

Article

Antifouling Performance and Sustained Release Behavior of Ethanol Extract from the Root of *Stellera chamaejasme*

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Abstract: Antifouling substances play a crucial role in inhibiting fouling and adhesion due to their broad-spectrum and non-toxic advantages. Nevertheless, the excessive release of the antifouling agents shortens the service life of the antifouling coating. In this study, we investigated the antifouling performance of an ethanol extract from the root of *Stellera chamaejasme* (Sc) through algal adhesion experiments. The interaction between Sc and algae (*Chlorella* and *Dunaliella tertiolecta*) was further studied by using a UV spectrophotometer. Then, Sc was encapsulated with polydopamine (PDA) microcapsules to prepare Sc@SiO₂@PDA microcapsules by the template method. The release behavior of Sc@SiO₂@PDA under different pH conditions was investigated. The result demonstrates that the interaction between Sc and algae belongs to single static quenching, and the Sc@SiO₂@PDA microcapsules exhibit good antifouling performance against *Chlorella* and *Dunaliella tertiolecta*. This work will provide guiding significance for the development of eco-friendly marine antifouling coatings.

Keywords: *Stellera chamaejasme*; PDA microcapsules; natural product; marine antifouling



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1. Introduction

The attachment and reproduction of marine organisms on underwater surfaces have significant negative impacts on ships, cooling pipelines, membrane filtration equipment, aquaculture systems, and marine sensors [1,2]. Various physical and chemical methods have been used to prohibit the attachment of fouling organism, such as mechanical cleaning, spraying antifouling paint, and fouling release coatings on the surface of the material. Among these methods, organic tin-based anti-fouling coating is the most effective [3–7]. However, this type of coating is highly toxic and cannot be completely degraded in the natural environment; in addition, it was prohibited by the International Marine Environment Organization in 2008 [8,9]. At present, other non-metallic- and metallic-based compounds, including Irgarol 1051, diuron, chlorothalonil, thiram, and zinc pyrithione, are widely used to prepare antifouling coatings as substitutes for organic tin-based compounds. Unfortunately, these fungicides also have a certain toxicity and some are difficult—biodegrade, posing a serious threat to the safety of the marine ecological environment [3,5,10]. Therefore, the development of non-toxic or eco-friendly marine antifouling coatings is a top priority.

In recent years, natural medicinal plant resources with physiological activities such as antibacterial, anti-tumor, antibiofilm, antifouling, and radiation resistance have been favored by researchers [11]. Natural product antifouling agents are natural substances extracted by biotechnology from various animals, plants, and microorganisms that can effectively prevent marine fouling [12]. They are secondary metabolites produced by organisms themselves with antifouling activity [13]. Firstly, it was found that some marine organisms, such as red algae, corals, sponges, etc., do not produce biological fouling on their own. On this basis, scientific and technological workers have conducted a series

of related studies on terrestrial plants and marine organisms. Some natural product extracts with antifouling activity have been found, such as terpenoids, peptides, amino acids, alkaloids, etc. [14,15]. These natural product extracts are expected to replace traditional antifouling agents [13]. For example, when the EC₅₀ of omaezallene extracted from the red algae *Microcystis aeruginosa* is 0.22, it can effectively inhibit the adhesion of barnacle larvae [16]. Dahee prepared a marine antifouling coating by using the red algae-derived polysaccharide carrageenan via Zr^{IV}-mediated multiple cross-linking reactions [17]. In this work, λ-CAR showed superior marine antifouling performance in diatom adhesion assays. Davis et al. isolated and extracted alkaloids g and h from the sea squirt *Eudistoma olivaceum*, which can effectively inhibit the attachment of barnacle larvae [18]. In addition, the furanone derivatives extracted from *Streptomyces purpurea* have a good inhibitory effect on the adhesion of *Ulva pertusa* and diatom *Navicular* algae. Gao and coworkers have studied the *Anthogorgia caerulea* of the Beibu Gulf gorgonian coral and isolated four homologues of avermectin, two of which are newly discovered derivatives of avermectin, avermectin B1c and B1e, as well as two known compounds B2a and A1a. These four homologues can effectively inhibit the adhesion of barnacle larvae [19]. There are also many types of antifouling substances isolated and extracted from some terrestrial plants and animals, such as indigo [20], diketopiperazine compounds (6S, 3S) -6-benzyl-3-methyl-2,5-diketopiperazine and (6S, 3S) -6-isobutyl-3-methyl-2,5-diketopiperazine [21], citrinin A, and aromatic ester compounds (phenol A acid) [22], amino acids [23], capsaicin [24], etc. However, it is still a huge challenge applying these effective antifouling components to available technologies with sustained release behavior [25].

The latest modern medical and traditional Chinese medicine studies show that the extract of *Stellera chamaejasme* is an ideal natural drug, which has anti-tumor, antibacterial, and insecticidal activity [26–29]. The main components of *Stellera chamaejasme* are terpenoids, flavonoids, and amino acid compounds which play a major role in the above performance. Some structures of ethanol extracts from *Stellera chamaejasme* are shown in Figure 1. In light of the inherent characteristics of these components, *Stellera chamaejasme* may have good antifouling properties. Herein, we investigated the antifouling properties of the ethanol extract from the root of *Stellera chamaejasme* (Sc) by a fluorescence quenching experiment and an algae adhesion experiment. Sc was encapsulated in polydopamine (PDA) to prepare Sc@SiO₂@PDA microcapsules with sustained release behavior. In the fluorescence quenching experiment, Sc and Sc@SiO₂@PDA microcapsules all exhibited good antifouling performance against *Chlorella* and *Dunaliella tertiolecta*.

