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Ionic liquid-based ultrasonic-assisted extraction of berberine from rhizome of *Coptis chinensis*

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ABSTRACT

Ionic liquids (ILs) solutions as green solvents were successfully applied in the ultrasonic-assisted extraction (UAE) of Berberine from *Coptis chinensis*. A series of 1-alkyl-3-methylimidazolium ionic liquids with different cations and anions were evaluated and compared for their extraction efficiency; the results indicated that the structure of ILs has significant influence on the extraction efficiency for target analytes. [PSMIM][H₂PO₄] was finally selected as the optimal IL. In addition, the concentration of the [PSMIM][H₂PO₄]-water solution was optimized. And the extraction parameters including ultrasonic power, extraction time and solid-liquid ratio were all optimized by response surface method also. Moreover, the extraction mechanism was discussed. Compared with the lixiviating method with dilute H₂SO₄ and regular UAE with MeOH, the approach gained higher extraction efficiency, reduced the extraction time and pollution.

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KEYWORDS

Ionic liquid;
Ultrasonic-assisted
extraction;
Berberine;
Coptis chinensis.

INTRODUCTION

Rhizome of *Coptis chinensis* is a traditional Chinese medicine for clearing heat and depriving dampness for treatment of diarrhea, dysentery and jaundice, and purging the sthenic fire and clearing away toxic material for the cases of seasonal febrile diseases, carbuncle, and sore throat. The herbal medicine has broad-spectrum antibacterial and antiprotozoal effects^[1]. Berberine, an isoquinoline derivative alkaloid (Figure 1), is the major active ingredient of the herb. The inhibition effects of Berberine on cancer and diabetes has also been reported in the past few years^[2,3]. There are some extraction methods for extracting berberine with conventional organic solvent and dilute H₂SO₄ solution extraction, but they have some drawbacks including

time-consuming, low efficiency, and using of a large amount of toxic and hazardous organic solvents. Therefore, it is highly desirable to develop an alternative extraction technique with higher selectivity, efficiency and environment friendliness.

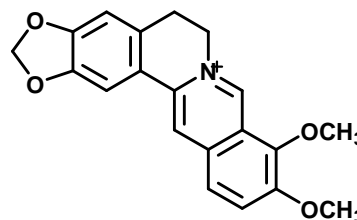


Figure 1 : The chemical structure of berberine

Ionic liquids (ILs), also known as molten salts, are composed of organic cations and inorganic or organic anions in liquid status near room temperature^[4]. With

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unique advantages of negligible vapor pressure, good thermal stability, good dissolving and extracting ability, ILs are regarded as an attractive alternative or replacement of conventional volatile organic solvents^[5]. In recent years, ILs have attracted extensive attention in modern chemistry and have been successfully applied in liquid-liquid partition, liquid-phase and solid-phase microextraction, or aqueous two phase systems extraction^[6-8]. Recently, ILs have been successfully used in the extraction of some active substances from medicine plants^[9-13]. Compared with organic solvents, ILs could reduce the environmental pollution in the process of separation as green solvents. But at room temperature ILs are difficult to be used to directly extract active ingredients from solid matrixes for the high viscosity and poor diffusivity. In this case, adding co-solvent and increasing temperature can reduce the viscosity of ILs and improve the diffusion of solvents, while ILs still maintain good dissolving capacity.

Moreover, UAE is a more rapid and effective extraction technique than conventional ways and this benefit has already been demonstrated in recent years^[14-17]. Under the circumstances, this paper is ready to introduce the development of a rapid and effective IL-based ultrasonic-assisted extraction approach for the extraction of berberine from rhizome of *Coptis chinensis*, which to our knowledge has not been reported by now. Besides although application of ILs as solvent in UAE of bioactive components from natural products has been reported by some research groups, they mainly focus on extraction of natural components which are difficultly to dissolve in water. Therefore, it is interesting to investigate the effects of ionic liquids on the extraction of berberine. In this paper, ILUAE mechanism was also discussed.

EXPERIMENTAL

Chemicals

All chemicals involved in this study were at least of analytical reagent grade. Acetonitrile and methanol used for HPLC were of chromatographic grade and purchased from KeLong, Chengdu, China. Water is redistilled. Standard berberine was used for HPLC was purchased from RuiQi Biological Technology Company (Shanghai, China). Rhizome of *Coptis chinensis* was

purchased from local drug-store. And all samples were milled and dried. And the sample practice size was controlled in 0.45~0.90 mm by passed through a stainless steel sieve. All samples were stored in closed desiccators until use. The same batch of sample was used through this study to be representative of variable hardness and density.

