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Article

Removal of Ionic Liquid (IL) from Herbal Materials After Extraction with IL and Comprehensive Investigation

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Abstract

At present, ionic liquids (ILs) are increasingly being used to extract natural products as green solvents, but their residues can lead to risks in terms of further use for the extracted herbal materials. Therefore, it is necessary to remove them with simple and effective methods. For example, after the toxic anthraquinones in *Polygonum multiflorum* are removed by extraction with the IL of [C_4Bim][PTSA], it needs to be recovered and reused, and the useful stilbene glycosides should not suffer from obvious loss as they are the main functional components. In this study, an ultrasonic method with *n*-propanol was used to remove the residual [C_4Bim][PTSA] in the solid powders of *Polygonum multiflorum* that had been extracted for anthraquinones. After single-factor optimization, the removal conditions were as follows: the removal temperature was 303.15 K, the solid–liquid ratio was 1:200 (w (1 g):v (200 mL)), the ultrasonic time was 40 min, and there were four operations. Under these conditions, ILs could be completely removed with almost no loss of stilbene glycosides in solid powders. After that, the IL in the extracting solution and scrubbing solution was recovered by the back-extraction method, and an IL with high purity could be obtained for reuse. The total recovery efficiency of the IL reached more than 98%. Then gas chromatography (GC) was conducted for the determination of residual ethanol and *n*-propanol in the solid powders of *Polygonum multiflorum*, which could be used to quickly detect the contents of two organic solvents within three minutes. Besides that, the method could also be applied to the determination of residual organic solvents in the raw materials of *Polygonum multiflorum*, and the results showed that the residue of ethanol and *n*-propanol in the solid powders were in accordance with the general provisions of the current *Chinese Pharmacopoeia*. According to the developed procedures and optimized conditions, the recovered IL could be reused in five runs at least. General applicability and greenness assessment for the developed process also proved that it is an ideal method, which has potential in large-scale application.

Keywords: ionic liquids; extraction; recovery; residue solvents; herbal materials; GC analysis

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1. Introduction

In recent years, ionic liquids (ILs) have increasingly been used to extract natural products as green solvents. However, the potential risks associated with their residues have not been adequately addressed in many studies [1]. Since the special properties of ILs are considered to offer many advantages over traditional organic solvents, their synthesis requires the use of volatile organic reagents, resulting in relatively high usage costs [2]. Meanwhile, if ILs are directly discharged without appropriate treatment after

application, a certain degree of environmental impact may be caused, thereby posing threats to the growth of natural organisms. Therefore, the recycling and reuse of ILs are considered essential not only for improving economic efficiency but also for reducing potential risks, thereby allowing ILs to be recognized as truly "green solvents" after water and supercritical carbon dioxide [3,4]. Generally, the recovery of ILs is an important factor affecting their industrial applications, so many researchers attach great importance to the research of IL recovery [5–7]. For example, a new method for recovering ILs based on a CO_2-induced two-phase system was proposed by Xiong et al., achieving a single recovery rate exceeding 99% [8]. Scurto's research group successfully recovered hydrophobic ILs by using supercritical CO_2 as the extraction solvent to recover imidazolium salts from aqueous solutions [9]. In addition, Yang et al. first used a polydimethylsiloxane (PDMS) membrane to recover ILs dissolved in methanol, and the results showed that the membrane separation method could effectively separate ILs from organic solvents [10]. During the synthesis of ILs, multiple chemical reagents are often required; therefore, the recycling and reuse of ILs are regarded as more economical and consistent with the expectations of both academia and industry for green solvents.

An increasing number of studies have indicated that the hepatorenal toxicity of *Polygonum multiflorum* can be largely attributed to the anthraquinone components contained in the herbal materials [11]; for instance, Yang et al. used resonance light scattering technology to evaluate the interaction between three anthraquinones and DNA and explored their potential toxicity mechanisms. The results indicated that these compounds were capable of intercalating into DNA and were demonstrated to exhibit distinct DNA toxicity [12]. Meanwhile, other chemical constituents in *Polygonum multiflorum* have been demonstrated to exhibit no significant toxic side effects, particularly stilbene glycosides, which are regarded as the major valuable components responsible for its pharmacological activity [13]. Therefore, if the anthraquinones contained in the raw material powders can be removed while stilbene glycosides are maximally retained, the medicinal risk associated with *Polygonum multiflorum* could be significantly reduced. In our previous work, the feasibility of achieving this goal through the use of an IL-based extraction method was investigated [14]. However, the applied IL also needs to be separated and recovered from residual medicinal materials to avoid introducing new solvent residues when removing toxic components. In existing research, residual ILs have not been adequately addressed, which greatly affects the practical application of related research in large-scale production [15].

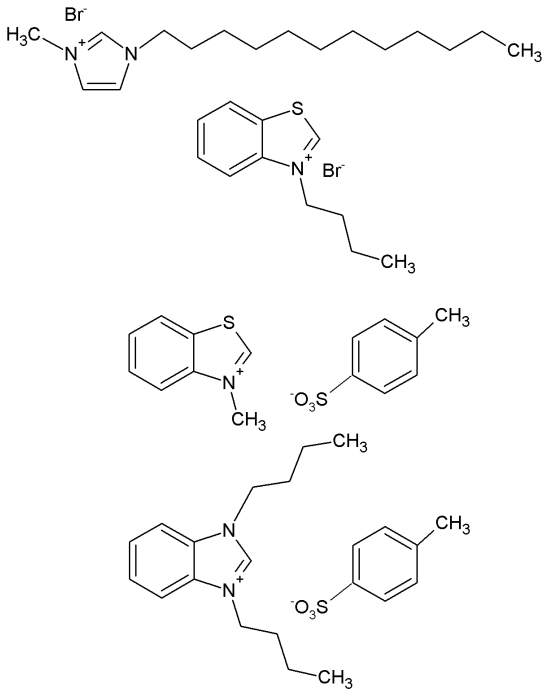
In order to ensure medication safety and drug quality, the General Principles section of the *Chinese Pharmacopoeia* provides clear regulations on residual solvents and their corresponding limits in drugs and raw materials. Therefore, many researchers are committed to establishing efficient, feasible, and systematic analytical methods for detecting residual organic solvents in active pharmaceutical ingredients. Lu and others developed a highly sensitive gas chromatography (GC) detection method for determining the residual amount of organic solvents in the raw material of the total glucosides of peony, in order to achieve the effective control of residual solvents in the raw material [16]. Zhang et al. established a systematic headspace gas chromatography (HS-GC) method to simultaneously determine the residual organic solvents in the total flavonoid extract [17]. The results showed that the method has high reliability and good sensitivity [18]. In addition, taxol was analyzed by Yang's group as an anticancer drug, and they successfully established an HS-GC-based detection method that met the predetermined analytical requirements for determining residual organic solvents in its raw materials, thereby ensuring clinical safety [19]. Another previous study reported the selective separation of anthraquinone components from *Polygonum multiflorum* with IL [20]. Therefore, in order to ensure the medication safety of *Polygonum multiflorum* powders, it is necessary to determine the content of residual solvents in solid powders.

Due to the porous nature and relatively large specific surface area of herbal raw materials, they are also very prone to absorbing IL, which can cause losses; moreover, if medicinal herbs need to be further utilized after extracted by IL, the residual IL on them will also pose certain risks and a potential safety hazard. At present, a large amount of research is almost entirely focused on the development and applications of ILs, and the effective removal of ILs from herbal materials has received little attention. Therefore, it is necessary to explore related avenues for possible large-scale application. Under these backgrounds, a comprehensive investigation was carried out on recovering the IL of 1,3-dibutyl benzimidazole *p*-toluene sulfonate ([C_4Bim][PTSA]) using *n*-propanol to achieve its reuse. At the same time, residual IL in solid powders was removed, and a detection method for ethanol and *n*-propanol residues in *Polygonum multiflorum* powders was established. This not only further ensures the safety of herbal medication but also provides a reference for the recovery of other ILs and the detection of organic solvent residues in natural medicine powders. This is also an important study in terms of the articles published in the Special Issue of "Green separation and purification technology"(https://www.mdpi.com/journal/separations/special_issues/QBT289Y51W), which focuses on the applications of green solvents more than their separation and treatment.