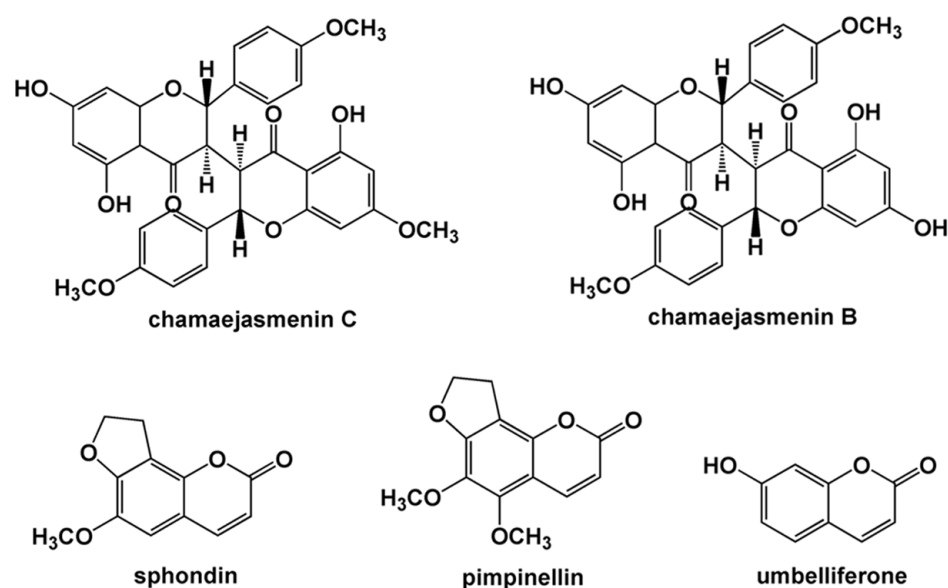


Figure 1. Some structures of ethanol extracts from *Stellera chamaejasme* [28,30].

2. Materials and Methods

2.1. Materials

Sc was provided by the Key Laboratory of Plant Resources Chemistry in Northwest China. Polyvinylpyrrolidone ($M_w = 40,000$) and dopamine were purchased from the Sigma-Aldrich Company (St. Louis, MO, USA). Trimethylol aminomethane (Tris), ethyl orthosilicate (TEOS), ammonia, styrene, azobisisobutamidine hydrochloride (AIBA) were all domestic analytical pure reagents. *Chlorella* and *Dunaliella tertiolecta* were provided by the Freshwater Algae Culture Collection at the Institute of Hydrobiology.

2.2. Methods

2.2.1. Preparation of Acrylic Resin Antifouling Coating

Preparation of acrylic resin: 7 g ethylene glycol methyl ether, 2 g butyl acetate, and 10 g dimethyl sulfoxide were added to the round-bottom flask, stirred to a uniform state, heated to 80 °C, and marked as A solution. A total of 0.25 g AIBN was dissolved in 1 g ethylene glycol methyl ether, 1 g butyl acetate, and 3 g dimethyl sulfoxide, 0.1 g dodecyl mercaptan was added, stirred until completely dissolved, and then the B solution was obtained. Then, 2 g acrylic acid, 1.5 g ethyl acrylate, 3 g methyl methacrylate, and 4 g butyl acrylate were stirred and added to the B solution, the above solution was mixed evenly and then added to the A solution. After dripping, the acrylic resin was obtained after holding for 3 h.

Preparation of acrylic resin antifouling coating: Sc with a mass fraction of 1% and 5% was dissolved in dimethyl sulfoxide, mixed with a certain amount of acrylic resin, and then sprayed onto the substrate and dried at room temperature to obtain an acrylic resin coating containing Sc.

2.2.2. Preparation of Hollow Silica Spheres (SiO_2)

The SiO_2 hollow spheres were fabricated by the sol–gel method [31]. In a nitrogen atmosphere, 1.5 g PVP was added to a 250 mL round-bottom flask, 100 g water was added, stirred to dissolve, and 10.0 g styrene was added dropwise. After stirring for 1 h, the system was heated to 70 °C, 0.26 g AIBA was added, the stirring speed was 300 rpm, and the reaction was performed at a constant temperature for 24 h to obtain a PS microsphere dispersion. After dialysis of the PS dispersion with a cellulose dialysis membrane, anhydrous ethanol was added to obtain a PS dispersion with a solid content of 6.5%.

The 3.5 g PS dispersion was added to 40.0 mL anhydrous ethanol, and heated to 50 °C with magnetic stirring. Then, 5 mL $\text{NH}_3\text{H}_2\text{O}$ and 1.0 g TEOS were added, and the reaction lasted 1.5 h. After centrifugation and washing with H_2O and ethanol three times, the SiO_2 hollow spheres were obtained by vacuum drying at 60 °C.

2.2.3. Preparation of Silica Spheres @ Polydopamine ($\text{SiO}_2\text{@PDA}$)

A total of 250 mg SiO_2 was uniformly dispersed in 25 mL Tris buffer solution (pH = 8.5), and then 25 mg dopamine was added. The reaction mixture was stirred at room temperature for 24 h. After the reaction, $\text{SiO}_2\text{@PDA}$ microcapsules were obtained by centrifugation and washing with H_2O and ethanol three times.

2.2.4. $\text{Sc@SiO}_2\text{@PDA}$ Microcapsules Sustained-Release Behavior

Loading: A total of 0.5 g of Sc was dissolved in 35 mL ethanol, then 0.5 g $\text{SiO}_2\text{@PDA}$ microcapsules were added and stirred at room temperature for 24 h. After the reaction, the product was centrifuged, washed with ethanol three times, and dried in a vacuum at 45 °C. The entrapment rate of $\text{Sc@SiO}_2\text{@PDA}$ microcapsules was 28%.

Release: A certain amount of $\text{Sc@SiO}_2\text{@PDA}$ microcapsules were placed in $\text{EtOH}/\text{H}_2\text{O}$ solutions with different pH values (7.0 and 8.3) (3:7, v/v), stirred at 100 rpm, and a

certain volume of the solution was taken at a time and detected by an ultraviolet–visible spectrophotometer.

$$\text{Sc loading rate (L\%)} = \frac{m_1}{W} \times 100\%, \quad (1)$$

$$\text{Sc embedding rate (E\%)} = \frac{m - m_2}{m} \times 100\%, \quad (2)$$

W is the mass of the loaded microcapsules, m_1 is the mass of Sc embedded in the microcapsules calculated by the concentration, m is the original amount of Sc in solutions, and m_2 is the amount of residual Sc.