Apparatus

KQ-2200DA ultrasonic water bath (Kunshan, Jiangsu, China) was used in the extraction step. HPLC analysis was performed with an LC-20AT pump, an SPD-M20A PDA detector (Shimadzu, Kyoto, Japan), a Waters symmetry C18 column, 5 μm , 3.9 \times 150 mm i.d. (Waters, Massachusetts, USA), and an HCT-360 LC column cooler/heater (Hengao Tech & Dev, Tianjin, China). A Class-VP workstation (Shimadzu, Kyoto, Japan) was used for data acquisition. The pH meter was purchased from Shanghai ShiNuo physical optical instruments (Shanghai, China).

Synthesis of ILs

Eight kinds of 1-alkyl-3-methylimidazolium ILs (as shown in TABLE 1) were synthesized according to the literature procedures^[18-22]. All ILs were dried for 4 h under vacuum at 90 μm and stored in closed desiccators before use. The purity of ILs was checked by HPLC and their purities were greater than 95% (w/w).

IL-based ultrasonic-assisted extraction

IL-based ultrasonic-assisted extraction was performed in ultrasonic baths at room temperature. 1.0 g of dried sample was mixed with 10 mL of different ILs aqueous solutions and then the suspension was extracted using ultrasound. IL solutions were prepared by dissolving corresponding IL in redistilled water. The optimal anion, cation, concentration of selected IL, ultrasonic power, extraction time, and solid-liquid ratio (g/mL) were systematically studied in this work. After ultrasonic extraction, the extracts obtained were cooled down to room temperature and filtrated through a Buser funnel, diluted to 50 mL with redistilled water, and filtrated through a 0.45 μm filter prior to HPLC analysis.

Optimization by response surface method

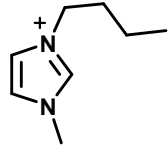
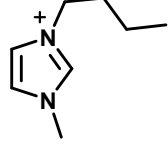
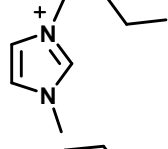
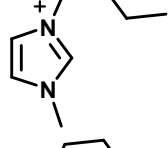
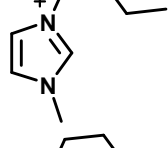
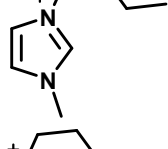
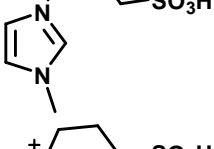
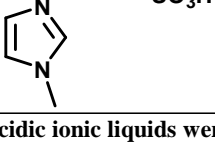
In order to optimize the operation factors and further study their interactions, a central composite de-

sign was used to investigate the effects of three independent variables, the ultrasonic power, extraction time and solid-liquid ratio on extraction efficiency of berberine. The complete design was consisted of 20 experimental points including six replications of the center points (see TABLE 2).

Compared with conventional reference extraction method

The lixiviating method with dilute H_2SO_4 was se-

TABLE 1 : The structure of studied ionic liquids

No.	IL	cation	anion	pH
A	[BMIM][PF ₆]		PF ₆ ⁻	Neutral
B	[BMIM][BF ₄]		BF ₄ ⁻	Neutral
C	[BMIM][Br]		Br ⁻	Neutral
D	[BMIM][CH ₃ SO ₃]		CH ₃ SO ₃ ⁻	Neutral
E	[BMIM][HSO ₄]		HSO ₄ ⁻	Acid 1.6*
F	[BMIM][H ₂ PO ₄]		H ₂ PO ₄ ⁻	Acid 2.2
G	[PSMIM][HSO ₄]		HSO ₄ ⁻	Acid 1.0
H	[PSMIM][H ₂ PO ₄]		H ₂ PO ₄ ⁻	Acid 1.5

*The pH values of the acidic ionic liquids were measured in the 20 mmol/100ml aqueous solution at 30°C by pH meter.

TABLE 2 : RSM experimental design^a

Run	A: ultrasonic power (W)	B: extraction time (min)	C: solid-liquid ratio (g/mL)	Response Extraction efficiency (%)
1	80	30	1:30	95.73783
2	80	30	1:30	98.20737
3	100	20	1:20	94.58196
4	60	20	1:20	86.7582
5	100	20	1:40	99.54314
6	80	30	1:30	96.64766
7	80	30	1:30	96.51769
8	100	40	1:20	94.62381
9	60	40	1:20	91.85364
10	80	30	1:46	97.56425
11	60	40	1:40	96.0191
12	100	40	1:40	100 ^b
13	80	30	1:13	88.96051
14	45	30	1:30	85.26685
15	80	46	1:30	99.01413
16	80	30	1:30	97.29754
17	80	13	1:30	94.23505
18	80	30	1:30	97.42752
19	110	30	1:30	95.68896
20	60	20	1:40	91.25718

^aThese experiments were designed by the Design Expert 7.0 software.

