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Innovative Eco-Friendly Microbeads for Skincare: A Sustainable and Effective Exfoliation Solution

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1. Introduction

Microbeads, commonly utilized in personal care products for exfoliation and skincare benefits (e.g. deep cleansing, acne treatment, moisturization) , are being phased out due to environmental concerns linked to synthetic polymers [1]. This shift necessitates sustainable alternatives derived from natural materials to meet rising consumer demand for eco-friendly cosmetics. Production methods such as microfluidic emulsification, spray drying, and electrospraying critically influence microbead functionality and stability. Electrospraying, in particular, enables uniform microbead formation without thermal degradation, preserves heat-sensitive ingredients, and minimizes solvent residues [2]. This technique has been applied to encapsulate bioactive compounds within sustainable matrices [3].

Chitosan, a biocompatible, biodegradable cationic polysaccharide, and gellan gum, a negatively charged polysaccharide with emulsion-stabilizing properties, form dense polyelectrolyte complexes through electrostatic interactions. These complexes offer structural integrity for microbead shells, while their natural origins align with sustainability goals. Fucoidan, a sulfated polysaccharide from brown algae with anti-aging and skin-protective properties, further enhances functionality.

This study developed eco-friendly microbeads via electrospraying, combining chitosan-gellan gum complexes with fucoidan extracted using deep eutectic solvents (DES). Characterization via SEM, FTIR, XRD, and ^{1}H NMR confirmed structural integrity, non-toxicity, cytocompatibility, and contamination resistance. The microbeads exhibited sustained fucoidan release, stability during swelling, and effective cleansing without skin irritation. These results highlight their potential as sustainable replacements for plastic microbeads, offering prolonged bioactive delivery and reduced ecological impact.

2. Materials and Methods

Chitosan (50–190 kDa, 85–90% deacetylation) and gellan gum (200–300 kDa, low-acyl) were sourced commercially. Eco-friendly microbeads were synthesized via electrospraying (TL-OMNI-BM device) [4]: chitosan (3.5% w/v) dissolved in 2% acetic acid (75°C), blended with gellan gum (2.5% w/v, 85°C), and combined with fucoidan (60°C) [5]. Electrospraying parameters (9.5 kV, 12 cm needle distance, 10 mL/h flow) deposited solutions into 10% TPP, followed by washing and drying. Commercial plastic microbeads (P-MBs) were isolated from cosmetics via centrifugation (12,000 rpm) and drying [4]. Fucoidan release (pH 5.5/3.7) was quantified via dialysis (37°C) and UV-vis [5]. Phenanthrene adsorption (30 µg/mL) was

analyzed using pseudo-first/second-order models [6], while degradability in tap water, seawater, and NaOH (pH 11) was assessed via weight loss and SEM. Cleansing efficacy of microbeads (40 mg in 10 mL cleanser) was tested against waterproof contaminants on human forearms, with residual sunscreen detected under UV light (365 nm). Data were processed using Case Viewer and Origin Pro 2024.

3. Results

3.1. Characterization of fucoidan and eco-friendly microbeads.

The structural and chemical properties of the microbeads were systematically characterized using complementary analytical techniques. All the images and analysis of CS-GgMBs and CS-GgMBs-ESF shown in Figure 1.