2.3. Testing and Characterization Methods

2.3.1. Characterization Instrument

TEM characterization was performed on a Japanese Shimadzu (Hitachi model JEM-2010, Shimadzu, Tokyo, Japan) at an accelerated voltage of 200 kV. The fluorescence intensity was measured by LS 55 fluorescence spectrophotometer (Perkin-Elmer, Boelingen, Germany). The morphology of microcapsules was observed under FE-SEM of JSM-6701F (Japan Electronics Co., Ltd., Tokyo, Japan), and the test voltage was 5–10 kV. Optical images were taken on OLYMPUS BX51 fluorescence microscope (Olympus, Tokyo, Japan). The UV–visible absorption spectra of the solution were measured on a Lambda 35 UV–visible spectrophotometer (Perkin-Elmer, Boelingen, Germany) and a quartz cuvette of 1 cm × 1 cm.

2.3.2. Sc Standard Curve Drawing

For drawing the standard curve of Sc, the UV spectrophotometer was used to test the absorbance of solutions with different concentrations. A total of 10 mg Sc was first added to a 100 mL volumetric flask, and then the EtOH/H₂O solution (3:7, v/v) was added to a constant volume. Similarly, 10.0, 6.0, 2.0, 1.6, 1.2, 0.8, 0.4, and 0.2 mL of the above-mentioned prepared solutions were taken in a 50 mL volumetric flask, and the EtOH/H₂O solution was added to a constant volume. Then, the absorbance of different solutions was measured by ultraviolet spectrophotometer, which was plotted into a curve to obtain a standard curve.

2.3.3. Fluorescence Quenching Experiment of Sc and Sc@SiO₂@PDA Microcapsules

Sc solutions with concentrations of 1, 5, 9, 13, and 17 mg/mL were prepared. At room temperature, the algae suspension was dispersed evenly, and 3 mL algae suspension was accurately added to a 4 mL quartz cuvette to determine the fluorescence intensity. Then, 25 and 50 µL with a different concentration of the Sc solution was added into the algae suspension and then the fluorescence intensity was measured after 40 s. Besides that, different mass of Sc@SiO₂@PDA microcapsules was added into algae suspension for the fluorescence quenching behavior. ($\lambda_{\text{ex}} = 405$ nm, because at $\lambda_{\text{ex}} = 405$ nm *Chlorella* suspension has strong fluorescence intensity, so this wavelength was chosen as fluorescence quenching λ_{ex}).

2.3.4. Fluorescence Quenching Constant

Static quenching is a process in which the interaction between the quencher and the fluorescent substance forms a quencher–fluorophore ground state complex. The quenching process is described by the Stern–Volmer equation:

$$\frac{F_0}{F} = K_{SV}[Q] + 1 = k_q\tau_0[Q] + 1, \quad (3)$$

In the formula, F_0 and F are the fluorescence intensity without and with the addition of the quencher Sc, respectively. τ_0 is the fluorescence lifetime of the fluorescent molecule without the quencher (the fluorescence lifetime of the biomacromolecule is about 10 ns),

$[Q]$ is the quencher concentration, k_q is the biomolecular quenching constant, and K_{SV} is the Stern–Volmer quenching constant.

2.3.5. Algae Adhesion Test

Chlorella and *Dunaliella tertiolecta* from the Freshwater Algae Culture Collection at the Institute of Hydrobiology were cultured at 25 °C on BG-11 and Dunaliella medium for 12 h of light and non-light, respectively. The concentration of algae used in the experiment was 10^6 /mL. The samples were cut into a size of 0.5 cm × 0.5 cm and washed with distilled water and ethanol. Three replicates of the samples were placed in a chlorella solution facing upwards. After incubation in a constant-temperature light incubator for 24 h, the sample was taken out and rinsed twice with the medium to remove the microorganisms floating on the surface of the sample, and observed under an optical microscope. The number of attached algae was obtained by averaging the number of attached algae in three groups of parallel samples and each group of samples in at least thirty random fields in the microscopic field of view.

3. Results and Discussion

Stellera chamaejasme is a common Chinese herbal medicine belonging to the genus *Stellera* of the family *Daphneaceae*. In recent years, it has been found that the ethanol extract of Sc has a good insecticidal effect on the pine wood nematodes (*Bursaphelenchus xylophilus*) and (*Bursaphelenchus mucronatu*) [29]. In this paper, Sc was added to an acrylic resin coating as a natural antifouling agent and the antifouling properties were investigated by adhesion experiments using *Chlorella* on their surfaces. Furthermore, it was embedded in polydopamine microcapsules and the sustained release behavior in solution was studied by altering the pH value.

Two acrylic resin antifouling coatings with 1 wt.% and 5 wt.% mass fractions of Sc were prepared and the adhesion behavior of *Chlorella* on their surfaces was investigated by fluorescence microscope (Olympus BX 51). Figures 2 and 3 show the adhesion densities of *Chlorella* on the surface of blank acrylic resin coatings at different time periods. The adhesion densities of *Chlorella* on the surface of blank acrylic resin coatings were 338/mm², 372/mm², 366/mm², and 393/mm². Meanwhile, the adhesion densities of *Chlorella* on the surface of acrylic resin coating containing 1 wt.% Sc were 117/mm², 228/mm², 186/mm², and 248/mm². It was more striking that the adhesion densities of acrylic resin coatings containing 5 wt.% Sc were 41/mm², 152/mm², 62/mm², and 55/mm². The experimental result shows that the adhesion density of *Chlorella* on the surface of blank acrylic resin coatings is higher than on the surface of acrylic resin coatings containing Sc, indicating that Sc can inhibit the adhesion of *Chlorella* on its surface. These results indicate that the higher the content of Sc, the better the inhibitory effect on *Chlorella*.