^bThe extraction efficiency is expressed as the observed values of berberine and the maximum amount in curve was taken to be 100%.

lected as the reference method for extraction of the berberine in rhizome of *Coptis chinensis*. 0.4% H_2SO_4 solution was selected as solvent. 1.0 g dried sample with 10 mL of 0.4% H_2SO_4 solution in a 50 mL flask, mixed round 24 hours. The suspensions obtained after extraction were filtered through a Busher funnel, then the filtrate was diluted to 50 mL with redistilled water and filtered through the 0.45 μ m filter for the subsequent HPLC analysis.

HPLC analysis

The filtrated and diluted extracts were directly injected into the liquid chromatography. And each injection volume was 5 μ L. The mobile phase was composed of 30% of acetonitrile and 70% of NaH_2PO_4 solution with 0.8mL/min of the flow rate. The column temperature was kept at 25°C and the UV detection wavelength was 345 nm. Under these conditions, ber-

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berberine obtained baseline separation and was identified by standard berberine solution. A comparison of the chromatograms of the berberine obtained from standard solutions with those contained in ILs extract is shown in Figure 2. Peak area was used for quantification, the berberine standard curve was made for the determination of extracts:

$$y = 4.01 \times 106x + 238288, R^2 = 0.9992$$

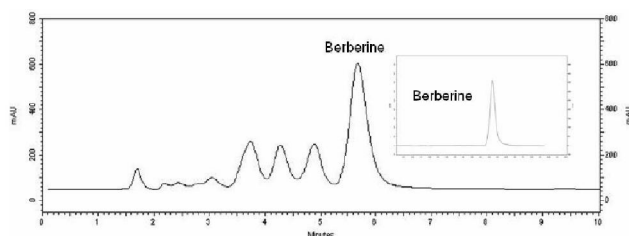


Figure 2 : HPLC chromatogram of berberine in the [BMIM][CH₃SO₃] extract. Insert: HPLC chromatogram of standard berberine solution.

RESULTS AND DISCUSSION

Screening of the IL-based extraction phase

The structure of ILs has significant influence on their physicochemical properties and their distinct multiple interactions with target analytes, which might greatly affect the extraction efficiency of active substances^[23]. Therefore the effects of the anion and cation of ILs (in TABLE 1) on the extraction efficiency were studied. The extraction efficiency of 8 kinds of pure ILs and their aqueous solution were also compared with each other in this work (as shown Figure 3 and Figure 4).

Figure 3 shows the pure [BMIM][CH₃SO₃] is more efficient than other pure ILs, but among their aqueous solutions, the most efficient solution is [PSMIM][H₂PO₄] solution. By comparing Figure 3 and Figure 4, it could be found that pure ILs are less efficient than the corresponding IL solutions due to their high viscosity and poor diffusivity at room temperature.

From Figure 4, acidic IL solutions are more efficient than neutral IL solutions on account of the berberine is a water-soluble alkaloid; but in Figure 3, the advantage of extraction has not been shown, it may be because that pure acidic IL has higher viscosity than neutral IL. Besides, the neutral IL solution extraction efficiency was decreased as [BMIM][CH₃SO₃] > [BMIM][Br] > [BMIM][BF₄] > [BMIM][PF₆]

decreasing hydrophilicity of these four anions, which is the same as pure IL. This result could be explained by the fact that the water miscibility of four neutral IL decreases as CH₃SO₃⁻ > Br⁻ > BF₄⁻ > PF₆⁻. In addition, [BMIM][PF₆] is relatively hydrophobic and is only sparingly water soluble, so sequentially its extraction efficiency is worst.

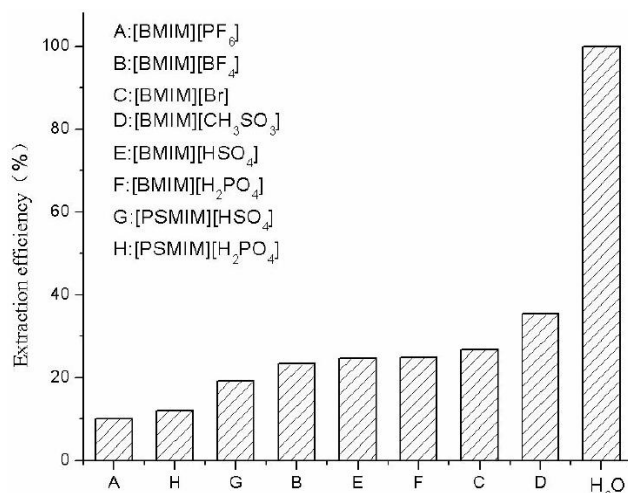


Figure 3 : Effect of pure ILs direct on the extraction efficiency of berberine from rhizome of *Coptis chinensis*, pure water as a blank experiment. Sample: 1.0 g, extractant volume: 10 mL, ultrasonic power: 100W, extraction time: 30 min. The extraction efficiency is expressed as the observed values of berberine and the maximum amount in curve was taken to be 100%.