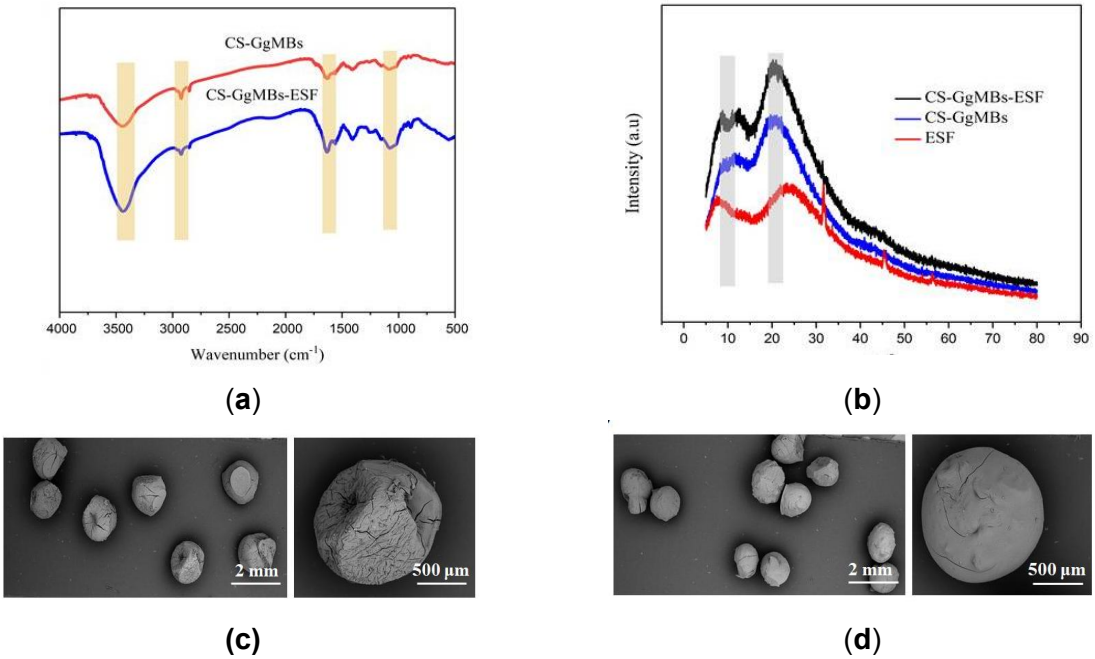


Figure 1. FTIR spectra analysis of CS-GgMBs and CS-GgMBs-ESF (a). X-ray diffraction (XRD) analysis of microbeads and fucoidan extract (ESF) (b). SEM images of CS-GgMBs and CS-GgMBs-ESF microbeads. Scale bars: 2 mm and 500 µm (c and d).

3.2. Swelling Activity of Microbeads

The effectiveness of cosmetic skin care products is significantly influenced by the swelling characteristics and delivery system [10]. The swelling tendencies of microbeads are detailed in Table 1, showcasing the swelling index measurements. The swelling index of CS-GgMBs microbeads after 10 days at pH 5.5 (69.16 ± 0.02%) was greater than that of the CS-GgMBs-ESF microbeads (57.57 ± 0.05%), as outlined in Table 1. In contrast, the swelling index of CS-GgMBs microbeads after 10 days at pH 3.7 (62.23 ± 0.04%) was marginally lower than that of the CS-GgMBs-ESF microbeads (63.55 ± 0.03%).
All microbeads retained structural integrity and insolubility during testing (Figure 2).

Table 1. Swelling index (%) with different time days at pH=5.5 and pH=3.3 for CS-GgMBS and CS-GgMBs-ESF, respectively. Values are mean ± SD

days	pH=5.5 CS-GgMBS	pH=3.7 CS-GgMBS	pH=5.5 CS-GgMBs-ESF	pH=3.7 CS-GgMBs-ESF
2	30.24 ± 0.14	28.32 ± 0.17	18.27 ± 0.03	19.24 ± 0.02
4	46.17 ± 0.12	43.13 ± 0.02	35.35 ± 0.07	36.57 ± 0.02
6	52.27 ± 0.07	49.26 ± 0.06	46.56 ± 0.23	49.59 ± 0.16
8	60.28 ± 0.04	57.48 ± 0.04	54.12 ± 0.09	62.19 ± 0.02
10	69.16 ± 0.02	62.23 ± 0.04	57.57 ± 0.05	63.55 ± 0.03

