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Simultaneous aqueous two-phase flotation of sodium chlorophyllin and removal of sugars from saponified solution of bamboo leaves

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ABSTRACT

An ethanol–tripotassium phosphate aqueous two-phase flotation (ATPF) system was first time studied for the separation of sodium chlorophyllin and sugars. The single factors influencing the recovery of sodium chlorophyllin in the top phase and removal of sugars in the bottom phase were investigated and optimized by response surface methodology (RSM). The maximum recovery percentage (88.28%) of sodium chlorophyllin were obtained at 0.55 g/mL of tripotassium phosphate, 25 mL/min of nitrogen flow rate, 26 min of flotation time and 5 mL of ethanol, meanwhile, the removal percentage of sugars reached 95.84%. Compared with aqueous two-phase extraction (ATPE), ATPF showed advantages of low consumption of organic solvent, high enrichment factors, and high separation effect. Sodium chlorophyllin were demonstrated theoretically and experimentally to have surfactivity. Finally, the scale-up experiments were conducted to further prepare sodium copper chlorophyllin, and the absorbance ratio ($A_{406.00\,nm}/A_{631.00\,nm}$) was 3.49. This method may blaze the trail for mass production of sodium copper chlorophyllin in industry.

1. Introduction

Chlorophyll, as a green pigment in nature, extensively exists in plants, algae and some bacteria. Belonging to porphyrins, chlorophyll (as shown in Fig. 1a) consists of a porphyrin ring and a long phytol chain [1]. Chlorophyll is so structurally unstable that acid, alkali, light, heat, oxygen, and enzymes are liable to degrade it [2,3]. The magnesium ion of the chlorophyll molecule can be easily replaced by hydrogen ion and metal ions (such as copper ion, zinc ion, ferric ion, etc.) during extraction and processing. Not only the weak stability but also the water-insoluble property of chlorophyll imposes some restrictions on its application. Sodium copper chlorophyllin (as shown in Fig. 1d and e) is a synthetic derivative of chlorophyll, possessing two types: disodium copper chlorophyllin and trisodium copper chlorophyllin. Compared with chlorophyll, water-soluble sodium copper chlorophyllin is more stable and more resistant to acid, light, heat and so on. With the advantages of sodium copper chlorophyllin, it is widely employed in the fields of food, medicine and cosmetic as a colorant or additive [4], which embodies its tremendous value and causes an increasing demand worldwide. Therefore, excogitating a suitable synthetic method of sodium copper chlorophyllin has been brought into focus.

Traditional technologies that sodium copper chlorophyllin was prepared through the successive steps of extraction, saponification, acidification, copper replacement, and salt formation had the defects of excessive organic solvent consumption and complex process. In addition, fat-soluble and water-soluble impurities was extracted together with target products, which resulted in the poor quality of sodium copper chlorophyllin. In view of this, our previous study has reported the simultaneous aqueous two-phase extraction (ATPE) and saponification reaction of chlorophyll from silkworm excrement [5]. Then, the sodium chlorophyllin was used to further produce sodium copper chlorophyllin. This method was vastly superior to the conventional methods in terms of simplifying operation steps and avoiding amounts of organic solvent. However, the consumption of ethanol was still relatively high, which violated the principle of saving reagents and caused the low enrichment coefficient of the sodium chlorophyllin. Besides, the removal percentage of water-soluble impurities (such as sugars) produced during extraction was not high [6] by one-step process using an aqueous two-phase system (ATPS). As a result, both the residues of fat-soluble and water-soluble impurities from silkworm excrement and the low enrichment coefficient of sodium chlorophyllin made it difficult to refine sodium copper

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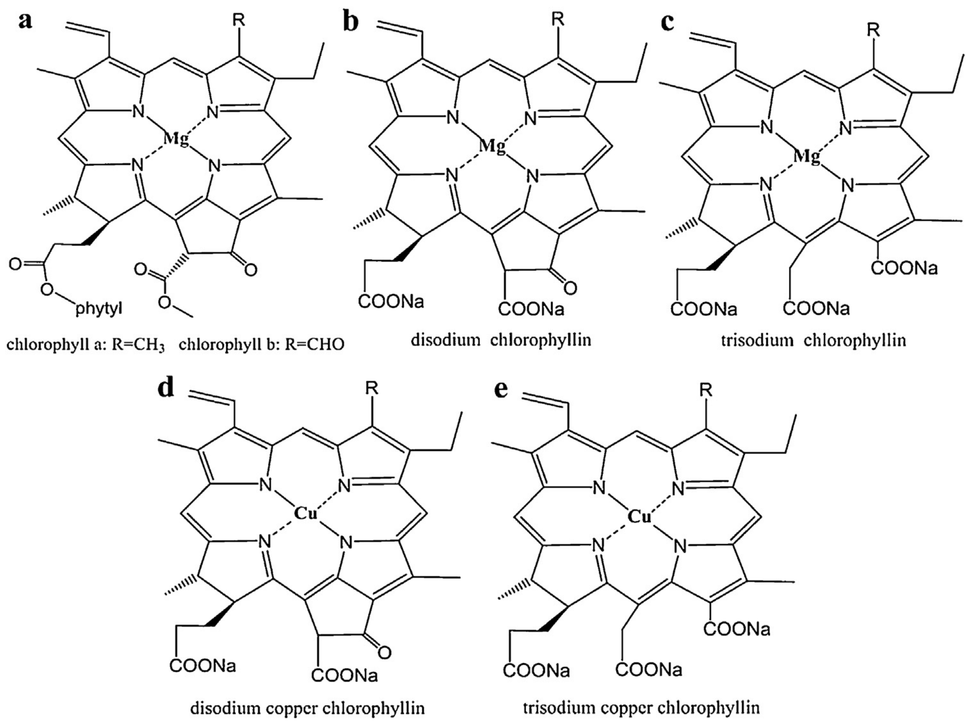