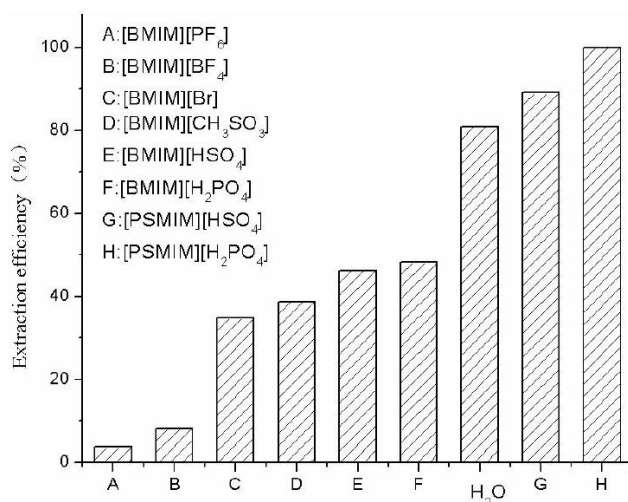


Figure 4 : Effect of ILs solution on the extraction efficiency of berberine from rhizome of *Coptis chinensis*, pure water as a blank experiment. The concentration of IL: 0.5M, sample: 1.0 g, extractant volume: 10 mL, ultrasonic power: 100W, extraction time: 30 min. The extraction efficiency is expressed as the observed values of berberine and the maximum amount in curve was taken to be 100%.

As shown in Figure 4, acidic IL [PSMIM][H₂PO₄] solution is the most efficient solution, and the second is [PSMIM][HSO₄]. TABLE 1 shows acidity about these four acidic ionic liquid solutions which were measured in this work. From this table, it can be seen that HSO₄⁻ ionic liquid solution is more acidity than H₂PO₄⁻ with the same cation, but under the same conditions H₂PO₄⁻ ionic liquid solution could extract more target analytes (Figure 4). This result could be interpreted by the fact that H₂PO₄⁻ anion could afford more protons at the same IL concentration level, which might facilitate the extraction of target alkaloids. Considering the above results, [PSMIM][H₂PO₄] was selected for the subsequent evaluation in this work.

The effect of the concentration of ILs

It has been proved that IL concentration had significant influence on the extraction of target analytes. Therefore, the concentration of IL on extraction effect was studied and the result was shown in Figure 5. Moreover, the above result had proved that the extraction mechanism of the neutral ionic liquid and acidic ionic liquid were different, so a neutral ionic liquid, [BMIM][Br] was selected as a control group (Figure 5).

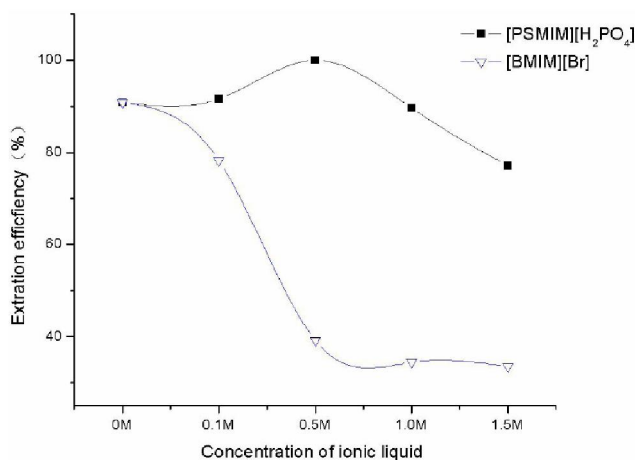


Figure 5 : Effect of the concentration of ionic liquid on the extraction efficiency of berberine. Sample: 1.0 g, extractant volume: 10 mL, ultrasonic power: 100W, extraction time: 30 min. The extraction efficiency is expressed as the observed values of berberine and the maximum amount in curve was taken to be 100%.

From Figure 5, it can be seen that the extraction efficiency gradually reduced with the increase of [BMIM][Br] concentration, and at the end the curve

tends to be flat. This is because that berberine is a kind of water-soluble alkaloid and has large polarity; and the polarity of the neutral IL is less, so the polarity of the IL solution decreased as the IL concentration increased. According to the theory of “similarity and intermiscibility”, the extraction efficiency of berberine would be reduced. But the acidic IL [PSMIM][H₂PO₄] does not show such a trend; the extraction efficiency increased when the IL concentration increased from 0.1M to 0.5M. However, when it further increased, the extraction efficiency decreased. It might be because acidic IL could provide proton which increase the extraction efficiency of target alkaloid, and increasing the IL concentration decreased the polarity of IL solution which decreased the extraction efficiency. Consideration of the above results, 0.5M of [PSMIM][H₂PO₄] was selected in the following experiments..

