Preparation of a water-based antibacterial ink based on microcapsules

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Abstract. In this paper a water-based antibacterial ink with a proper recipe is obtained where antibacterial microcapsules is prepared by \( \beta \)-cyclodextrin embedding cinnamon essential oil, a waterborne acrylate resin is used as a binder and the ethanol and water are the solvents, and followed that pigments, fillers and various additives are added to prepare water-based antibacterial ink for PE film printing. The viscosity, fineness, gloss, initial drying, water resistance and antibacterial properties of the ink are detected successively, and the influence of the addition of antibacterial microcapsules on the performance of the ink is discussed accordingly. The results show that the water-based antibacterial ink possesses the good physical performances in the following fraction of \( w(\text{waterborne acrylate resin liquid}) = 40\% \), \( w(\text{ethanol}) = 30\% \), \( w(\text{water}) = 10\% \), \( w(\text{carbon black}) = 8\% \), \( w(\text{adjuvant}) = 5\% \), and \( w(\text{antimicrobial microcapsules}) = 7\% \) (all relative to the total amount of ink). As a result, this ink shows a viscosity of 34.5 mPa\( \cdot \)s, a fineness of 15 \( \mu \)m, a glossiness of 85\%, an initial dryness of 15 mm/30 s, a water resistance of 4 grades and an inhibition zone diameter of 22 mm and 14 mm for escherichia coli and penicillium, respectively.

1. Introduction

Recently, "food safety incidents" have occurred frequently, which has not only caused great harm to the health of the public, but has also triggered a crisis of integrity in the society and has become a social focus problem. Ink is an important food packaging material and has been criticized for its large VOC emissions, severe environmental pollution and other problems. Water-based inks are a kind of environment-friendly inks made of water or alcohol as main solvent, water-based resin, pigments, fillers and various additives after being dispersed and ground [1]. Because it does not contain volatile solvents, reducing the pollution discharge to the environment, it has become the recognized environmental protection ink in the current ink industry. Food packaging is exposed to various types of dust and bacteria in the process of storage and transportation, and these factors will affect people's health [2]. If ink can be used not only to print information on objects, but also to inhibit the growth of bacteria, it will certainly bring great benefits to people's lives. Antibacterial ink is a kind of functional ink prepared by adding a substance with bactericidal ability to a given ink formulation, so that the ink has bactericidal capacity under the condition of ensuring the good basic performance.

Nowadays, antibacterial materials are developing rapidly all over the world especially in Japan, the United States, and Germany. However, due to the influence of many factors, the research and application of antibacterial materials started late and developed relatively slowly in China. As
antibacterial ink have broad prospects for development, numerous scientific research institutes, enterprises and colleges at home and abroad have carried out a large amount of research and have made certain progress. Young et al. believed that chitosan with amino positive ions can occur surface adsorption of most negatively charged microorganisms, thus forming a layer of polymer barriers that hinder the normal metabolism of bacteria [3]. Knobloch et al. found that plant essential oil can destroy the membrane of fungi and inhibit their respiration [4]. And Bower et al. demonstrated that diatomite can effectively inhibit the growth of L. monocytogenes after Nisin adsorption [5]. Gutiérrez et al. used cinnamon essential oil as an antibacterial agent and immobilize it on a microporous polypropylene film with a thickness of 30 μm. The shelf life of baked foods was prolonged to 3-10 days [6]. Wang et al. developed the tipping paper antibacterial water-based inks, and use nano-titanium dioxide and sulfa-drugs as antibacterial agents [7]. These results show that the ink had a good inhibitory effect on Escherichia coli and Staphylococcus aureus. Duan et al. used sodium oleate as a modifier to modify the nano-magnesia powder to develop antibacterial ink as an antibacterial agent, and the results show that nano-magnesia modified by sodium oleate can improve its dispersibility and exhibit better antibacterial properties [8]. Yu et al. prepared inorganic metal antimicrobial agents by using Zn2+ and Cu2+ metal ions on zeolites through ion exchange method, which are equipped with antibacterial UV ink and antibacterial water-based inks, respectively, and the results show that the antibacterial rate of antibacterial UV ink against Escherichia coli and Staphylococcus aureus is 99%, and the antibacterial rate of antimicrobial water-based inks is 90% [9].