2. Materials and Methods

2.1. Reagents and Materials

Ethanol, phosphoric acid, *n*-propanol, isopropanol, and ethyl acetate were all purchased from Kelong chemical factory (Chengdu, China). Acetonitrile was purchased from Titan Technology Co., Ltd. (Shanghai, China). Ultrapure (UP) water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). 1-Dodecyl-3-methylimidazolium bromide ([C_{12}mim][Br]) was purchased from Aladdin Chemical Reagent Company (Shanghai, China). Benzothiazolium ILs ([BBth][Br] and [HBth][PTSA]) and [C_4Bim][PTSA] were self-synthesized according to the methods in the literature [14]. All the IL structures can be found in Scheme 1.



Scheme 1. All the involved ILs and their structures (from top to bottom: [C_{12}mim][Br], [BBth][Br], [HBth][PTSA] and [C_4Bim][PTSA]).

2.2. Instruments

A JSM-7001F scanning electron microscope (SEM) from JEOL Co., Ltd. (Tokyo, Japan) was applied to observe the raw material. A DF-101S oil bath pot was procured from Yinyu-yuhua Instrument Co., Ltd. (Gongyi, China). AnFA2004B electronic balance was sourced from Tianmei Balance Instrument Co., Ltd. (Shanghai, China). The SHZ-D (III) circulation vacuum pump used was from Dufu Instrument Factory (Zhengzhou, China). The RE-2000 rotary evaporator used was from Yarong Biochemical Instrument Factory (Shanghai, China). The 85-2 magnetic stirrer used was from Sile Instrument Factory (Shanghai, China).The AOE 380 UV-Vis Spectrometer used was from Aoyi Instrument Co., Ltd. (Shanghai, China). The YM-031S ultrasonic cleaner used was from Fangao Microelectronics Co., Ltd. (Shenzhen, China). The TDZ6-WS centrifuge used was from Hunan Hesi Instrument and Equipment Co., Ltd. (Changsha, China). The EC2006 high-performance liquid chromatography (HPLC) system used was obtained from Dalian Elite Co., Ltd. (Dalian, China). The GC7900 gas chromatography (GC) system used was obtained from Shanghai Tianmei Scientific Instrument Co., Ltd. (Shanghai, China).

2.3. Extraction of Toxic Anthraquinones in Polygonum Multiflorum by Using [C_4Bim][PTSA]

The herbal raw material used was obtained from a local drug store, which was identified by Prof. Yanfang Li in the department of pharmaceutical and biological engineering, Sichuan University. After cleaned using water and dried, the raw material was ground and sieved to obtain 60-mesh powders, which were extracted with 0.6 mol/L [C_4Bim][PTSA] aqueous solution (pH = 7) under the following conditions: solid–liquid ratio of 1:60 (w (1 g):v (200 mL)), 40 °C, 60 min. After extraction, herbal powders were collected by filtration and high centrifugation (500 rpm) for further treatment.

2.4. Development of Analytical Conditions for IL Analysis

The concentration of the IL was determined using HPLC [21]. Initially, the ultraviolet absorption wavelength of [C_4Bim][PTSA] was identified. [C_4Bim][PTSA] was dissolved in methanol and subjected to a full-wavelength scan from 200 to 550 nm using a UV-Vis spectrophotometer. Prominent absorption peaks were observed at 220 nm and 260 nm. Based on these observations, 264 nm was chosen as the optimal detection wavelength. HPLC analysis was performed using a Welchrom-C_{18} column (250 mm × 4.6 mm, 5 μm) maintained at 30 °C. The mobile phase consisted of a mixture of acetonitrile and 0.1% aqueous phosphoric acid solution. The flow rate was set at 1.0 mL/min. A calibration curve was constructed using the external standard method. The regression equation of the calibration curve was obtained as $y = 8668.9242x + 151.9885$, with a correlation coefficient (R^2) of 0.9996, indicating excellent linearity.

A methodological validation of the HPLC method was performed [14]. The calibration curve exhibited a linear range from 32.16 to 482.4 mg/L. A repeatability assay showed a relative standard deviation (RSD) of 2.39% for the IL peak area (n = 6). Stability testing after 16 h of storage yielded an RSD of 2.46% for peak area measurements. The recovery of the HPLC method ranged from 98.1% to 103.0%. The method demonstrated a limit of detection (LOD) of 0.019 mg/L and a limit of quantification (LOQ) of 0.061 mg/L. Overall, the HPLC method applied in this study exhibited good reliability and was suitable for the quantitative determination of IL in samples.

2.5. Method for Recovery of IL

The recycling of IL is essential, as it mitigates potential environmental pollution risks and reduces economic costs [22]. The recovery of IL was performed after the extraction process, where centrifugation yielded the extract and the corresponding solid residue.

Ethanol was added to the solid residue at a ratio of 1:50 (*w*/*v*), followed by shaking at 25 °C for 30 min and centrifugation, resulting in the separation of a removal solution and the solid fraction. Subsequently, the solid residue was washed with deionized water at a ratio of 1:100 g/mL, producing the filtrate. The extract and removal solution were combined and evaporated under reduced pressure to produce a yellow-brown solid, whereas the drying of the filtrate yielded a comparable yellow-brown solid. The mixed yellow-brown solid was dissolved in *n*-propanol, and the resulting filtrate was rotary-evaporated to yield crude IL. Finally, the crude IL was purified by washing it with ethyl acetate to afford white solid powders, which was further recrystallized in propanol to obtain a purified sample of the recovered IL. For clarity, a technical flowchart of this study is presented in Figure 1.

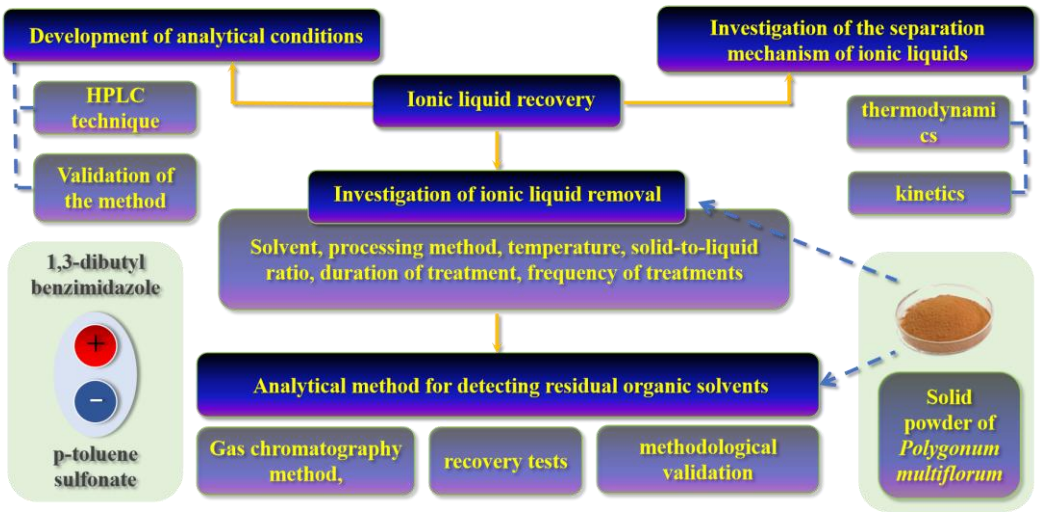


Figure 1. Technical roadmap of whole process.