Optimization of UAE conditions

The univariate method was used in all instances to optimize the following three parameters: solid-liquid ratio, ultrasonic power and extraction time.

The solid-liquid ratio is an important factor which should be studied to increase the extraction efficiency of berberine. Superfluous solvent volume could make unnecessary waste and the burden of solvent recovery increase, and smaller volume would make the targets extraction incomplete. To examine the effect of the solid-liquid ratio on the extraction efficiency, extraction was carried out with different solid-liquid ratios (1:10, 1:20, 1:30, and 1:40 g/mL). The extraction efficiency increased when solid-liquid ratio was changed from 1:10 to 1:40 as shown in Figure 6a, and no significant increase was found when it was increased to 1:40. Thus, a solid-liquid ratio of 1:30 was selected in present study.

To examine the effect of the ultrasonic power on the extraction efficiency, extraction was carried out at 40, 60, 80, 100 and 120 W, respectively. As shown in Figure 6b, it can be seen that ultrasonic power did not significantly influence the extraction efficiency, and the extraction efficiency increased with the enhancement of ultrasonic power before the power reached 100w, and then the efficiency was not improved with the further increase of the power. Finally, the ultrasonic power of 100 w was selected.

To optimize the extraction time, extractions were

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carried out at 100 W when extraction time was changed. As shown in Figure 6c, when the extraction time increased from 10 to 30 min, the extraction efficiency increased. When the variable was increased from 30 to 40 min, slight improvement was obtained. Therefore, 30 min was selected for further experiments.

Based on the above experiments, the optimum UAE conditions were established as follows: 0.5M [PSMIM][H₂PO₄] as extraction solvent, ultrasonic power of 100 W, extraction time of 30 min, solid-liquid ratio of 1:30 (gmL⁻¹). The extraction efficiency of berberine increased 22.08% by using the proposed UAE approach under optimal conditions.

Optimization parameters by response surface method (RSM)

In order to further research the interactions between the operation parameters, the solid-liquid ratio, ultrasonic power and extraction time were optimized by RSM. As shown in TABLE 3, the model F-value of 44.14 indicated that the model was significant, and there was only 0.01% chance that a “model F-Value” this large could occur due to noise. Values of “Probability > F” less than 0.0500 indicated model terms were significant. In this case, A, B, C, AB, A² and C² were significant model terms. The “Lack of Fit F-value” of 1.14 indicated the lack of fit was not significant relative to the pure error. There was a 44.37% chance that a “Lack of Fit F-value” could occur due to noise. Insignificant lack of fit was good. Moreover, the effect of solid-liquid ratio and ultrasonic power was the greatest ($P < 0.0001$) and that of extraction time was the smallest ($P=0.0002$) as shown in TABLE 3.

In TABLE 4, the “Predicted R-Squared” of 0.8843 was in reasonable agreement with the “Adjust R-Squared” of 0.9533. “Adequacy Precision” measured the signal to noise ratio. A ratio greater than 4 was desirable. The present ratio of 21.658 indicated an adequate signal. This model can be used to navigate the design space.

The response surfaces for the effect of independent variables on extraction efficiency of berberine were shown in Figure 7. Figure 7a represented the 3D-plot about the effect of ultrasonic power and extraction time on the reaction. Figure 7b depicted ultrasonic power and solid-liquid ratio effect on the response. The mutual