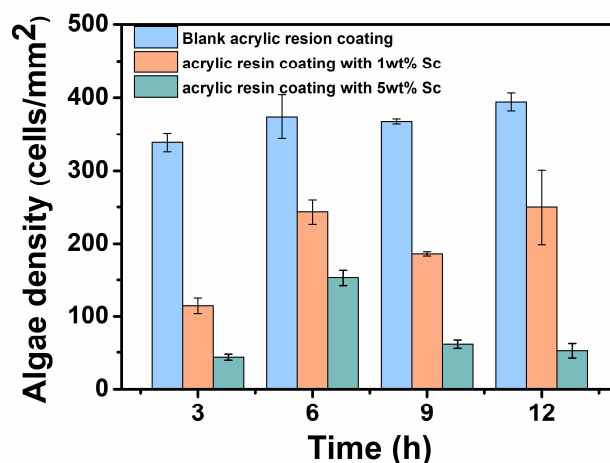


Figure 2. Adhesion density of *Chlorella* on different coating surfaces.

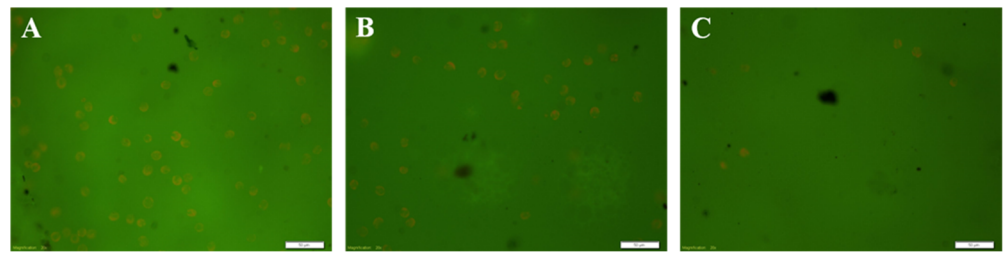


Figure 3. Fluorescence microscope pictures of *Chlorella* on different surfaces after incubation for 12 h in algae solution. (A) blank acrylic resin coating, (B) acrylic resin coating with 1 wt.% Sc, (C) acrylic resin coating with 5 wt.% Sc. The scale bar is 50 μm .

To further investigate the antifouling mechanism of Sc, the fluorescence quenching experiments of *Chlorella* and *Dunaliella tertiolecta* were carried out. Figure 4 shows the fluorescence intensity of *Chlorella* decreased with the increase in the volume and Sc concentration. Figure 5 shows the fluorescence intensity of *Dunaliella tertiolecta* decreased with the increase in the volume and Sc concentration. It is proved that Sc has a fluorescence quenching effect on both algae and exhibited an obvious dose–effect relationship. Figure 4B,D and Figure 5B,D are obtained by drawing with F_0/F as the ordinate and the concentration of Sc as the abscissa. According to the Stern–Volmer equation, the quenching constants of *Chlorella* were determined as $K_{SV} = 0.06229 \pm 0.01175 \text{ mL/mg}$ and $K_{SV} = 0.23347 \pm 0.02784 \text{ mL/mg}$. The quenching constants of *Dunaliella tertiolecta* were determined as $K_{SV} = 0.06043 \pm 0.01058 \text{ mL/mg}$ and $K_{SV} = 0.18797 \pm 0.02289 \text{ mL/mg}$. As shown in Figures 4 and 5, the relation between F_0/F and concentration is linear and the fluorescence quenching mechanism of algae and Sc is the static quenching. The quenching effect was also enhanced with the increase in Sc dose. When the adhesion experiment was combined with the fluorescence quenching data of *Chlorella* and *Dunaliella tertiolecta*, Sc can reduce the activity of algae and prevent biological fouling. This mechanism is different from hydrophilic coating and oleophobic coating which depends on surface wettability [32].

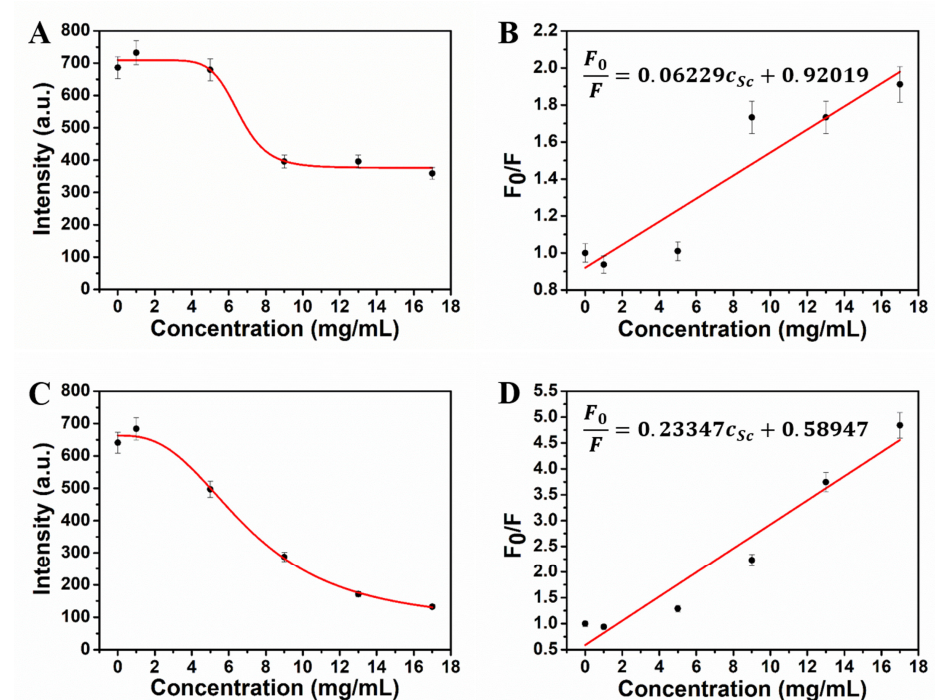


Figure 4. Fluorescence quenching curve of *Chlorella* at different concentrations of Sc ((A), 25 μL) and ((C), 50 μL), Stern–Volmer curve of *Chlorella*/Sc system ((B), 25 μL) and ((D), 50 μL).