The treatment method applied to the solid residue determined the final residual content of IL. A higher removal efficiency resulted in the improved safety of the remaining solid product and enhanced recovery of the IL. The separation efficiency of the IL was optimized by systematically evaluating various parameters, including removal solvents (water, anhydrous ethanol, *n*-propanol), removal methods (ultrasonication, mechanical stirring), removal temperature, the solid–liquid ratio, removal duration, and the number of removal cycles.

2.6. Kinetic and Thermodynamic Investigation of IL Removal

To obtain a deeper understanding of the removal process of ILs from *Polygonum multiflorum* solid residues, both kinetic and thermodynamic investigations were conducted [23,24]. These studies enabled the assessment of the spontaneity and feasibility of IL removal, thereby offering a theoretical foundation for the potential scale-up of this process. For kinetic experiments [25], 0.10 g of dried solid powders was dispersed in *n*-propanol at a solid–liquid ratio of 1:200 (w (1 g):v (200 mL)). Following ultrasonic treatment, the suspension was maintained at a controlled temperature. Aliquots were collected every 5 min, filtered through syringe filters, and analyzed by HPLC to quantify the ionic liquid concentration in the removal medium. The thermodynamic analysis followed a similar procedure [26], with the modification that sampling was conducted at different temperatures rather than fixed time intervals, thereby enabling the evaluation of the temperature dependence of ionic liquid removal.

2.7. Development of Analytical Method for Detecting Residual Organic Solvents in Solid Powders

Residual organic solvents in *Polygonum multiflorum* powder can present safety risks; therefore, ensuring that their concentrations fall within acceptable safety limits is essential. Gas chromatography (GC) was employed to quantify residual organic solvents [27]. Throughout extraction and purification, the solid residue primarily came into contact with ethanol and *n*-propanol. Analysis was performed under the following GC conditions: HP-5 capillary column (30 m × 0.32 mm i.d., 1.0 μm film), injector temperature 220 °C, column oven temperature 100 °C, FID temperature 250 °C, split ratio 1:200, and carrier gas nitrogen at a flow rate of 36 mL min^{-1}.

A methodological validation of the GC procedure was performed to confirm its robustness, stability, and suitability for quantitative analysis [28]. For repeatability evaluation, 10 μL of a reference mixture containing ethanol and *n*-propanol was subjected to GC analysis, with the peak areas of the two solvents recorded. Six replicate measurements were performed, and the RSDs of the peak areas were determined. In the recovery experiment, an accurately weighed powder sample was refluxed with 50 mL of water for 4 h, and the resulting distillate was collected as the test solution. Nine aliquots of 2 mL test solution were divided into three groups, each spiked with standard solutions at different concentrations. After homogenization, GC analysis was conducted, and recoveries were calculated. The limits of detection (LOD) and quantification (LOQ) were determined following the guidelines of the *Chinese Pharmacopoeia* (2020 edition) [29]. At last, the on-line free tools of Complexity-Greenness Analysis and Process Index(ComplexGAPI, https://bit.ly/ComplexMoGAPI, accessed on 1 September 2025) and Analytical Greenness Evaluation (AGREE, https://mostwiedzy.pl/AGREE, accessed on 1 September 2025) were used to evaluate the developed method.

3. Results and Discussion

3.1. Analysis of Residual Raw Material and Extract After Extraction

Before extraction with IL, the particle size of sample powders was controlled by stainless steel sieves with a 60-mesh size. After extraction, the average specific surface area was determined to be 0.0568 $m^2 \cdot g^{-1}$ through nitrogen gas adsorption measurement. The scanning electron microscopy (SEM) results of *Polygonum multiflorum* powders before and after extraction are shown in Figure 2. By comparison, it can be found that the solid powders after extraction are different in morphology from the original powders, and there is a certain degree of difference between the two. Before extraction, the powders of the raw material have a soft texture, and the particle size after sieving is uniform. From the SEM image magnified 3000 times, it can be seen that the surface of the raw material powders is relatively smooth. After ultrasound-assisted IL–ethanol solution extraction, the solid powders obtained darkened in color and aggregated into larger particles. After sieving, the surface structure of solid powders showed a loose and rough state. Moreover, the extract contained 87.9% anthraquinones, and their extraction efficiency reached 97.7% according to the reported quantitative method [14]. These results indicated that the removal of toxic anthraquinones had been basically achieved, and after extraction, the solid residue contained the IL extractant of $[C_4Bim][PTSA]$ and useful components including stilbene glycosides.

According to the SEM image magnified 3000 times, it can be found that there are still many pores and wrinkles on the surface of the extracted solid powders. This indicates that during the extraction process, the cell wall of the raw material was greatly damaged due to the penetration of the IL–ethanol solution and the ultrasonic cavitation effect. Consistent with the results reported by Koel Saha et al. [30], the treatment of sugarcane bagasse with ionic liquids disrupted cellular bonds, leading to surface cracking and the depolymerization of amorphous lignin and hemicellulose in the outer layer, which resulted in the formation

of aggregates and irregular textures. Therefore, it can be beneficial to increase the contact probability and contact area between the extractant and the target components, thereby improving the extraction efficiency of the latter. At the same time, this also provides a space for the residual extraction solvents to be accommodated, which poses certain difficulties for subsequent separation and post-treatment.

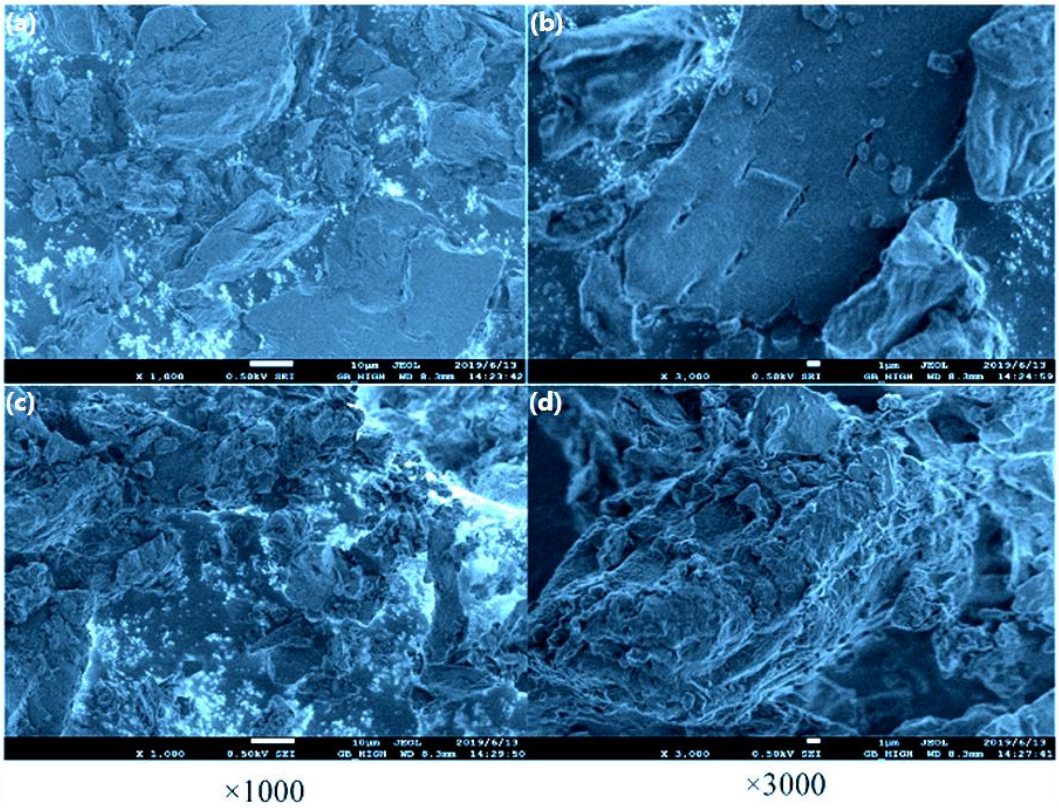


Figure 2. SEM images of raw material powders before (**a**,**b**) and after (**c**,**d**) extraction (an accelerating voltage of 0.5 kV was applied, with magnifications set at 1000× and 3000×).