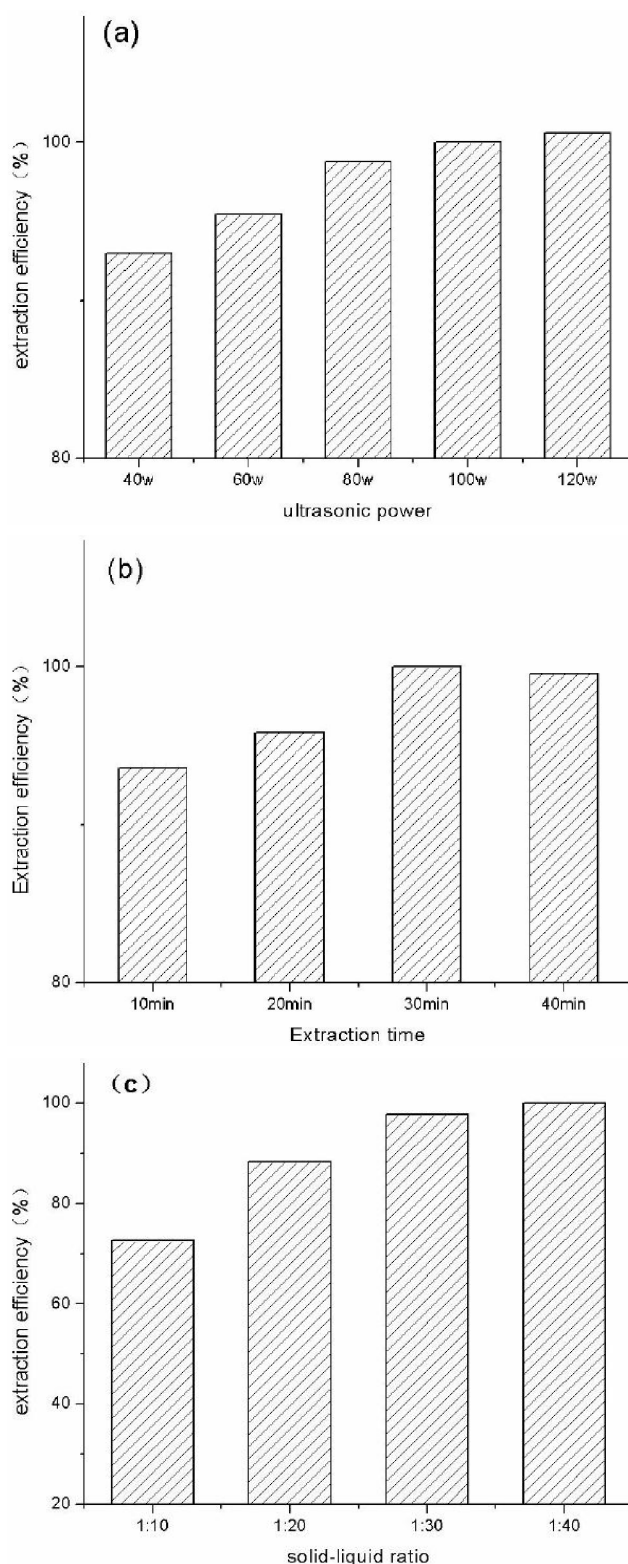


Figure 6 : Effect of ultrasonic power (a), extraction time (b) and solid-liquid ratio (c) on the extraction efficiency of berberine with 0.5M [PSMIM][H₂PO₄] as extracting phase. Sample: 1.0 g. The extraction efficiency is expressed as the observed values of berberine and the maximum amount in curve was taken to be 100%.

TABLE 3 : Analysis of variance (ANOVA) for the quadratic model for the berberine yield

Source	Sum of Squares	df	Mean Square	F-Vaule	P-Vaule Pro>F
modle	1.85	9	0.21	44.14	<0.0001
A-Ultrasonic power	0.71	1	0.71	151.87	<0.0001
B-Time	0.15	1	0.15	31.53	0.0002
C-soild-liquid ratio	0.49	1	0.49	104.14	<0.0001
AB	0.065	1	0.065	13.95	0.0039
AC	0.00211	1	0.00211	0.45	0.5163
BC	0.000006989	1	0.000006989	0.0015	0.9699
A2	0.36	1	0.36	78.24	<0.0001
B2	0.0009565	1	0.0009565	0.21	0.6602
C2	0.100	1	0.100	21.45	0.0009
Residual	0.047	10	0.0046	-	-
Lack of Fit	0.025	5	0.004969	1.14	0.4437
Pure Error	0.022	5	0.004350	-	-
Cor total	1.90	19	-	-	-

TABLE 4 : The credibility analysis of the regression equations.

Std.Dev	0.068	R-Squared	0.975
Mean	7.30	Adj R-Squared	0.9533
C.V.%	0.94	Pred R-Squared	0.8843
PRESS	0.22	Adeq Precision	21.658