Although the above studies have achieved certain successes, they still have some disadvantages including the difficult preparation process, a high price, and the harm to environment and so on. Cinnamon essential oil is a kind of natural antibacterial substance derived from cinnamon plants and has the characteristics of low boiling point and easy volatilization. β-cyclodextrin shows a special structure of "external hydrophilicity, internal hydrophobicity" and is non-toxic and environmentally friendly [10]. It can encapsulate a variety of core materials. Therefore, this work adopts β-cyclodextrin embedding technology to prepare the microcapsules of cinnamon essential oil, and followed that a water-based antibacterial inks was prepared, which provides a theoretical guidance for the development of functional inks.

2. Experimental section

2.1 Equipment Materials

For obtaining the water-based antibacterial inks, the following apparatus are employed. And they are JB-CJ-1500FX type clean bench, Suzhou Jiabao Purification Engineering Equipment Co., LTD, HHS type electric constant temperature water bath, Shanghai Boxun Industrial Co., Ltd. medical equipment factory, JY98-IIIDN type ultrasonic cell shredder, Ningbo Xinzhi Biotechnology Corporation, GZX-9246MBE type electric thermostatic blast drying oven, Shanghai Bo Xun Industrial Co., Ltd. Medical Equipment Factory, DZF-6020 type vacuum drying oven, Shanghai Yiheng Technology Co., Ltd., AL204 type electronic balance, METTLER - Toledo Instruments Co., Ltd., ZFS High-speed Disperser, Shanghai Sheng Electromechanical Technology Co., Ltd., DHP-9082 Electric Thermostatic Incubator, Shanghai Yiheng Chemical Instrument Co., Ltd., UV-1800 Ultraviolet Spectrophotometer, Beijing Rayleigh Analysis Instrument Co., Ltd., LC-P20 eccentric disc type sand mill, Dongguan City, Chi Chi Machinery Co., Ltd., QXD scraper fineness meter, Shanghai High Precision Instrument Co., Ltd., LVDV-11+ type viscometer, the United States Brookfield Co., Ltd., QMN60 gloss meter, Tianjin Heli Technology Co., Ltd., and LC-162B refrigerator, Qingdao Haier Group.

Moreover, the raw medicines are listed as follows: β-Cyclodextrin (AR), Sinopharm Group Chemical Reagent Co., Ltd., Cinnamon Essential Oil (CP), Guangzhou Hengxin Spice Co., Ltd., Waterborne Acrylic Emulsion (Industrial Grade, Viscosity: 400-800CPS (NDJ-1, 25°C), Solids content: 45±1%, PH: 8.5±0.5), Dongguan Xinmao Chemical Co., Ltd., Dispersant: Sodium dodecyl sulfate (CP), Guangdong Guanghua Chemical Co., Ltd., Pigment: Carbon black (Industrial Grade), Guangzhou Feiluo Chemical Pigment Co., Ltd., Defoamer: Silicone oil (AR), Guangzhou Oudi Chemical Co., Ltd., Wetting agent: Alkylphenol polyoxyethylene ether (CP), Germany Corning Co., Ltd., Water Ethanol (AR), Ammonia Water (25%), Nanjing Chemical Reagent Co., Ltd., Escherichia
coli, Penicillium, Institute of Light Industry and Food, South China University of Technology, Medium, beef extract, peptone, AR, Beijing Aoboxing Biotechnology Co., Ltd., agar powder (AR), Weida Chemical Co., Ltd., sodium chloride (AR), Guangzhou Donghong Chemical Factory, potato, commercially available, and purified water, homemade.

2.2 Sample preparation

1) Preparation of culture medium [11]. For obtaining an escherichia coli culture medium, the beef extract of 5g, peptone of 10 g, and sodium chloride of 5g in 1000 ml conical flask were add water to 1000 ml while adjusting the pH to from 7.2 to 7.6. Then it was sterilized at 121°C for 30 min. Moreover, PDA medium is prepared in the following process: potato was peeled diced, take 200 g, and 700 ml pure water was added into them and boiling for 30 minutes. Then 15g agar and 20g sucrose were dissolved in water of 1000 ml, and this sample was sterilized at 121°C for 30min and placed in 1000 ml conical flask.