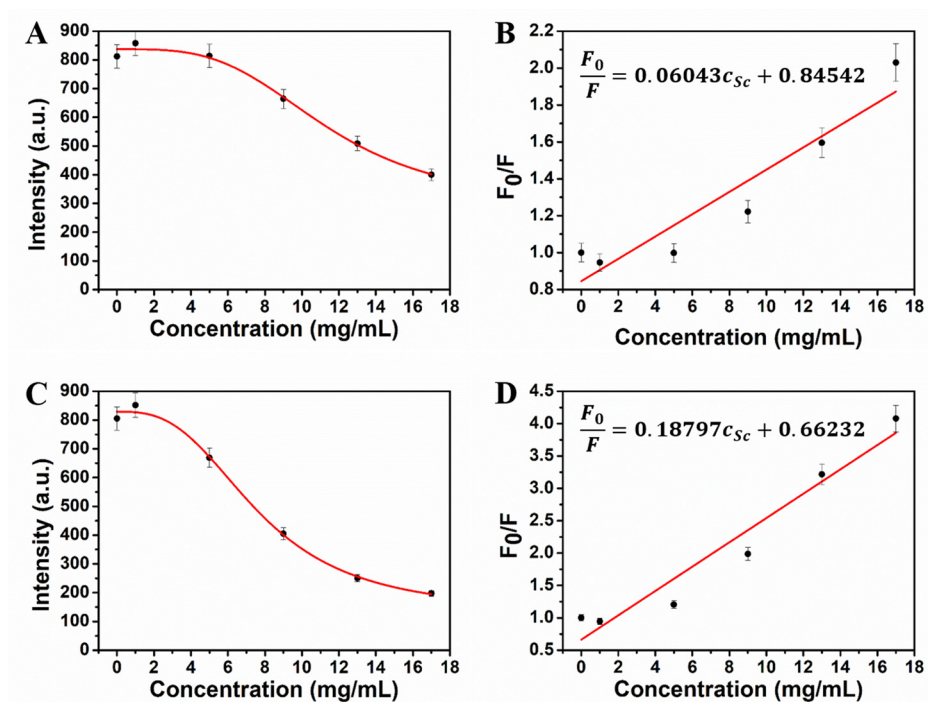
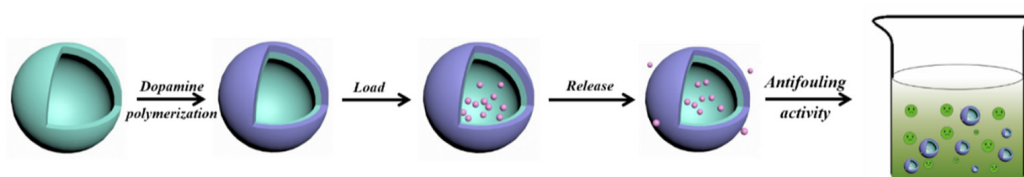


Figure 5. Fluorescence quenching curve of *Dunaliella tertiolecta* at different concentrations of Sc ((A), 25 μ L) and ((C), 50 μ L), Stern–Volmer curve of *Dunaliella tertiolecta*/Sc system ((B), 25 μ L) and ((D), 50 μ L).

However, the adhesion density of *Chlorella* on acrylic resin coating with Sc tends to increase with the passage of test time, as shown in Figure 3. It may be due to the diffusion of Sc on the surface of the coatings into the algae solution, which results in a decrease in the Sc content and weakens the antifouling effect of the coating surface. The release rate of antifouling agents determines the failure rate of antifouling coatings. Thus, it is crucial for antifouling coatings to achieve a slow and continuous release of antifouling agent into the seawater to maximize the long-term antifouling life in practical applications. To solve the problem of the excessive release speed of antifouling agents in the coating, Sc was encapsulated into PDA microcapsules to achieve a sustained release behavior.

Polydopamine microcapsules were prepared using hollow silica spheres as templates, and the detailed preparation method is shown in Scheme 1. Hollow SiO_2 microspheres were prepared according to reference [31]. TEM and SEM images of SiO_2 microspheres and SiO_2 @PDA microcapsules are shown in Figure 6. In Figure 6A,C, the SiO_2 microspheres are uniformly dispersed and have a hollow structure with a particle size of about 200 nm. After dopamine polymerization, the size of the microsphere increases slightly (the thickness of the capsule is about 20 nm) and the surface is smoother in Figure 6B,D. Therefore, based on the structure of the SiO_2 hollow sphere, it is possible to load Sc. Figure 7 shows the TGA curve of different samples, showing that the thermal performances of SiO_2 @PDA and Sc@SiO_2 @PDA are different. It indicates that Sc was successfully buried into the microcapsule.



Scheme 1. The preparation of SiO_2 @PDA microcapsules.

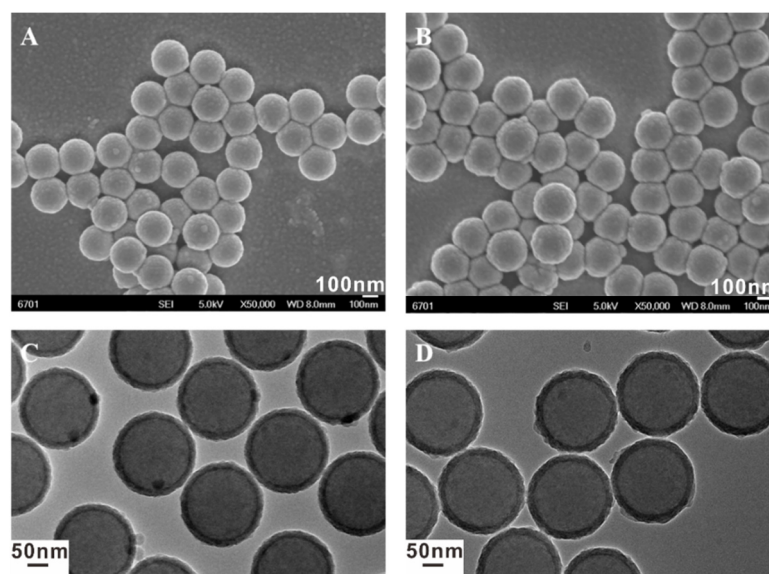


Figure 6. SEM images of (A) SiO_2 and (B) SiO_2 @PDA microcapsules, TEM images of (C) SiO_2 and (D) SiO_2 @PDA microcapsules.