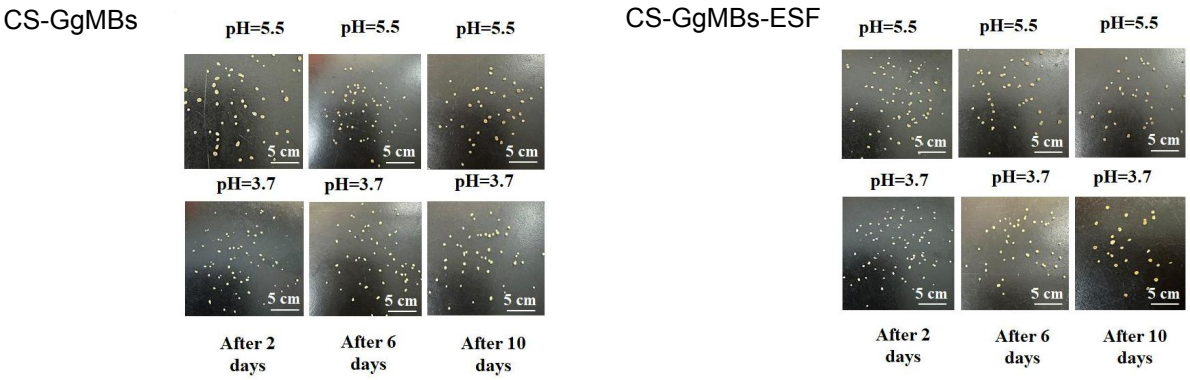


Figure 2. Initial photographs of CS-GgMBs and CS-GgMBs-ESF microbeads obtained during the swelling study after 2, 6, and 10 days (a and b).

3.3. Investigating of release behavior of fucoidan algae extract from microbeads

The release profiles of fucoidan (ESF) and CS-GgMBs-ESF microbeads were analyzed in vitro using buffer media at pH 3.7 and 5.5, as depicted in (Figure 3a and b), respectively. The findings demonstrated that the release rate of microencapsulated fucoidan from the microbeads was more sustained at pH 3.7, with approximately 73.2% being released over a duration of 180 minutes. In contrast, pure fucoidan only released 38.2% within the same time frame. Similarly, at pH 5.5, the release rate of fucoidan from the microbeads was slightly lower but still significant, with around 65.11% being released in 180 minutes, compared to 36.2% released from pure fucoidan.

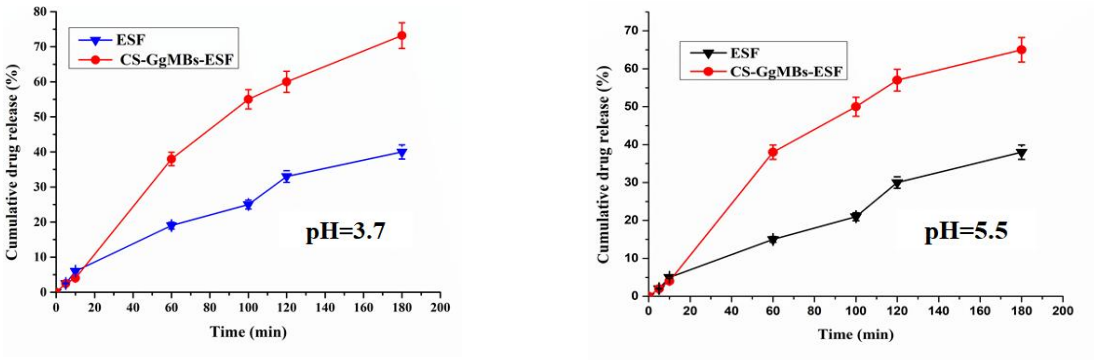
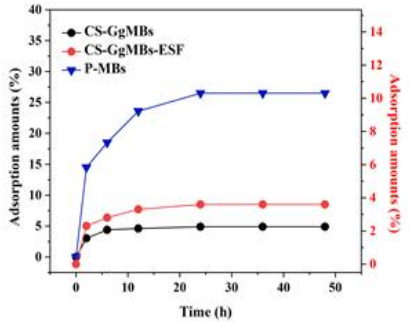


Figure 3. Drug release behavior of fucoidan algae extract ESF and CS-GgMBS-ESF microbeads at (a) pH3.7 and (b)pH5.5 . All measurements were implemented in triplicates (n = 3) and data were presented as mean standard deviation (± SD).