2) Preparation of cinnamon essential oil microcapsules [12]. According to the previous article, 40 g of β-cyclodextrin was dissolved in 100 ml of distilled water and was stirred continuously until a saturated solution of β-cyclodextrin was form. Then 5 ml of cinnamon essential oil was dissolved in 50 ml of anhydrous ethanol to form a mixed solution of cinnamon essential oil and ethanol. Subsequently, the cinnamon essential oil-ethanol mixed solution was dripped into the wall material solution dropwise under the condition of ultrasonic cell disintegrator (1000 r/min). After the reaction was finished, the mixture was kept at 80 °C for 1 hour. After cooling to room temperature, it was placed in a refrigerator and allowed to stand still for 24 hours, vacuum-filtered with a vacuum pump, and the filter residue was washed three times with a small amount of distilled water and anhydrous ethanol. Finally, the product of cinnamon essential oil microcapsules was obtained by drying it to constant weight in an electric heated constant temperature blast drying oven at 50 °C.

3) Preparation of water-based antibacterial inks [13]. According to the reference formula of antibacterial water-based inks (as shown in Table 1), the cinnamon essential oil microcapsules, waterborne acrylate emulsion, pigments, fillers and auxiliaries were weighed and placed in a clean beaker and dispersed for 1 hour with a high-speed disperser under 3000 r/min conditions. Moreover, the water-based antibacterial inks could be obtained by grinding and filtering with a sand mill.

| Table 1. Formulation for antimicrobial water based inks. |
|---------------------------------|---------------------------------|
| Ink components                  | Mass fraction(wt%) |
| Waterborne acrylate             | 40                      |
| Ethanol                         | 30                      |
| Water                           | 10                      |
| Antimicrobial microcapsules     | 7                       |
| Carbon black                    | 8                       |
| Calcium carbonate               | 1                       |
| Silicone oil                    | 2                       |
| Alkylphenol ethoxylates         | 1                       |
| Ammonia water                   | 1                       |

2.3 Performance Test

By referring the standard of China GB/T 13217.4-2008, the liquid ink viscosity was tested. And the GB/T 13217.3-2008 liquid ink fineness test method was also used in fineness testing, GB/T 13217.5 - liquid ink initial drying test method for initial dryness, GB/T 13217.2—2009 color luster method for liquid ink for glossiness, and GB/T 1733-1993 paint film water resistance test for water resistance grade (Grade 1, severely discolored, Grade 2; Obvious discoloration, Grade 3, slightly discolored, Grade 4, Basically not discolored, Grade 5, not discolored, respectively). By taking 0.1ml of cinnamon essential oil capsule antibacterial water-based ink on a circular 7mm diameter white cardboard piece and putting the circular piece of paper on a watch glass coated with bacteria and incubate in a 37°C
incubator for 24 hours, the diameter of the inhibition zone was measured.

3. Results and Discussion

3.1 Effect of Antibacterial Microcapsules on the Comprehensive Performance of Water-based Antibacterial Inks

The basic fraction of the ink remains unchanged. And the different amounts of cinnamon essential oil with various mass fractions (relative to the total amount of ink) of 0, 1%, 3%, 5%, 7%, and 9% were added to the aqueous ink, respectively. Then the water-based antibacterial ink was prepared. And the relative performances of the ink was presented in Table 2.

According to Table 2, the viscosity, fineness and incipient dryness of the ink increase continuously as the increases of the amount of antibacterial microcapsules. However, the gloss and water resistance have the reverse trend. The reason is that the antibacterial microcapsules are cinnamon essential oil embedded with β-cyclodextrin, and it will become the solid powder which results in the increase the viscosity of the ink. The fineness of the microcapsules prepared by the experiment is larger than the fineness of the ink, leading to the increase of overall fineness of the ink. Moreover, the cinnamon oil will release slowly over time, and it will cause tiny voids on the surface of the ink layer. These changes will reduce the reflection of light as well as the glossiness. At the same time, the volatilization of the cinnamon essential oil provides the conditions for ink drying and lead to an increase of the initial dryness. Moreover, β-Cyclodextrin is easily soluble in water, which may cause the phenomenon that the water resistance of the ink reduces constantly as increases of the adding amount.