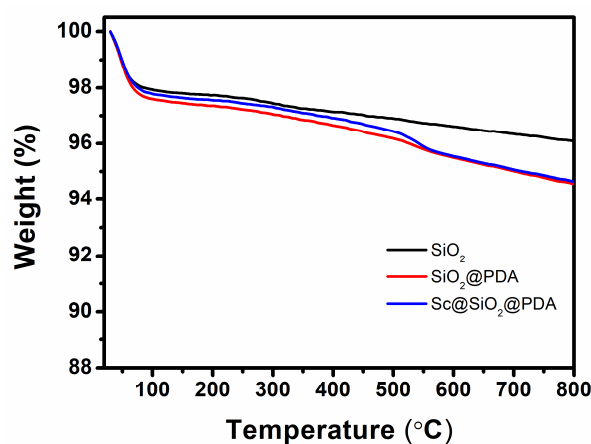


Figure 7. TGA curve of different samples.

Since the pH of seawater is from 8.2 to 8.4, we chose weak alkaline conditions to study the sustained release behavior of Sc@SiO_2 @PDA microcapsules. The Sc@SiO_2 @PDA microcapsules were placed in a cellulose dialysis bag. Then, the bag was placed in 200 mL EtOH/ H_2O solutions with pH = 7.0 and pH = 8.3 (close to seawater pH). First, the position of the absorption peak was determined by measuring the UV absorption curve of Sc at different concentrations, as shown in Figure 8A. The absorption peak of Sc is 300 nm. Figure 8B is the UV absorption standard curve of Sc. The relationship between ultraviolet absorption intensity (A) and the concentration of Sc (c_{Sc}) is $A = -0.01179 + 18.80196 c_{\text{Sc}}$. Based on this formula, the instantaneous concentration of released Sc can be determined by the obtained standard curve.

The sustained release behavior of Sc@SiO_2 @PDA microcapsules under different pH conditions is shown in Figure 9. The release equilibrium time of Sc@SiO_2 @PDA microcapsules in pH 7.0 and 8.3 solutions was 12 h and 24 h, respectively. Approximately 20.1% w/w of Sc (in percentage terms, Sc released divided by the total load of Sc, w/w) was released into the solution at pH = 7. The cumulative release of Sc@SiO_2 @PDA microcapsules reached 52% at pH = 8.3 when the release time was 96 h. This may be due to the deprotonation of polydopamine under weakly alkaline conditions [33]. At a high pH value, the amino of polydopamine will be deprotonated and negatively charged, thus increasing the repulsive

force between Sc and polydopamine, so the release rate of Sc is accelerated, and the release amount is also increased. Therefore, the release rate and amount of Sc increased with the increase in pH value. Because the seawater is also weakly alkaline (pH = 8.2–8.4), the capsule can be used as an additive to prepare a coating with a sustainable and efficient release of antifouling agents.

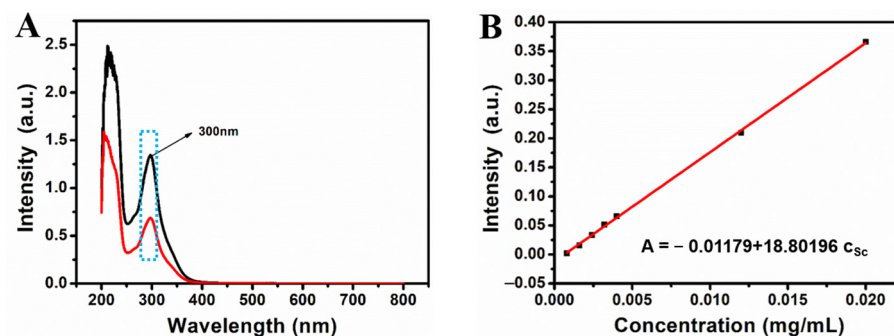


Figure 8. (A) UV absorption spectra of Sc, (B) standard curve of Sc between concentration and absorption intensity.

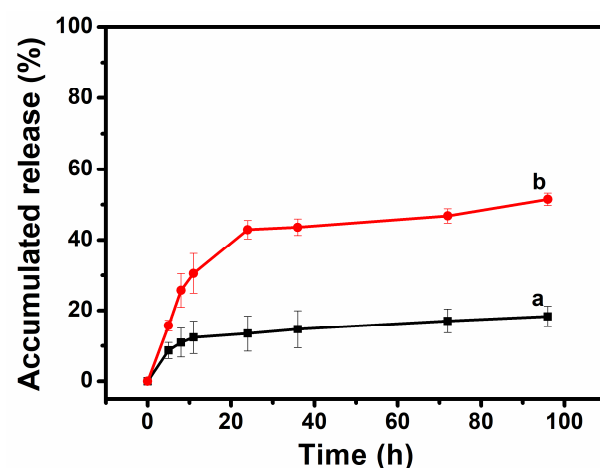


Figure 9. The effect of different pH on the sustained release behavior of Sc@SiO₂@PDA microcapsules: (a) pH = 7, (b) pH = 8.3.

It is proved that the effect between algae and Sc is the static quenching in the fluorescence quenching test. In order to prolong the antifouling time of Sc, Sc@SiO₂@PDA microcapsules were prepared. The fluorescence quenching test of c@SiO₂@PDA microcapsules was investigated. Microcapsules were added to *Chlorella* and *Dunaliella tertiolecta*, shaken well, and tested for fluorescence intensity after 3 min. Figure 10 shows the influence curve of the fluorescence intensity of algae solution on the quality of microcapsules. With the addition of Sc@SiO₂@PDA microcapsules, the fluorescence intensity of the *Chlorella* solution decreases from 437 to 119, and the fluorescence intensity of the *Dunaliella tertiolecta* solution decreases from 367 to 38. The result shows that the fluorescence intensity of the algal solution gradually decreases with the increase in the added capsule mass, especially for the fluorescence quenching of *Dunaliella tertiolecta*. It's due to the release of Sc from microcapsules. These experimental results show that Sc is an effective natural product antifouling agent and has potential applications in the preparation of marine antifouling coatings. However, natural product Sc is difficult to achieve mass production. It is important to study how to efficiently extract and separate the compound, and its relationship between structure and activity, to provide guidance for further structural modification and chemical synthesis, to achieve the production of antifouling agents.