3.4. Comparison of the adsorption behavior of plastic and eco-friendly microbeads

The adsorption capacity of phenanthrene shown in Figure 4a, P-MBs displayed a significantly higher adsorption capacity, around 28%, after 48 hours compared to chitosan-based microbeads (CS-GgMBs and CS-GgMBs-ESF), which only adsorbed 5% of the contaminant. Chitosan-based microbeads possess a smooth and regular surface, unlike the irregular and coarse structure observed in P-MBs after exposure to the contaminant, as shown in Figure 4d. We evaluated the degradation of chitosan-based microbeads in tap water, seawater, and NaOH solution, revealing reduced degradability in NaOH. After 6 weeks in NaOH, polysaccharide microbeads retained significant weight and developed extensive cracks, indicating structural compromise (Figure 4e).



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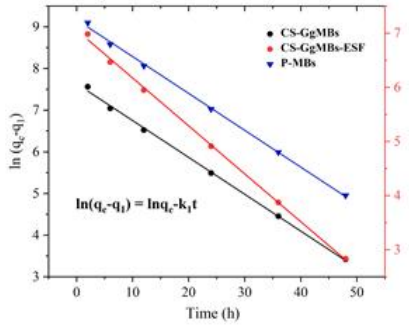

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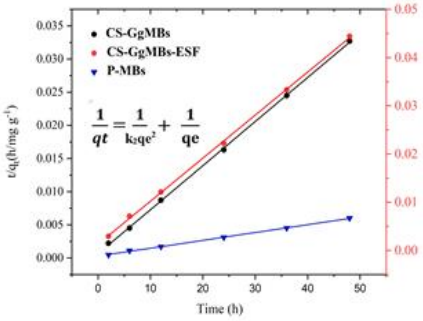

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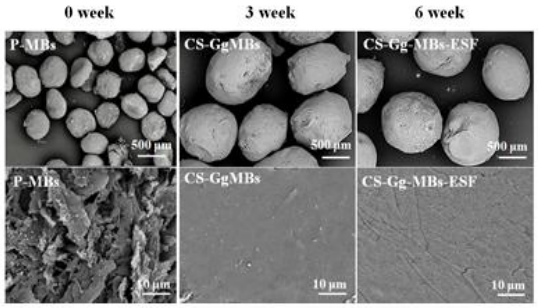

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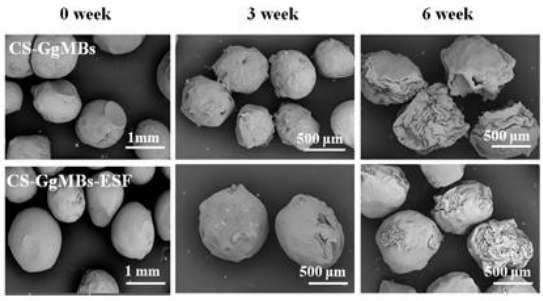

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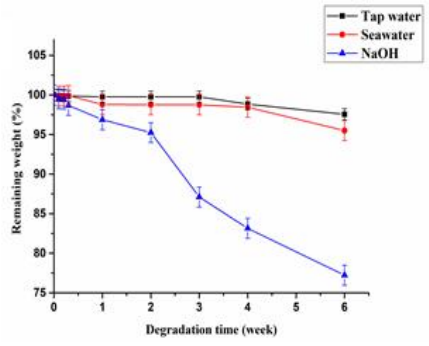

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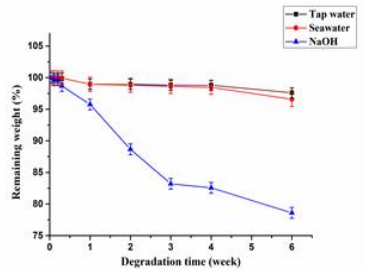