3.2. Screening of Removal Solvent for IL

The key objective of this study is to recover the residual IL in the raw material powders while retaining stilbene glycoside as much as possible in the solid residue, in order to reduce the IL's impact on the further utilization of medicinal materials. Therefore, choosing the appropriate solvent is crucial for the removal of IL. The selection of a suitable solvent for IL removal is crucial to minimizing the loss of valuable stilbene glycosides. Comparable approaches have been reported for separating ILs from other natural products, for example, the use of aqueous systems to separate ILs from isoflavones [31]. Following this rationale, three solvents—water, ethanol, and *n*-propanol—were screened based on their distinct solubilities toward ILs and the target glycosides. As shown in Figure 3a, within the monitored time range, a conical flask was placed in a constant-temperature water bath for 12 h to allow the IL to naturally dissolve. From the perspective of dissolving the IL, the results indicate that water can have the best removal effect among the three selected solvents, with an IL removal rate of over 80%; although using *n*-propanol for removal has the worst removal effect compared to water and ethanol, its removal rate can still reach around 70%.

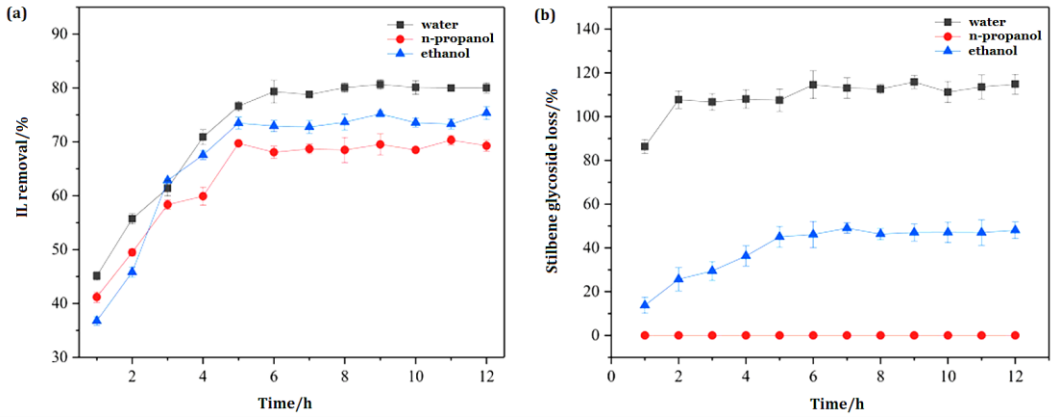


Figure 3. Three solvents(water, *n*-propanol, ethanol) for the dissolving of (**a**) IL and (**b**) stilbene glycoside.

Considering the loss of stilbene glycoside during the removal of IL (Figure 3b), it is found that the loss rate of stilbene glycoside is higher than 110% when water was used as the removal agent; the loss rate of stilbene glycoside using ethanol as a removal agent was nearly 48%. However, when *n*-propanol was used as the solvent for IL removal, the presence of stilbene glycoside in the solvent was not detected by HPLC, indicating no loss of stilbene glycoside in the solid powder. When using *n*-propanol as the solvent for the IL solution instead of ethanol, the extractant was unable to extract anthraquinone components and stilbene, indicating that the solubility of stilbene glycoside in *n*-propanol is very low. From the perspective of "similar solubility", this should be related to the polarity difference between stilbene glycoside and *n*-propanol. Therefore, considering the acceptable recovery rate of IL and the loss of the useful component of stilbene glycoside, *n*-propanol is a more reasonable solvent for the removal of IL.

3.3. Screening of Removal Methods for IL

In this section, ultrasound and stirring are compared in terms of their use to remove residual IL from residual powders [32]. In this experiment, no stilbene glycoside was detected in the *n*-propanol obtained after five removal cycles, so it can be considered that stilbene glycoside was not lost in either removal method considered in this study. Here, only the removal rate of IL was used as an indicator for screening removal methods. As shown in Figure 4a, it is evident that the ultrasonic removal of IL is much faster than stirring. After five cycles of removal, ultrasound can achieve a cumulative removal rate of over 80% for the IL; after being removed five times by stirring, the cumulative removal rate of the IL is near 75%. Moreover, stilbene glycoside was not detected in the removal solution of either experimental group. As mentioned earlier, the cavitation effect of ultrasound can increase the degree of damage to plant cells, thereby improving the extraction rate of target compounds [30]. Here, the use of ultrasound removal can also promote the mass transfer process of IL from solid powders to the removal solvent, thereby accelerating its removal rate. As reported in previous studies, extraction methods show significant advantages in isolating and separating ILs, while ultrasonic assistance further enhances the efficiency of this process [33].

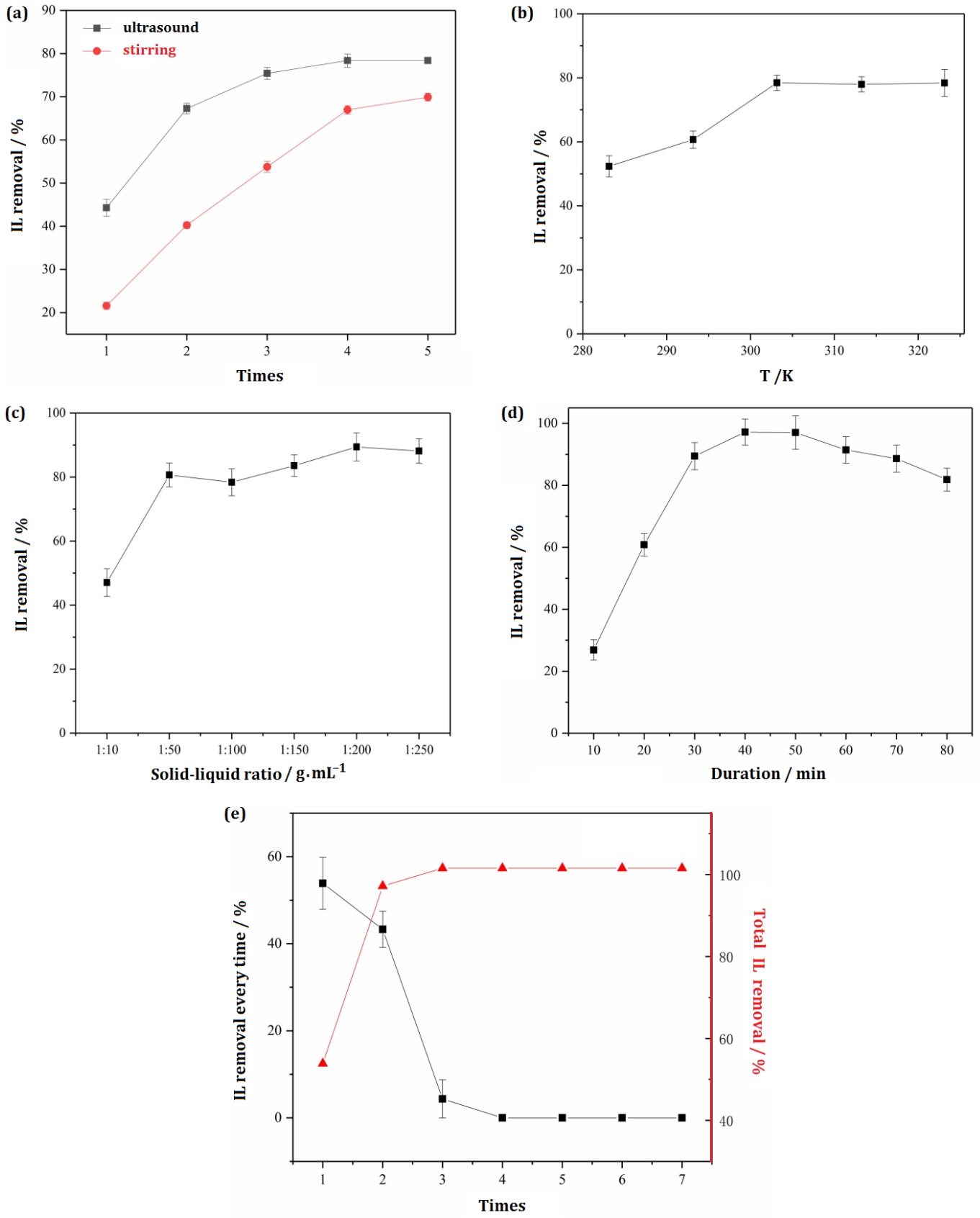


Figure 4. Influence of various (**a**) removal modes, (**b**) temperatures, (**c**) solid-to-liquid ratios, (**d**) treatment durations, and (**e**) operation times on separation efficiency of IL.