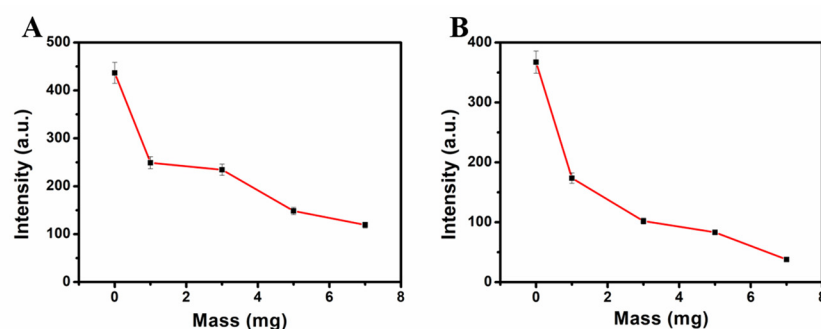


Figure 10. Fluorescence spectra of (A) *Chlorella* and (B) *Dunaliella tertiolecta* at different mass of Sc@SiO₂@PDA at 300 nm and 298 K.

4. Conclusions

In this work, an eco-friendly Sc@SiO₂@PDA microcapsule with antifouling performance and sustained release behavior is fabricated. It is proved that the natural product Sc has good antifouling properties through the algae adhesion experiment and fluorescence quenching experiment. Combined with Cui's work, Sc should be a broad-spectrum antifouling agent against algae and animals [29]. For long-term controlled release, Sc@SiO₂@PDA microcapsules have higher release capacity at pH = 8.3, and effectively quench the fluorescence of *Chlorella* and *Dunaliella tertiolecta*. In other words, the Sc@SiO₂@PDA microcapsules could exhibit long-term anti-fouling performance in sea water (seawater is weakly alkaline from 8.2 to 8.4). Therefore, Sc and Sc@SiO₂@PDA microcapsules can be used as a natural product antifouling agent to prepare antifouling coatings with the sustainable and efficient release of the antifouling agent.

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Conflicts of Interest: The authors declare no conflict of interest.

References

- Katharios-Lanwermeier, S.; Xi, C.; Jakubovics, N.S.; Rickard, A.H. Mini-review: Microbial coaggregation: Ubiquity and implications for biofilm development. *Biofouling* **2014**, *30*, 1235–1251. [[CrossRef](#)] [[PubMed](#)]
- Hu, P.; Xie, Q.; Ma, C.; Zhang, G. Silicone-Based Fouling-Release Coatings for Marine Antifouling. *Langmuir* **2020**, *36*, 2170–2183. [[CrossRef](#)] [[PubMed](#)]
- Qian, P.-Y.; Li, Z.; Xu, Y.; Li, Y.; Fusetani, N. Mini-review: Marine natural products and their synthetic analogs as antifouling compounds: 2009–2014. *Biofouling* **2015**, *31*, 101–122. [[CrossRef](#)] [[PubMed](#)]
- Yang, W.; Lin, P.; Cheng, D.; Zhang, L.; Wu, Y.; Liu, Y.; Pei, X.; Zhou, F. Contribution of Charges in Polyvinyl Alcohol Networks to Marine Antifouling. *ACS Appl. Mater. Inter.* **2017**, *9*, 18295–18304. [[CrossRef](#)]
- Yoshikawa, C.; Takagi, R.; Nakaji-Hirabayashi, T.; Ochi, T.; Kawamura, Y.; Thissen, H. Marine Antifouling Coatings Based on Durable Bottlebrush Polymers. *ACS Appl. Mater. Inter.* **2022**, *14*, 32497–32509. [[CrossRef](#)]
- Wang, X.; Yang, J.; Jiang, X.; Yu, L. Preparation and Properties of Environmentally Friendly Marine Antifouling Coatings Based on a Collaborative Strategy. *Langmuir* **2022**, *38*, 6676–6689. [[CrossRef](#)]
- Jeong, Y.; Kang, S.M. Catechol-conjugated Dextran for Marine Antifouling Applications: The Adverse Effects of High Catechol Content. *B. Korean Chem. Soc.* **2020**, *41*, 1068–1072. [[CrossRef](#)]