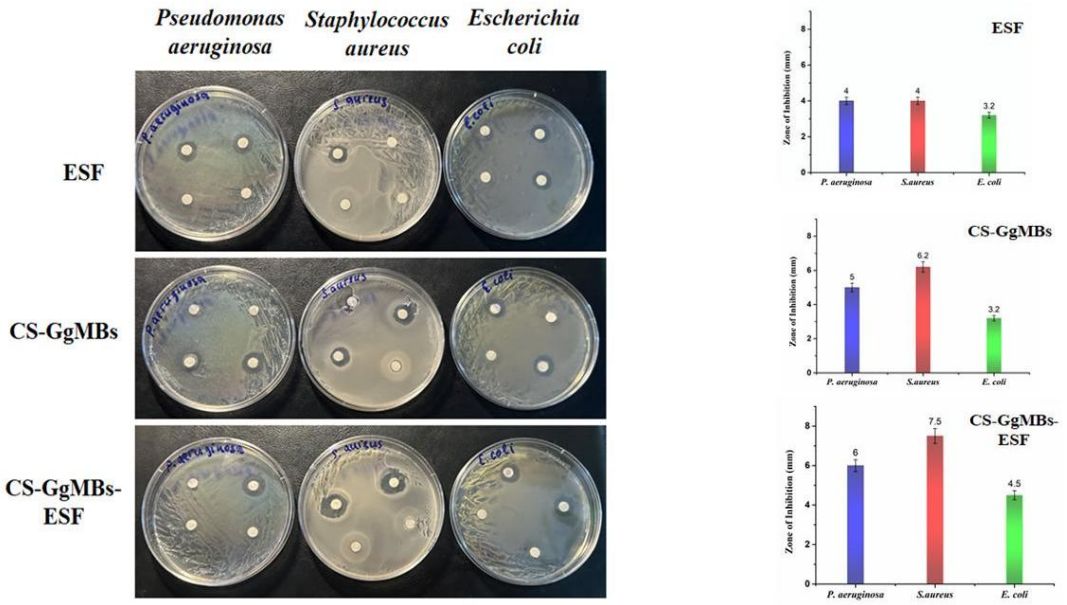
(**g**)

Figure 4. Adsorption capacity of phenanthrene on commercial (P-MBs) and eco-friendly microbeads (a). Adsorption kinetics corresponding to pseudo-first and pseudo-second order kinetic (b and c). SEM images of P-MBs, CS-GgMBs and CS-GgMBs-ESF microbeads after adsorption capacity (d). SEM images of CS-GgMBs and CS-GgMBs-ESF microbeads with different degradation times in NaOH solution (e). Hydrolytic degradation of CS-GgMBs and CS-GgMBs-ESF microbeads in different aqueous conditions (f and g).

3.5. Cytotoxic and antibacterial activity of fucoidan extract and produced microbeads.

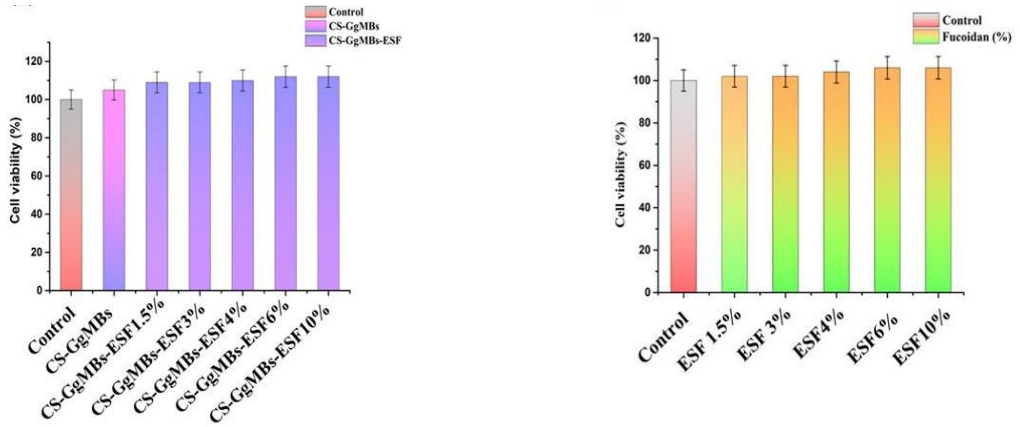
The antimicrobial activity of the microbeads was demonstrated in Figure 5a, b. The samples exhibited antibacterial activity against all tested microorganisms. The CS-GgMBs sample displayed zone inhibition values of 5.0, 6.2, and 3.3 mm for P. aeruginosa, S. aureus, and E. coli, respectively. Notably, the CS-GgMBS-ESF microbeads, which contained microencapsulated fucoidan, exhibited higher zone of inhibition values of 6.0, 7.5, and 4.5 mm for P. aeruginosa, S. aureus, and E. coli, compared to the extract fucoidan alone, which had values of 4.0, 4.0, and 3.2 mm, respectively.