3.4. Selection of Removal Temperature and Solid–Liquid Ratio

The appropriate removal temperature can promote the complete diffusion of IL into *n*-propanol by reducing the viscosity of *n*-propanol, increasing the contact area and probability between *n*-propanol and IL. During the experiment, no stilbene glycoside was detected in the *n*-propanol removal solution after removing the IL at different temperatures, indicating no loss of stilbene glycoside. Here, only the cumulative removal rate of IL is used as an indicator for screening removal temperature and the solid–liquid ratio (see Figure 4b). When the temperature reaches 303.15 K or above, the cumulative removal rate of the IL reaches 80% after five repeated processes. Therefore, considering the removal efficiency and energy saving, 303.15 K is selected as the optimal removal temperature for removing IL from solid powders. In addition, using a larger solid–liquid ratio is more advantageous for the removal process of IL. When the solid–liquid ratio reaches 1:200 (w (1 g):v (200 mL)), the concentration difference between the solvent and the solid in the IL is large, which promotes the smooth mass transfer and diffusion process of the IL. In order to recover IL as much as possible, 1:200 (w (1 g):v (200 mL)) was selected as the optimal solid–liquid ratio for the removal process.

3.5. Selection of Operation Duration

During the removal process at different times, no stilbene glycoside was detected in the removal solution of *n*-propanol, indicating that this compound was not lost during the removal of the IL. From Figure 4c, it can be seen that as the removal time increases, the cumulative removal rate of the IL shows a trend of first increasing and then decreasing. This may be because as the ultrasound time increases, more and more IL diffuses from the interior of the solid into the removal solvent, resulting in an increase in removal efficiency; when the removal equilibrium stage is reached, the entire system remains relatively stable, and the cumulative removal rate of the IL reaches its maximum level. As the removal time continues to increase, due to the fact that the powder has already undergone the extraction and removal stages, its internal structure is very loose. Continuous ultrasound radiation at this time may cause the IL in the removal solution to enter the solid powders again through ultrasonic action, resulting in a decrease in the cumulative removal rate. Therefore,40 min is appropriate as the removal time in this study.

3.6. Selection of Operation Times

In order to ensure the thorough removal of residual IL in *Polygonum multiflorum* powders and ensure the safety of the subsequent use of the powders, it is necessary to screen operation times (see Figure 4d). After each removal operation, the presence of stilbene glycoside was not detected in *n*-propanol, so it can be considered that there was no loss of stilbene glycoside. Here, only the removal rate of IL is used as an indicator to screen the number of removal operations. After four times, no IL was detected in the removal solution of *n*-propanol, and the cumulative removal rate of IL in the powders was calculated to be 101.55%. This may be due to the high content of IL in the first two rounds of *n*-propanol. In order to ensure that the concentration of IL is within the linear range of the standard curve, it is necessary to first dilute the sample and then use HPLC to determine the IL content in *n*-propanol after each removal. This may introduce experimental errors, resulting in its total removal rate slightly exceeding 100%. Overall, after four removal operations, the IL could no longer be detected in *n*-propanol by HPLC, and the total removal rate of the IL was also close to 100%. In summary, in order to fully remove the residual IL in the solid powders, the removal frequency is determined to be four times.

3.7. Study on Removal Kinetic Process

Exploring the relationship among the removal rate of IL, time, and temperature is crucial for a deep analysis of the mass transfer process between the solid and liquid phases during the separation process, and it provides a reference for future practical applications. This experiment investigated the removal kinetic process within the temperature range of 283.15 K to 323.15 K. In order to investigate the kinetic process of separating IL from solid powders within 45 min, first-order and second-order models were used for kinetic discussion. Based on this study, the linearized form of the kinetic equation is as follows (see Figure 5 and Table 1 for the results):

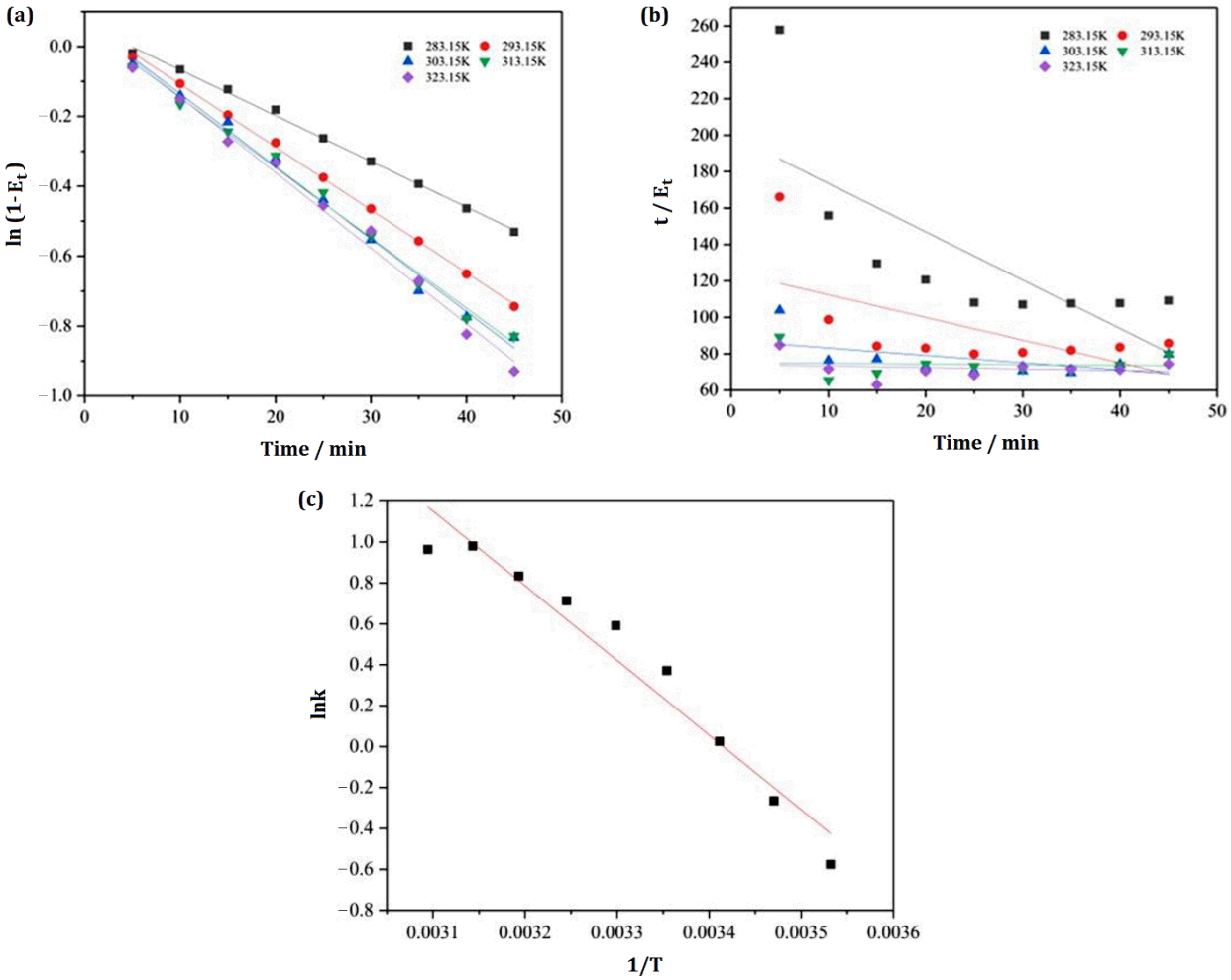


Figure 5. Models of kinetics governing ionic liquid removal: (**a**) first-order kinetic model and (**b**) second-order kinetic model; (**c**) fitting results of thermodynamic process.