8. Evans, S.M. TBT or not TBT? That is the question. *Biofouling* **1999**, *14*, 117–129. [\[CrossRef\]](#)
9. Xie, C.; Guo, H.; Zhao, W.; Zhang, L. Environmentally Friendly Marine Antifouling Coating Based on a Synergistic Strategy. *Langmuir* **2020**, *36*, 2396–2402. [\[CrossRef\]](#)
10. Li, M.; Nan, L.; Zhang, B.; Kong, J.; Wang, Y.; Ba, M. Polyether-thiourea-siloxane copolymer based on H-bonding interaction for marine antifouling. *Molecules* **2023**, *28*, 3574. [\[CrossRef\]](#)
11. Mohd-Ramzi, M.; Rahman, N.I.A.; Rawi, N.N.; Bhubalan, K.; Ariffin, F.; Mazlan, N.W.; Saidin, J.; Danish-Daniel, M.; Siong, J.Y.F.; Bakar, K. Antifouling potential of *Diadema setosum* and *Sonneratia lanceolata* extracts for marine applications. *J. Mar. Sci. Eng.* **2023**, *11*, 602. [\[CrossRef\]](#)
12. Sun, L.; Wang, W.-F.; Li, M.; Zhang, J.; Chai, T.; Cao, W.; Yan, T.; Zhao, X.; Yang, W.; Yu, B.; et al. Natural Product *Zanthoxylum bungeanum* Based Multi-Functionalized Self-Polishing Interface for Sustainable Marine Antifouling. *Adv. Mater. Inter.* **2022**, *9*, 2201195. [\[CrossRef\]](#)
13. Fusetani, N. Antifouling marine natural products. *Nat. Prod. Rep.* **2011**, *28*, 400–410. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Wang, K.-L.; Dou, Z.-R.; Gong, G.-F.; Li, H.-F.; Jiang, B.; Xu, Y. Anti-larval and anti-algal natural products from marine microorganisms as sources of anti-biofilm agents. *Mar. Drugs* **2022**, *20*, 90. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Sedanza, M.G.; Yoshida, A.; Kim, H.-J.; Yamaguchi, K.; Osatomi, K.; Satuito, C.G. Identification and Characterization of the Larval Settlement Pheromone Protein Components in Adult Shells of *Crassostrea gigas*: A Novel Function of Shell Matrix Proteins. *Int. J. Mol. Sci.* **2022**, *23*, 9816. [\[CrossRef\]](#)
16. Umezawa, T.; Oguri, Y.; Matsuura, H.; Yamazaki, S.; Suzuki, M.; Yoshimura, E.; Furuta, T.; Nogata, Y.; Serisawa, Y.; Matsuyama-Serisawa, K.; et al. Omaezallene from Red Alga *Laurencia* sp.: Structure Elucidation, Total Synthesis, and Antifouling Activity. *Angew. Chem. Int. Ed.* **2014**, *53*, 3909–3912. [\[CrossRef\]](#)
17. Kim, D.; Kang, S.M. Red Algae-Derived Carrageenan Coatings for Marine Antifouling Applications. *Biomacromolecules* **2020**, *21*, 5086–5092. [\[CrossRef\]](#)
18. Davis, A.R.; Wright, A.E. Inhibition of larval settlement by natural products from the ascidian, *Eudistoma olivaceum* (Van Name). *J. Chem. Ecol.* **1990**, *16*, 1349–1357. [\[CrossRef\]](#)
19. Gao, C.; Wang, Y.; Chen, Y.; He, B.; Zhang, R.; Xu, M.; Huang, R. Two new avermectin derivatives from the Beibu Gulf Gorgonian *Anthogorgia Caerulea*. *Chem. Biodivers.* **2014**, *11*, 812–818.
20. Majik, M.S.; Rodrigues, C.; Mascarenhas, S.; D'Souza, L. Design and synthesis of marine natural product-based 1H-indole-2,3-dione scaffold as a new antifouling/antibacterial agent against fouling bacteria. *Bioorg. Chem.* **2014**, *54*, 89–95. [\[CrossRef\]](#)
21. Cho, J.Y.; Kang, J.Y.; Hong, Y.K.; Baek, H.H.; Shin, H.W.; Kim, M.S. Isolation and structural determination of the antifouling diketopiperazines from marine-derived *Streptomyces praecox* 291-11. *Biosci. Biotech. Bioch.* **2012**, *76*, 1116–1121. [\[CrossRef\]](#)
22. Nong, X.H.; Zheng, Z.H.; Zhang, X.Y.; Lu, X.H.; Qi, S.H. Polyketides from a marine-derived fungus *Xylariaceae* sp. *Mar. Drugs* **2013**, *11*, 1718–1727. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Lin, P.; Ding, L.; Lin, C.W.; Gu, F. Nonfouling property of zwitterionic cysteine surface. *Langmuir* **2014**, *30*, 6497–6507. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Peng, B.; Wang, J.; Peng, Z.; Zhou, S.; Wang, F.; Ji, Y.; Ye, Z.; Zhou, X.; Lin, T.; Zhang, X. Studies on the synthesis, pungency and anti-biofouling performance of capsaicin analogues. *Sci. China Chem.* **2011**, *55*, 435–442. [\[CrossRef\]](#)
25. Liu, H.; Yang, W.; Zhao, W.; Zhang, J.; Cai, M.; Pei, X.; Zhou, F. Natural product inspired environmentally friendly strategy based on dopamine chemistry toward sustainable marine antifouling. *ACS Omega* **2020**, *5*, 21524–21530. [\[CrossRef\]](#)
26. Zhang, Z.-Q.; Zhang, Y.-H.; Sun, H. The reproductive biology of *Stellera chamaejasme* (Thymelaeaceae): A self-incompatible weed with specialized flowers. *Flora-Morphol. Distrib. Funct. Ecol. Plants* **2011**, *206*, 567–574. [\[CrossRef\]](#)
27. Weijian, F.; Tetsuro, I.; Mitsuzi, Y. The antitumor activities of gnidimacrin isolated from *Stellera chamaejasme* L. *Chin. J. Cancer Res.* **1996**, *8*, 101–104. [\[CrossRef\]](#)
28. Yang, G.; Liao, Z.; Xu, Z.; Zhang, H.; Chen, D. Antimitotic and Antifungal C-3/C-3''-Biflavanones from *Stellera chamaejasme*. *Chem. Pharm. Bull.* **2005**, *36*, 776–779. [\[CrossRef\]](#)
29. Cui, H.; Jin, H.; Liu, Q.; Yan, Z.; Ding, L.; Qin, B. Nematicidal metabolites from roots of *Stellera chamaejasme* against *Bursaphelenchus xylophilus* and *Bursaphelenchus mucronatus*. *Pest. Manag. Sci.* **2014**, *70*, 827–835. [\[CrossRef\]](#)
30. Dehghan, H.; Sarrafi, Y.; Salehi, P.; Nejad-Ebrahimi, S. α -Glucosidase inhibitory and antioxidant activity of furanocoumarins from *Heracleum persicum*. *Med. Chem. Res.* **2017**, *26*, 849–855. [\[CrossRef\]](#)
31. Deng, Z.; Chen, M.; Zhou, S.; You, B.; Wu, L. A novel method for the fabrication of monodisperse hollow silica spheres. *Langmuir* **2006**, *22*, 6403–6407. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Faÿ, F.; Champion, M.; Guennec, A.; Moppert, X.; Simon-Colin, C.; Elie, M. Biobased anti-adhesive marine coatings from polyhydroxyalkanoates and polysaccharides. *Coatings* **2023**, *13*, 766. [\[CrossRef\]](#)
33. Jia, X.; Sheng, W.-B.; Li, W.; Tong, Y.-B.; Liu, Z.-Y.; Zhou, F. Adhesive polydopamine coated avermectin microcapsules for prolonging foliar pesticide retention. *ACS Appl. Mater. Inter.* **2014**, *6*, 19552–19558. [\[CrossRef\]](#) [\[PubMed\]](#)

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