Consequently, the MTT assay was employed to investigate the cytotoxicity effect of microbeads on cell proliferation against L929 as depicted in Figure 6a,b. All microbeads (blank and fucoidan-loaded) showed >90% L929 cell viability.



(**a**) (**b**)

Figure 5. Antibacterial activity of CS-GgMBs, CS-GgMBs-ESF microbeads, and fucoidan algae extract (ESF) against P. aeruginosa, S. aureus, and E. coli (a). Graphical representation of the antibacterial activity of CS-GgMBs, CS-GgMBs-ESF microbeads, and ESF (b).

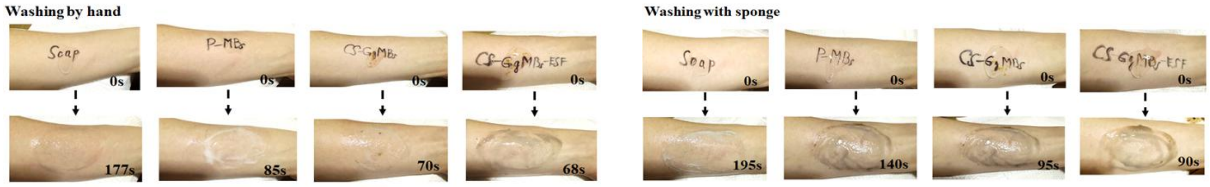


(**a**) (**b**)

Figure 6. In vitro cytotoxicity of the chitosan-gellan gum microbeads with and without fucoidan extract at different concentrations (a) and only fucoidan extract (b) at different concentrations regarding L929 cells by MTT assay.

3.6. Investigating of cleansing ability effect of plastics and sustainable microbeads.

The study demonstrated that CS-GgMBs and CS-GgMBs-ESF microbeads significantly enhanced cleansing efficiency in cosmetic exfoliants. In hand-washing tests, soap with these microbeads removed contaminants in ~70 and 68 seconds, respectively, versus 177 seconds without microbeads (Figure 7a). Similarly, sponge-based cleansing with the microbeads took 95 and 90 seconds, compared to 195 seconds for microbead-free cleanser (Figure 7b). Polysaccharide microbeads outperformed both traditional plastic microbeads (P-MBs) and microbead-free formulations, with results aligning with prior bead-based detergent studies [9] (Figure 7c).



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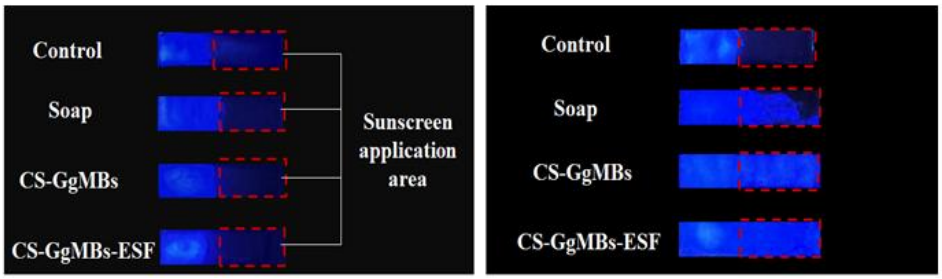

(**c**)

Figure 7. Photograph of washing by hand and washing with sponge using various microbeads (a and b). Observation of the cleansing efficiency of CS-GgMBs and CS-GgMBs-ESF microbeads against sunscreen applied to human skin (c).

4. Discussion

Environmental pollution from plastic microspheres (MPs) has become a critical global concern. Their small size allows millions of tons to bypass wastewater treatment systems annually, accumulating in marine ecosystems. Developing biodegradable alternatives is now imperative, with biopolymers emerging as a promising solution offering functional microbeads capable of eco-friendly degradation, thereby addressing marine plastic pollution innovatively.