Table 1. Fitting results of first-order kinetics and second-order kinetics.

T/K	First-Order Kinetics			Second-Order Kinetics		
	k_1/min^{-1}	R^2	RMSE	k_2/min^{-1}	R^2	RMSE
283.15	0.01309	0.9971	9.0895×10^{-3}	2.6547	0.5444	31.3524
293.15	0.01800	0.9992	6.6355×10^{-3}	1.2455	0.3799	20.5434
303.15	0.02077	0.9929	2.2641×10^{-2}	0.4007	0.2705	8.4946
313.15	0.02109	0.9919	2.3510×10^{-2}	0.0376	0.00565	6.4418
323.15	0.02162	0.9912	2.6247×10^{-2}	0.07736	0.03317	5.3913

For the first-order kinetic model,

$$ln(1 - R_t) = -k_1 t \quad (1)$$

For the second-order kinetic model,

$$t/\mathrm{R}_t = 1/k_2 + t \quad (2)$$

where R_t is the removal rate of ILs at different removal times, %; t is the removal time, min; $k_1$and $k_2$are the rate constants, min^{-1}, for the first-order and second-order kinetic models, respectively.

Based on Figure 5a,b and Table 1, it can be seen that under experimental conditions, $ln(1 - R_t)$ exhibits a good linear relationship with t, indicating that the dissolution behavior of residual IL from *Polygonum multiflorum* solid powders is more in line with first-order mass transfer kinetics. In addition, the apparent first-order kinetic model has been proven to be widely applicable in the extraction research of medicinal plants, and the magnitude of its rate constant is affected by temperature changes. The experimental results show that as the operating temperature increases, the rate constant gradually increases, indicating that the removal rate is gradually accelerating. Therefore, higher removal temperatures are beneficial for the diffusion of IL molecules into related solvents. Furthermore, based on the intercepts of the lines at different temperatures, it can be concluded that as the temperature increases, the intercept value of the lines decreases. This further indicates that changes in operation temperature can affect the magnitude of the removal rate. Here, the actual dissolution time required for ILs from solid particles becomes shorter as the temperature increases.

Based on the dissolution rate constants at different removal temperatures, the activation energy required for the removal of ILs in this experiment can be calculated. Generally speaking, the relationship between the rate constant of the removal process and the removal temperature can be described by the Arrhenius equation as follows:

$$ln\, k_1 = ln\, A - E_a/(RT) \quad (3)$$

where k_1 is the rate constant of the removal process, min^{-1}; A is the pre-exponential factor, min^{-1}; E_a is the activation energy, $\mathrm{J{\cdot}mol}^{-1}$; R is the molar gas constant, with a value of 8.314 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

According to the relationship between variables in the Arrhenius equation, plotting $lnk1$ as the y-axis and $1/T$ as the x-axis is applied to determine the value of activation energy. The magnitude of activation energy can be used to indicate the difficulty of the removal process of the IL. Generally, the higher the value of activation energy, the more energy needs to be provided for the removal process to proceed smoothly, resulting in a slower removal process. After calculation, the activation energy required for the removal of IL in this study is 14.82 kJ/mol. Compared to the activation energy required for the dissolution of polyphenols in tea leaves [34], the activation energy here is relatively small, indicating that the removal process can be easily carried out.

3.8. Thermodynamic Study

Similarly to kinetic analysis, we can also use the van der Waals equation to study the thermodynamics of IL removal processes. According to the equation, a straight line can be obtained through linear fitting after plotting $1/T$ as the horizontal axis and lnk as the

vertical axis (as shown in Figure 5c). According to the fitting results, the thermodynamic fitting equation for the removal process of IL is determined as follows:

$$lnk = -3650.8742 \times (1/T) + 12.4689, R^2 = 0.9490 \quad (4)$$

The thermodynamic parameters of the entire removal process are shown in Table 2. From this, it can be seen that the ΔH of the removal process is greater than zero, indicating that the removal process is an endothermic process. Therefore, increasing the removal temperature is beneficial for promoting the dissolution of ILs in solid powders. In addition, $\Delta S > 0$ indicates that during the removal process, the IL is transferred from the solid medicinal powder to the removal solvent, suggesting a transition from order to disorder. Meanwhile, ΔG decreases with increasing temperature, and its value changes from positive to negative, indicating that the dissolution of IL is a transition from a non-spontaneous process to a spontaneous process.

Table 2. Thermodynamic parameters of IL removal process at different temperatures.

T/K	PartitionCoefficient (k)	ΔG/(kJ·mol^{-1})	ΔH/(kJ·mol^{-1})	ΔS/[(kJ·(mol·K^{-1})]
283.15	0.5619	0.9907		
288.15	0.7669	0.4722		
293.15	1.0249	−0.0463		
298.15	1.4493	−0.5648		
303.15	1.8055	−1.0833	30.3534	0.1037
308.15	2.0388	−1.6018		
313.15	2.3011	−2.1203		
318.15	2.6652	−2.6388		
323.15	2.6212	−3.1573		

3.9. Determination of Solvent Residue

On the basis of the GC external standard method described earlier, the standard curve equation for detecting ethanol residue can be obtained as follows:

$$y = 9.8882 \times 10^5 x - 109385.2857, R^2 = 0.9995 \quad (5)$$

where x is the concentration of ethanol, mg/mL, and y is the peak area corresponding to the ethanol chromatographic peak, mV. The linear range of the ethanol standard curve is 0.0960 mg/L~0.6000 mg/L.

The standard curve equation for detecting residual *n*-propanol is as follows:

$$y = 8.9751 \times 10^5 x - 94135.7857, R^2 = 0.9996 \quad (6)$$

where x is the concentration of *n*-propanol, mg/mL, and y is the peak area corresponding to the chromatographic peak of *n*-propanol, mV. The linear range of the standard curve for *n*-propanol is 0.1120 mg/L~0.6400 mg/L. In the repeatability test experiment, the RSD% of the peak area corresponding to the ethanol chromatographic peak was 2.83% (n = 6), and the RSD% of the peak area corresponding to the *n*-propanol chromatographic peak was 1.46% (n = 6). In addition, the recovery rates of the analytical methods were determined, with ethanol recovery rates ranging from 97.6% to 99.1% and *n*-propanol recovery rates ranging from 98.4% to 102.5%. The minimum detection limit and minimum quantification limit for ethanol were 6.5404 mg/L and 19.8192 mg/L, respectively, while the minimum detection limit and minimum quantification limit for *n*-propanol were 6.5965 mg/L and 19.4881 mg/L, respectively. In summary, the methodological investiga-

tion of the experimental results shows that the GC analysis method used in this study has good reliability and can be used for a quantitative analysis of the residual amounts of ethanol and *n*-propanol in samples.