| Antibacterial microcapsules added amount/% | Viscosity /mPa·s | Fineness /μm | Glossiness /% | initial drying/mm/30s | water resistance |
|-----------------------------------------|------------------|-------------|--------------|------------------------|----------------|
| 0                                       | 26.2             | 5           | 95           | 8                      | 5              |
| 1                                       | 27.5             | 8           | 93           | 10                     | 5              |
| 3                                       | 28.9             | 10          | 90           | 12                     | 4              |
| 5                                       | 31.6             | 12          | 86           | 14                     | 4              |
| 7                                       | 34.5             | 15          | 85           | 15                     | 4              |
| 9                                       | 38               | 20          | 80           | 16                     | 3              |

3.2 Effect of Antimicrobial Microcapsules Addition on Antibacterial Performance of Water-based Ink

The effect of the addition of cinnamon essential oil microcapsules on the antibacterial properties of water-based inks was shown in Figure 1.

![Figure 1](image-url)
Apparently, the diameter of the inhibition zone of antimicrobial water-based ink against Escherichia coli and Penicillium is gradually increased with the addition of cinnamon essential oil microcapsules. When the added amount of cinnamon essential oil microcapsules is less than 3%, the diameter of the inhibition zone grows slowly. And when it exceeds to 3%, the increases of the diameter of the inhibition zone show almost linear. Figure 1 also shows that the high amount of cinnamon essential oil microcapsules has good antibacterial effect. In addition, the antimicrobial effect of cinnamon essential oil microcapsules on Escherichia coli is stronger than that of Penicillium, which may be due to the fact that Escherichia coli belongs to bacteria while Penicillium is fungi, and the composition of bacteria has a slightly different from that of fungi. It also shows that cinnamon essential oil has a strong ability to kill bacteria. As is known, when the diameter of the inhibition zone is greater than 10 mm, the bacteriostatic effect is effective. Therefore, the optimum amount of cinnamon essential oil microcapsules can be determined as 7%.

3.3 Antibacterial Detection of Water-based Antibacterial Ink

By referring the antibacterial detection method, the diameter of the inhibition zone was measured with a dosage of 7% of the antibacterial microcapsules. And the results are shown in Figure 2.

![Antibacterial effect of water-based antibacterial ink on Escherichia coli and Penicillium](image)

**Figure 2.** Antibacterial effect of water-based antibacterial ink on Escherichia coli and Penicillium.

As shown in Figure 2, when the added amount of antibacterial microcapsules is 7%, the water-based antibacterial ink have significant antibacterial effect on both Escherichia coli and Penicillium. After the determination, the diameter of the inhibition zone of the water-based antibacterial ink against Escherichia coli was 22 mm, and the diameter of the inhibition zone of Penicillium is 14 mm, which satisfies the requirement of antibacterial property.

4. Conclusion

The antimicrobial microcapsules and the relative water-based ink were prepared by β-cyclodextrin embedding technology with a series of auxiliaries including aqueous acrylic resin, ethanol, water, pigments, fillers and et al. The viscosity, fineness, gloss, initial dryness, water resistance and antimicrobial properties of ink were tested, which shows that when the ink contains the following reagents of w (aqueous acrylic resin solution) = 40%, m (ethanol): m (water) = 30:10, w (carbon black) = 8%, w (adjuvant) = 5%, and w (antibacterial microcapsule) = 7% (all relative to the total amount of ink), it shows a favorable water-based ability. Moreover, the ink has the proper physical performances including a viscosity of 34.5 mPa·s, a fineness of 15 μm, a gloss of 85%, an initial dryness of 15 mm/30 s, a water resistance of 4 grades and an inhibition zone diameter of 22 mm and 14 mm for Escherichia coli and Penicillium, respectively. Generally, by adding antibacterial substances into the pulp, the antibacterial properties of the ink are obtained, and the water-based antibacterial ink is
developed in combination with the environmental characteristics of the water-based ink. This work will enhance the application value of water-based ink in food packaging and increases the additional value of the ink printing.

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