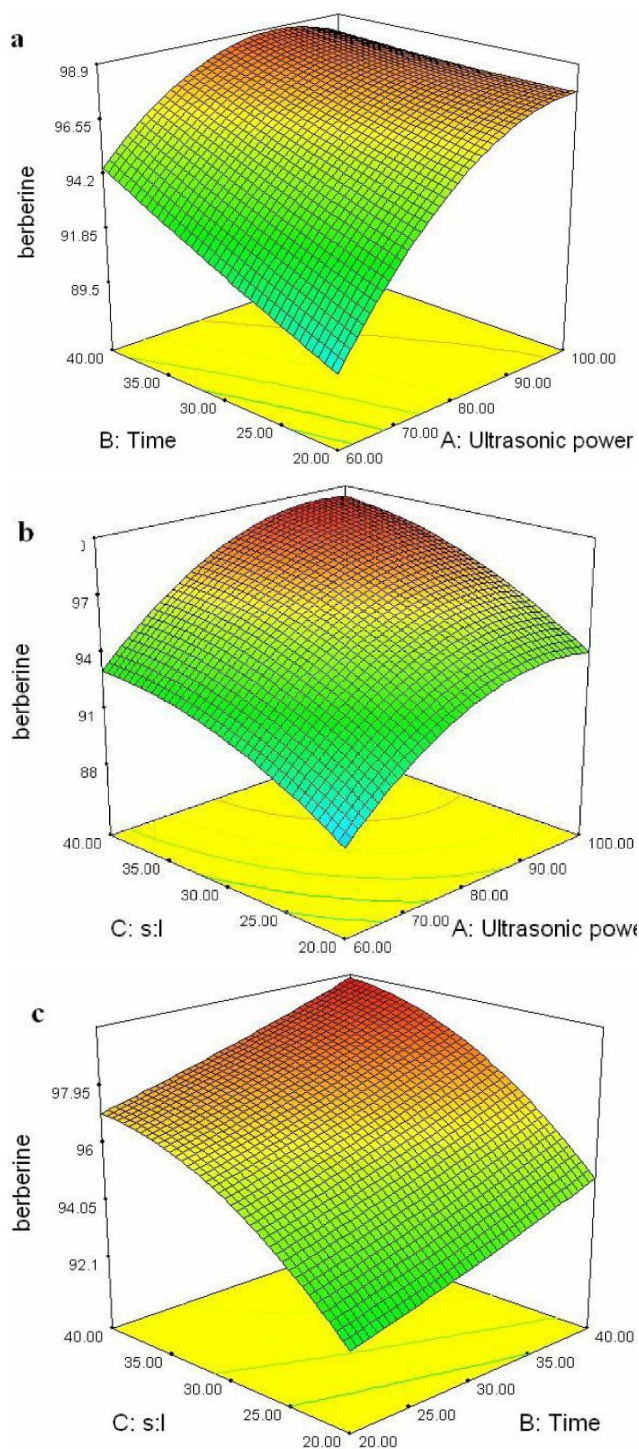
effect of solid-liquid ratio and extraction time on the reaction was shown in Figure 7c. The final extraction efficiency (Z) was given by:

$$Z = 7.46 + 0.23A + 0.10B + 0.19C - 0.090AB + 0.016AC + 0.000935BC - 0.16A^2 + 0.00814B^2 - 0.083C^2$$

From this equation, according to the linear coefficient and Figure 7, the response surface experiment indicated that the descending order of influencing factors for the extraction efficiency was as follows: ultrasonic power, solid-liquid ratio and extraction time. And the predict consequence was: 88.03w and 39.81min ultrasonic extraction, 1:37.05 solid-liquid ratio. Under this optimized conditions, the extraction efficiency of berberine could reach to 101.6%.

Comparison of the proposed IL- based ultrasonic-assisted extraction approach with the conventional methods

For the comparison of the extraction efficiency of IL-based ultrasonic-assisted extraction with other conventional extraction techniques, such as the lixiviating

**Figure 7 : 3D-plot between any two parameters for the extraction of berberine.**

method with 0.4% H₂SO₄ and regular UAE extraction which are carried out to extract berberine from rhizome of *Coptis chinensis*.

In order to further demonstrate the use of ILs, the regular UAE process was compared with the proposed UAE approach with ionic liquid. In this work,

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MeOH was used as solvent in regular UAE, and this experiment was carried out under the same UAE conditions.

The result was shown in TABLE 5, the IL-based ultrasonic-assisted extraction method not only increased the extraction efficiency, but also dramatically reduced the total extraction time (from 24 h to 30min). This

means that the proposed IL-based UAE procedure has great potential to be a rapid and effective method for extraction of berberine from rhizome of *Coptis chinensis*. The extracts were spiked with known quantities of standards. The recoveries of the 3 methods were in the range of 94.75 % and 103.71 % with RSD lower than 2.28 % which were shown in TABLE 2.

TABLE 5 : Comparative study of extraction efficiency using different extraction methods.

Extraction method	IL- based ultrasonic-assisted extraction	The lixiviating method with 0.4% H ₂ SO ₄	UAE extraction with regular organic solvent MEOH
Relative extraction efficiency ^a (mean± SD, %)	100.00 ± 1.00	68.37 ± 1.84	71.22 ± 1.50
Recovery yields (mean± SD, %)	98.53±1.76	103.71±1.59	97.45±2.28
Extraction time	30 min	1440min	30 min

^aThe extraction efficiency is expressed as the observed values of berberine and the maximum amount in curve was taken to be 100%.

ILs present are more expensive than organic solvent and H₂SO₄, the ILUAE method is still economical considered the saved time and potential recycle of ILs. And compare with dilute H₂SO₄ and Regular UAE with methanol methods, no organic solvent have been discharged into the air during the extraction and ILs could not cause the corrosion of equipment as H₂SO₄. Besides ILs can be recycled which decrease the waste water further. Overall the IL-based ultrasonic-assisted extraction method is a much safer and greener process.