According to the general rules of the *Chinese Pharmacopoeia* (2020 edition) [29], common residual solvents in drugs and active pharmaceutical ingredients must have certain limits. Among them, the residual amounts of ethanol and *n*-propanol in drugs and raw materials do not exceed 0.5%. The detection results of residual ethanol and *n*-propanol content inside the solid powders of *Polygonum multiflorum* after removing anthraquinone components and residual IL in this study are shown in Figure 6. According to the gas chromatogram (Figure 6b), no chromatographic peaks appeared within the retention time range of ethanol and *n*-propanol (Figure 6a). This indicates that the residual amounts of ethanol and *n*-propanol in the solid powders are both below 0.5%, which complies with the regulations for the content of these two organic solvents in the general rules.

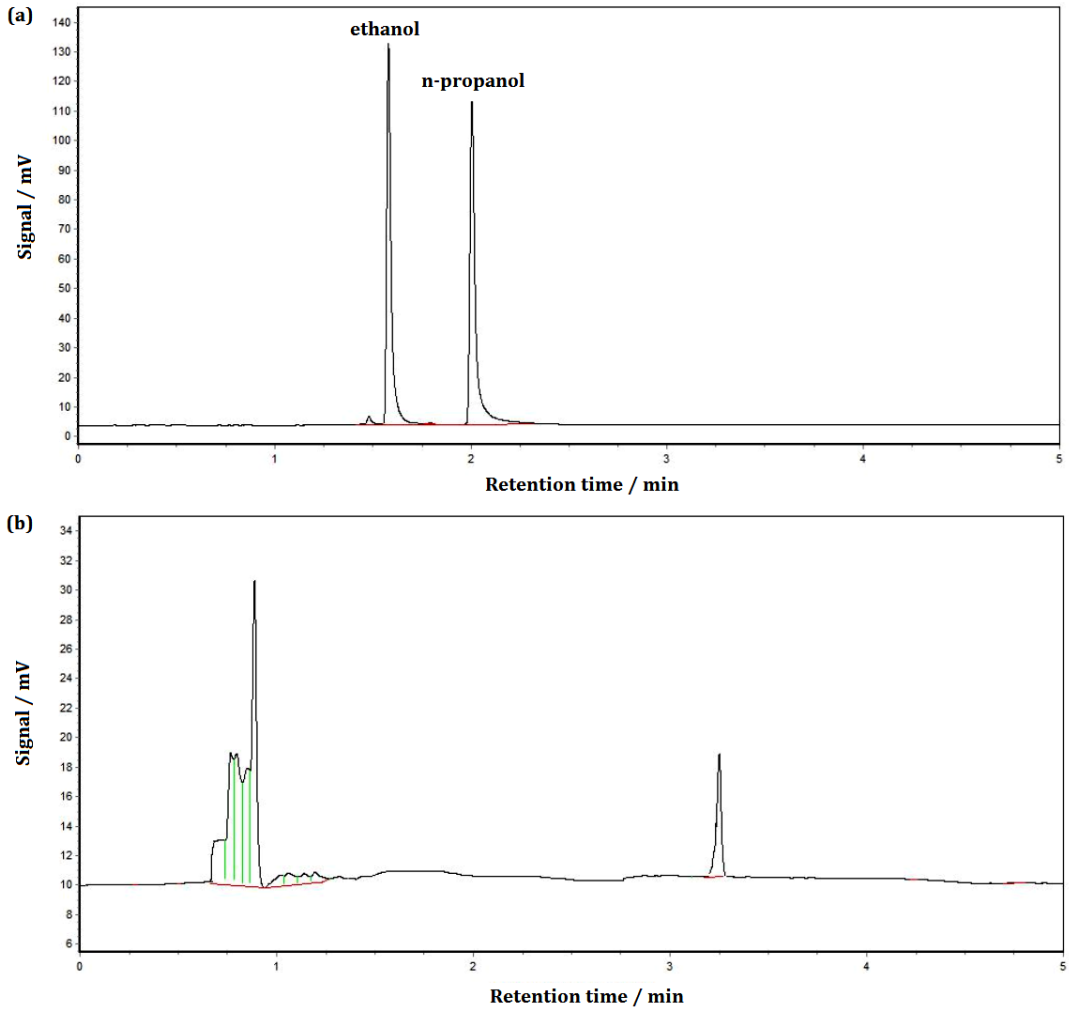


Figure 6. GC chromatograms of (**a**) two standard solvents and (**b**) actual sample after post-treatment.

3.10. Analysis of Recovered IL and Its Reuse Performance

According to the developed procedures and optimized conditions, the recovered IL was reused in five runs, and its chromatographic analysis results together with reuse performance are shown in Figure 7a. It can be found that the decreasing trend in the extraction efficiency of anthraquinones and stilbene glycosides is not obvious, because the developed post-treatment methods are strict and effective. Meanwhile, the IL's purity can be ensured. In order to remove anthraquinones and retain stilbene glycosides as much as

possible, IL selectivity plays a key role. The thermodynamic parameters in Figure 7b also show the difference in IL extraction for the two objectives. In particular, the Δ*H* values of anthraquinone components during the extraction process are smaller than those of stilbene glycosides, indicating that in order to dissolve more stilbene glycosides in the extraction agent, more heat energy needs to be provided.

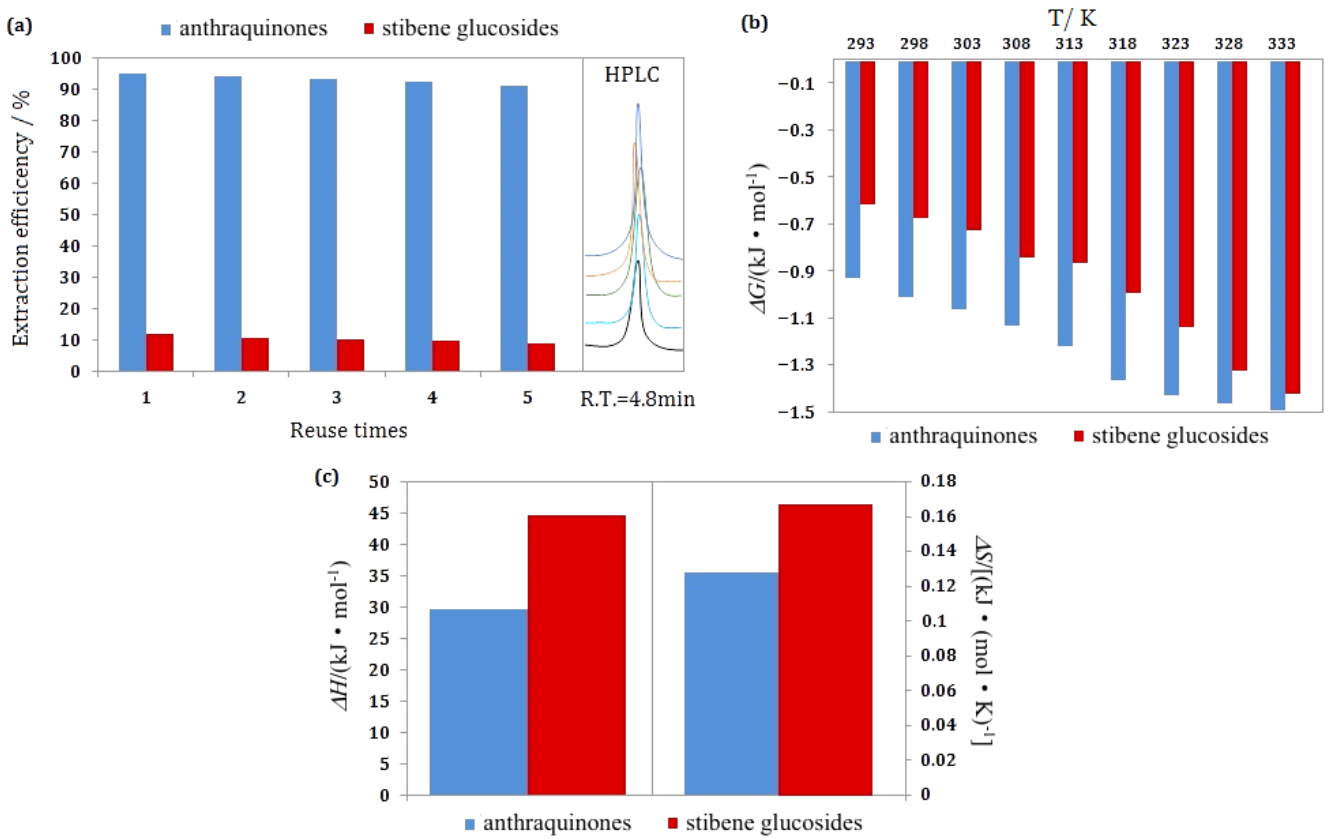


Figure 7. (**a**) Reuse performance of IL and HPLC analysis; (**b**) comparison of Δ*G*; (**c**) Δ*H* and Δ*S* comparison in terms of IL extraction for two natural products.

