, both models describe the system well, but the Langmuir model provides a slightly better fit (R^2≈1), indicating that MO adsorption mainly follows monolayer behavior, while the Freundlich parameters suggest some degree of surface heterogeneity enhanced by crosslinking.

Conclusion

This study successfully demonstrates the synthesis, characterization, and application of chemically crosslinked κ-carrageenan hydrogel beads for the removal of Methyl Orange dye from aqueous solutions. The modification of κ-carrageenan using acrylic acid (AA), ammonium persulfate (APS), N,N′-methylenebisacrylamide (MBA), and glutaraldehyde significantly enhanced the structural and functional properties of the matrix. Characterization through scanning electron microscopy (SEM) revealed a transition from a compact morphology to a more porous structure, while FTIR and EDX analyses confirmed the incorporation of functional groups such as carbonyl, amide, and nitrogen-containing moieties that contributed to improved adsorption performance. Batch adsorption experiments showed that the modified κ-carrageenan achieved a high removal efficiency of up to 95.26% under optimal conditions, which were determined at a pH range of 6–8, temperature of 35 °C, and contact time of 150 minutes. The adsorption process reached equilibrium rapidly and remained stable across different dosages and environmental conditions. Isotherm modeling indicated that both the Langmuir and Freundlich models fitted the data well, with the Langmuir model suggesting monolayer adsorption on a uniformly modified surface. The high adsorption capacity and fast equilibrium attainment emphasize the potential of the modified κ-carrageenan for practical dye removal in wastewater treatment. However, further investigations are recommended to examine adsorption behavior at higher initial dye concentrations (beyond 25 ppm) to better assess surface saturation effects and adsorption site limitations. Future work should also reinvestigate the effect of adsorbent dosage at higher initial concentrations to clarify its influence on removal efficiency. Additionally, a comparative study with literature-reported adsorption capacities (q_{max} and isotherm constants) should be conducted to benchmark the performance of this material against other biopolymer-based adsorbents.

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