Fig. 1. Structure of chlorophyll (a), sodium chlorophyllin (b,c) and Sodium copper chlorophyllin (d,e).

chlorophyllin. Therefore, the approaches of synthesizing sodium copper chlorophyllin need improving.

Aqueous two-phase flotation (ATPF) which is an integration of solvent sublation (SS) and ATPE is a significant preconcentration and separation technique. There are three main kinds of ATPF: hydrophilic organic solvent/salt ATPF [7], polymer/salt ATPF [8,9], and ionic liquid/salt ATPF [10]. Because SS and ATPE are complementary to each other and comprise the benefits from both methods, ATPF contains many advantages, including high separation efficiency and enrichment coefficient, soft condition, simple operation, and reduced dosage of organic solvents. Due to these superiorities, various ATPF systems have been successfully applied to deal with surface-active compounds in bioseparation and bioengineering, for example lipase [7], penicillin G [11], baicalin [8], chloramphenicol [12], etc. However, only the small molecule alcohol/salt ATPF can overcome the limitations of both high cost and hard recycling of phase components in the recovery of target products. Bamboo leaves are rich in chlorophyll and have plentiful resources and low cost. Furthermore, less lipid and waxiness in bamboo leaves can benefit the preparation of sodium copper chlorophyllin. Herein, ethanol/tripotassium phosphate ATPF of sodium chlorophyllin from the saponified solution of bamboo leaves was investigated.

Thus far, there is no literature concerning the simultaneous ATPF of target product and removal of impurities in one system. Moreover, this is the first paper to demonstrate the surfactivity of target compound by experiment. In this work, sodium chlorophyllin in the aqueous phase was absorbed on the gas bubble surfaces of an rising gas stream floating to the top of the aqueous phase, and then dissolved in the ethanol phase after bubbles ruptured, while impurity sugars tended to gather in the aqueous phase (Fig. 2). The mechanism of the ATPF was studied not only theoretically but also experimentally. Several variables, namely type and concentration of inorganic salt, flotation time, gas flow rate, and volume of ethanol affecting the recovery of the sodium chlorophyllin and removal of the total sugars were discussed and further optimized using RSM [13]. The kinetic process of the sodium chlorophyllin in ATPF was analyzed. The results obtained by ATPF were in comparison to that of ATPE under the optimal conditions. Furthermore, the salt and ethanol were recycled in the purpose of establishing a sustainable ATPF. Finally, the scale-up experiment was attempted to yield sodium copper chlorophyllin.

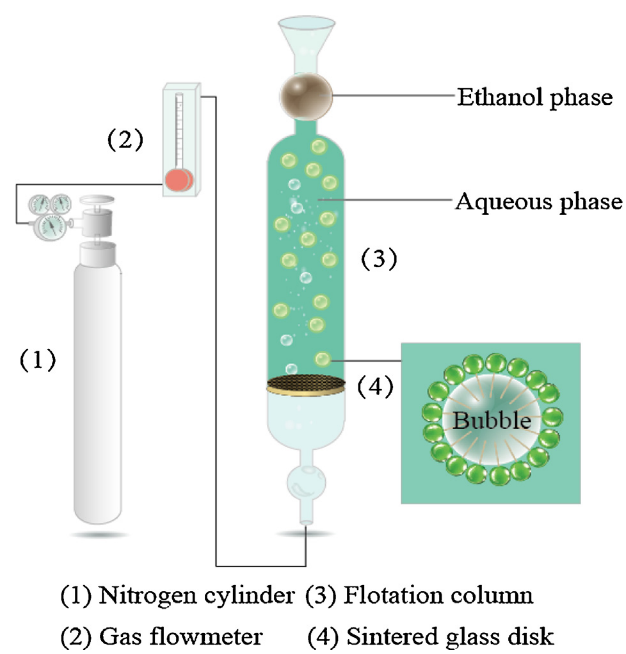

Fig. 2. ATPF apparatus.