The microbeads' structural and chemical properties were characterized using FT-IR, SEM, and XRD. FT-IR showed key peaks for CS-GgMBs (3442 cm^{-1} hydroxyl, 2923 cm^{-1} C-H, 1630 cm^{-1} C=C, 1407 cm^{-1} carboxylate, 1076 cm^{-1} C-O) and confirmed ESF integration in CS-GgMBs-ESF. Altered spectral intensity around 1500 cm^{-1} and an 892 cm^{-1} peak indicated polyelectrolyte complex formation and fucoidan incorporation. SEM revealed a smoother, firmer morphology in CS-GgMBs-ESF (~988 μm) compared to CS-GgMBs (~983 μm). XRD showed enhanced crystallinity in CS-GgMBs-ESF (9.7° vs. 9.28° in CS-GgMBs) with prominent peaks at ~20.9 °. Electrospraying maintained structural integrity and crystallinity, supporting the use of eco-friendly microbeads as sustainable alternatives to plastic microbeads [7,8].

The study revealed pH-dependent swelling characteristics in chitosan-gellan gum microbeads (CS-GgMBs and CS-GgMBs-ESF), critical for their performance in skincare formulations. CS-GgMBs exhibited a higher swelling index than CS-GgMBs-ESF after 10 days at pH 5.5 conditon.This reduction in CS-GgMBs-ESF is attributed to fucoidan's sulfate groups reinforcing the chitosan-gellan gum polyelectrolyte complex, limiting water-polysaccharide interactions and creating a rigid structure. At pH3.7 conditon , the swelling indices reversed slightly, with CS-GgMBs-ESF slightly exceeding CS-GgMBs. The lower pH likely enhanced electrostatic repulsion, promoting hydration in fucoidan-loaded microbeads.

The chitosan-gellan gum/fucoidan microbeads (CS-GgMBs-ESF) exhibit pH-responsive release kinetics, outperforming pure fucoidan in sustained delivery. The pH-responsive release mechanism arises from chitosan-gellan gum's hydration behavior , lower pH (3.7) promotes matrix swelling, facilitating buffer penetration through surface cracks and fucoidan diffusion (linked to the swelling data). Electrospraying enables controlled encapsulation, ensuring efficient fucoidan delivery across skin-relevant pH levels (5.5–3.7). This sustained release profile supports prolonged skin benefits (e.g., anti-aging, hydration) in cosmetic formulations, aligning with demands for natural, pH-adaptive skincare systems.

Recent research underscores the environmental and health risks of plastic microbeads, including marine contamination and links to human inflammatory responses and cancer. This study analyzed the adsorption capabilities of chitosan-based microbeads (CS-GgMBs and CS-GgMB-ESF) against commercial plastic microbeads (P-MBs) from exfoliants, using phenanthrene as a representative organic pollutant.The commercial microbeads P-MBs displayed a significantly higher adsorption capacity, around 28%, after 48 hours compared to CS-GgMBs and CS-GgMBs-ESF microbeads, which only adsorbed 5% of the contaminant. （Figure 4a） This difference can be attributed to the presence of numerous hydroxyl and amino groups (-OH-NH2) in the polysaccharide structure of chitosan and gellan gum. These functional groups facilitate hydrogen bonding and electrostatic interactions, resulting in a more rigid and compatible structure [11]. As a result, the density and surface smoothness of the microbeads increase, hindering the penetration of phenanthrene and limiting the adsorption capacity. Phenanthrene adsorption on microbeads followed pseudo-second order kinetics (R^2 = 0.999, Figure 4b-c), dominated by physisorption via van der Waals forces, attributed to the microbeads' smooth surface and electrostatic properties. The pseudo-first order model (R^2 = 0.998) showed weaker alignment, excluding chemisorption as a primary mechanism. These results confirm that adsorption capacity hinges on microbead surface area and physical interactions [12], supporting their eco-friendly design for cosmetic applications。