3.11. General Applicability and Greenness Assessment

Universality is another important indicator for measuring the usefulness of a method, because if the developed ultrasound–*n*-propanol method established here is only suitable for a specific system, its reference value will be very limited, and the significance of the entire study will not be obvious. Here, three other ionic liquids ([BBth][Br], [HBth][p-TSA], and [C_{12}mim][Br]) were used as extraction solvents for *Polygonum multiflorum*, as in existing studies [35,36], and we compared the total recovery rate of the ILs using the same extraction and post-treatment conditions as before. In order to reduce experimental errors, all the ionic liquids were quantitatively analyzed using reported HPLC conditions (Waters C_{18} chromatographic column, 3.9 × 150 mm, 5 μm i.d.; the mobile phase was composed of methanol–water (23:77, *v*/*v*) for benzothiazolium ILs of [BBth][Br] and [HBth][p-TSA] and acetonitrile–water (10:90, *v*/*v*) for methyl imidazolium IL of [C_{12}mim][Br], with a flow rate of 1.0 mL/min, injection volume of 10 μL, and a column temperature of 25 °C, and a2000ES evaporative light scattering detector, Alltech, San Diego, USA, was used) [35]. As shown in Figure 8a, the final recovery rates of all the tested ILs are all above 95%, indicating that the general applicability of the developed method is ideal.

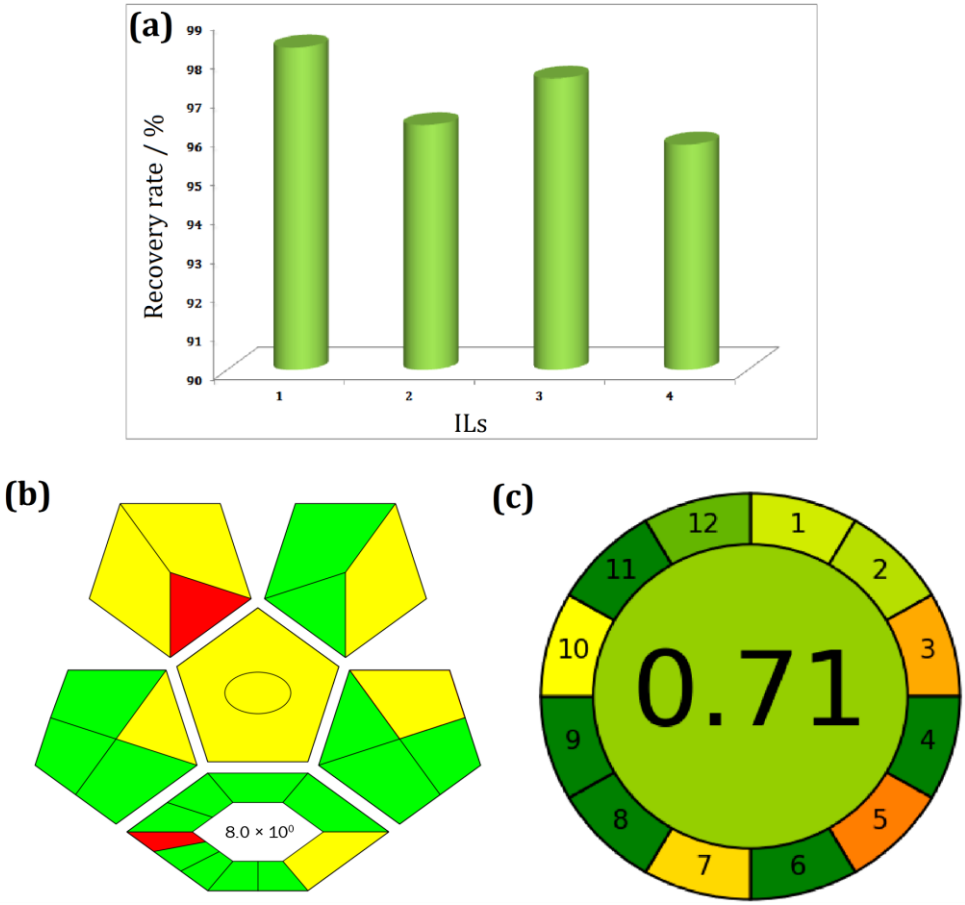


Figure 8. (**a**) Recovery of four ILs (1: [C_4Bim][PTSA]; 2: [BBth][Br]; 3: [HBth][PTSA]; 4: [C_{12}mim][Br]); (**b**) ComplexGAPI and (**c**) AGREE analysis for developed method of IL removal.

Beneficial processes should use energy-saving instruments as much as possible, reduce the use of toxic reagents or compounds, and minimize waste generation. The concept of greenness and friendliness has been widely recognized in both academia and industry. It is necessary to develop and apply simple, comprehensive, and flexible green indicators to evaluate the impact of processes on the environment, human health, and human safety. To showcase the utility of the proposed metric, it was used to evaluate separation protocols for actual potential applications. As two useful free tools, ComplexGAPI and AGREE have gained attention and eventually trust and acceptance from the chemical community. Here, they were employed to evaluate the above method and provide initial references for possible large-scale production. The results are included in Figure 8b,c. Most of the evaluation indicators are acceptable, and the possible risk mainly comes from the flammability of *n*-propanol. When stored, it should be kept in a cool and ventilated warehouse, and when used, it should be kept away from sources of fire and heat. It is currently widely used in cosmetics, dental detergents, insecticides, food additives, and other fields. If users receive specialized training and take personal protective measures before coming into contact with *n*-propanol, it can reduce harm to the human body.

4. Conclusions

In order to reuse green extractants and avoid possible residues in *Polygonum multiflorum* after extraction, this study used back-extraction to recover ionic liquid from the extraction and removal solutions, achieving a total recovery rate of over 98% for the IL. Through single-factor investigation, the optimal process conditions were obtained as fol-

lows: ultrasonic mode with *n*-propanol, 303.15 K, a solid–liquid ratio of 1:200 (w (1 g):v (200 mL)), 40 min, and four times. Under these conditions, the residual ionic liquid in the solid powders can be fully removed, and the stilbene glycosides in the powders are hardly lost. A first-order kinetic equation is suitable for describing this removal process. Meanwhile, an increase in removal temperature will accelerate the removal rate, and the activation energy required for the removal process is relatively small, indicating that residual IL can be easily separated from solid powders. In addition, the removal process is an endothermic process. Gas chromatography was used to quickly detect the content of the residue of two organic solvents within three minutes. The results showed that the residual amounts of ethanol and *n*-propanol in the solid powders comply with the relevant regulations of the *Chinese Pharmacopoeia*. The reuse performance of ionic liquids can be ensured, and the selectivity for two types of components was also revealed. General applicability and greenness assessment for the developed process also proved that it is an ideal method, which has potential in large-scale application.

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