CONCLUSION

An efficient UAE method has been developed for extraction of berberine from rhizome of *Coptis chinensis* with ionic liquid. The structure of ILs has significant influence on the extraction efficiency of berberine. And the results indicate that if IL is more hydrophilicity and could afford more protons, the extraction efficiency of berberine would be better. In this work, the optimum UAE conditions were optimized by RSM. Compared with the lixiviating method with dilute H₂SO₄ and regular UAE with MeOH, the approach gained higher extraction efficiency and saved more time. Moreover, based on the advantages of ionic liquids, the UAE method will have great potential and broad space when it is applied in the food and pharmaceutical industry as an environmental friendly approach.

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REFERENCES

- [1] M.Ou; Chinese-English Manual of Common-used Traditional Medicine, Clarendon Press: Guangdong Science and Technology Publishing House, China, 598-599 (1992).
- [2] M.S.Choi, J.H.Oh, S.M.Kim; Int.J.Oncol., **34**, 1221-1230 (2009).
- [3] J.Zhou, S.Zhou, J.Tang, K.Zhang, L.Guang, Y.Huang, Y.Xu, Y.Ying, L.Zhang, D.Li; Eur.J. Pharmacol., **606**, 262-268 (2009).
- [4] A.Berthod, M.J.Ruiz-Angel, S.Cardá-Broch; J.Chromatogr.A, **1**, 6-18 (2008).
- [5] T.Welton; Chem.Rev., **99**, 2071-2076 (1999).
- [6] J.G.Huddleston, H.D.Willauer, R.P.Swatloski, A.E.Visser, R.D.Rogers; Chem.Comm., **16**, 1765-1766 (1998).
- [7] J.H.Wang, D.H.Cheng, X.W.Chen, Z.Du, Z.L.Fang; Anal.Chem., **79**, 620-625 (2007).
- [8] Z.Du, Y.L.Yu, J.H.Wang; Chem.Eur.J., **34**, 9679-9685 (2007).
- [9] W.Y.Ma, Y.B.Lu, J.H.Hu, Z.Z.Chen, Y.J.Zhang, J.Pan; Talanta, **80**, 1292 (2010).
- [10] X.J.Cao, X.M.Ye, Y.B.Lu, Y.Yu, M.W.Mo; J.Anal. Chim., **640**, 47-51 (2009).

Full Paper

- [11] L.J.Zhang, Y.L.Geng, W.J.Duan, D.J.Wang, M.R.Fu, X.Wang; *J.Sep.Sci.*, **32**, 3550-3554 (2009).
- [12] F.Y.Du, X.H.Xiao, X.J.Luo, G.K.Li; *Talanta*, **78**, 1177-1184 (2009).
- [13] K.K.Wu, Q.L.Zhang, Q.Liu, F.Tang, Y.M.Long, S.Z.Yao; *J.Sep.Sci.*, **32**, 4220-4226 (2009).
- [14] J.H.Chen, X.P.Liu, X.Q.Xu, F.S.C.Lee, X.R.Wang; *J.Pharmaceut.Biomed.Anal.*, **43**, 879-885 (2007).
- [15] D.A.Lambropoulou, I.K.Konstantinou, T.A.Albanis; *Analytica Chimica Acta*, **573**, 223-230 (2006).
- [16] L.Paniwnyk, H.Cai, S.Albu, T.J.Mason, R.Cole; *Ultrasonics Sonochem.*, **2**, 287-292 (2009).
- [17] L.Nunez, J.L.Tadeo, A.I.Garcia-Valcarcel, E.Turiel; *J.Chromatogr.A*, **1**, 178-182 (2008).
- [18] Y.Y.Wang, W.Li, L.Y.Dai; *Chemical Papers*, **3**, 313-317 (2008).
- [19] P.Bonhote, A.P.Dias, N.Papageorgiou, K.Kalyanasundaram, M.Gratzel; *Inorg.Chem.*, **35**, 1168-1178 (1996).
- [20] Y.Chu, H.Deng, J.P.Cheng; *J.Org.Chem.*, **72**, 7790-7793 (2007).
- [21] D.Fang, H.Cheng, K.Gong, Q.R.Shi, X.L.Zhou, Z.L.Liu; *J.Fluorine.Chem.*, **129**, 108-111 (2008).
- [22] L.Li, S.T.Yu, C.X.Xie, F.S.Liu, H.J.Li; *J.Chem. Technol.Biot.*, **84**, 1649-1652 (2009).
- [23] Y.B.Lu, W.Y.Ma, R.L.Hu, X.J.Dai, Y.J.Pan; *J.Chromatogr.A*, **1**, 42-46 (2008).