This study demonstrated that while CS-GgMBs and CS-GgMBs-ESF microbeads exhibited significantly reduced degradability in NaOH (retaining >80% mass after 6 weeks), they developed extensive surface cracks due to polysaccharide chain scission (Figure 4e), contrasting sharply with plastic microbeads' chemical inertness in NaOH (no cracks observed) [13]. This divergence stems from the inherent chemical sensitivity of biobased polysaccharides: NaOH likely disrupts electrostatic interactions in the chitosan-gellan gum polyelectrolyte complex, triggering hydrolytic chain cleavage. Notably, both microbead types showed minimal degradation in tap water and seawater (Figure 4f-g), with stability attributed to polyvalent ions (e.g., Ca^{2+}/Mg^{2+}) inducing crosslinking within the polyelectrolyte network [14], forming a dense structural barrier against swelling-driven degradation.

Incorporating eco-friendly microbeads with anti-bacterial properties is crucial when formulating cosmetics. This not only ensures the product's environmental friendliness but also its ability to maintain hygiene and safety standards [15]. The enhanced antibacterial activity of CS-GgMBs-ESF arises from synergistic effects: chitosan's cationic amino groups ($-NH_3^+$) electrostatically disrupt bacterial membranes [17], while fucoidan's sulfated polysaccharides inhibit microbial adhesion [16]. The pH-stable polyelectrolyte complex ensures sustained release of bioactive components, amplifying efficacy.

Non-cytotoxicity (>90% viability) confirms biocompatibility, aligning with fucoidan's reported role in promoting fibroblast proliferation[18]. Increased viability with fucoidan concentration suggests dose-dependent bioactivity, likely due to antioxidant and anti-inflammatory properties. These results validate the microbeads' safety and dual functionality (antibacterial + cytocompatibility) for cosmetic applications, particularly in formulations targeting skin health and hygiene [15].

Having compared the behavior of plastic and eco-friendly microbeads in the environment, we then tested their cleansing properties on human skin. It is worth noting that certain plastic microbeads are manufactured using polyethylene, a substance that has been associated with skin irritation and inflammation. The superior cleansing efficiency of CS-GgMBs-ESF stems from their dense surface structure, where fucoidan enhances rigidity and friction via hydrophilic interactions with chitosan-gellan gum. Chitosan's cationic nature promotes

adhesion to negatively charged skin surfaces, improving impurity removal [19]. The antibacterial properties (Figure 5) further enhance hygiene by inhibiting skin pathogens. Electrospraying ensures uniform encapsulation, balancing mechanical robustness (resisting stress) with controlled biodegradability. These attributes align with consumer demand for safe, non-irritating, and eco-friendly cosmetics, positioning polysaccharide microbeads as viable alternatives to P-MBs.

5. Conclusion

This study demonstrates the successful development of chitosan-gellan gum/fucoidan microbeads via electrospraying, offering a sustainable alternative to plastic microbeads with enhanced biocompatibility and pH-responsive drug release. The microbeads are produced using a blend of chitosan and gellan gum, enhanced by the addition of fucoidan extract sourced from Ecklonia stolonifera algae, and are fabricated using a syringe system operating under pump conditions for the polysaccharide solution.Key findings include:

Structural Integrity: FT-IR, ^{1}H NMR, XRD, and SEM confirmed the successful synthesis of microbeads with preserved fucoidan bioactivity and crystalline organization.

Functional Efficacy: The microbeads exhibited pH-responsive fucoidan release (73.2% at pH 3.7, 65.11% at pH 5.5), superior cleansing efficiency (68 – 70 s vs. 177 s for hand cleansing), and high adsorption resistance to pollutants (5% vs. 28% for plastic microbeads).

Safety and Compatibility: Demonstrated non-cytotoxicity (>90% cell viability), antibacterial activity against S. aureus, P. aeruginosa, and E. coli, and no skin irritation.

These results highlight the microbeads' potential as multifunctional cosmetic ingredients, combining exfoliation, sustained bioactive delivery, and environmental safety. Electrospraying parameters and ingredient selection (e.g., tea tree oil, aloe vera) can further enhance functionality for anti-aging, anti-inflammatory, and moisturizing applications. This approach aligns with the growing demand for eco-friendly, high-performance skincare solutions.

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