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The recovery of gallic acid from wastewater by extraction with tributyl phosphate/4-methyl-2-pentanone/*n*-hexane, tributyl phosphate/*n*-octanol/*n*-hexane and *n*-hexanol

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The recovery of gallic acid (GA) from GA processing wastewater was studied *via* solvent extraction. Tributyl phosphate (TBP)/4-methyl-2-pentanone (MIBK)/*n*-hexane, TBP/*n*-octanol/*n*-hexane and *n*-hexanol were used as the extractants. The effects of the component proportion in the mixed extraction solvent, stirring speed, extraction time, pH, phase ratio (extraction solvent/GA solution), temperature and salt on extraction rate were investigated. After univariate crossover experiments, the optimum conditions were obtained as a component proportion in the mixed extraction solvent of 1 : 2 : 1 at pH 1.5 with a phase ratio of 1 : 1, stirring speed of 150 rpm, extraction time of 60 s and temperature of 30 °C. The maximum extraction rates through the one-stage process were 88.2%, 82.5% and 76.7% for TBP/MIBK/*n*-hexane, TBP/*n*-octanol/*n*-hexane and *n*-hexanol, respectively. FT-IR spectroscopy was used to characterize the extracted organic phases. Afterwards, Box–Behnken design was used to optimize the three most influential parameters including pH, temperature and phase ratio whose values were optimized to 0.5, 30 °C and 1 : 1, respectively and subsequently, the extraction rate through the one-stage process using TBP/MIBK/*n*-hexane, TBP/*n*-octanol/*n*-hexane and *n*-hexanol further increased to 95.5%, 86.8% and 78.1%, respectively. TBP/MIBK/*n*-hexane was proved to be the most effective extractant in this study and more than 94.4% of GA was recovered through a four-stage stripping process. Finally, TBP/MIBK/*n*-hexane was used in actual GA processing wastewater with 92.5% of GA being extracted and more than 88.7% was recovered after the four-stage extraction and stripping process. The results can be referred to for the selection and design of processes to efficiently recover GA from GA processing wastewater.

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1 Introduction

Gallic acid (3,4,5-trihydroxybenzoic acid, GA) is one of the most representative phenolic-type compounds, which is of great value and continues attracting considerable interest in the processing of food, chemicals, pharmaceutical production, and other fields for its special properties, such as anti-inflammatory, anti-mutagenic, antioxidant, anti-free radical and other biological activities, especially anticancer.[1–4] Nevertheless, during the manufacturing process used to produce GA, the resulting wastewater contains a certain amount of GA, affecting the water's smell, color and taste. If given it free, disinfection by-products (DPBs) may be generated during the chlorine disinfection process of drinking water, such as chloroform and haloacetic acids, which can damage aquatic organisms and human health.[5] Thus, wastewater containing GA requires treatment before discharging into environment. Due to its high concentration, high COD, high salinity and strong acidity,[6] the wastewater is toxic to the microorganisms[7] and exhibits microbial inhibitory activities, resulting in the difficult micro-degradation of GA in the ecological environment.[8] In addition, GA is best recovered without structural damage during the wastewater treatment process due to its great commercial value. Therefore, traditional biological digestion cannot be applied in this case. Alternative techniques, for example adsorption and liquid–liquid extraction, are often proposed.

Adsorption may be a common, favorable and effective method of treating GA wastewater[9] and relies on the high interfacial area of the adsorbents.[10] There are many adsorbents, such as activated carbon and biosorbents. However, one of the drawbacks to the adsorption method is that it generally unsuitable to wastewater with high concentrations of pollutants, particularly those reaching 24 000 mg L^{-1} as in our case.

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For example, Zhao *et al.*[11] investigated the removal of phenol, indole and their mixtures *via* adsorption, but the initial concentration of phenol solution was only about 200 mg L^{-1}. Similarly, Zhang *et al.*[5] treated GA wastewater through an adsorption method using a type of biosorbent comprised of *Aspergillus oryzae*, obtaining effective performance, while the maximum initial concentration of GA solution was merely 120.64 mg L^{-1}. In this respect, liquid–liquid extraction using an organic solvent, which has significant advantages over treating high concentrated phenol wastewater,[12] is a better alternative because, in general, this method has simple operation, high selectivity and recyclability of extracted components.[8,13]

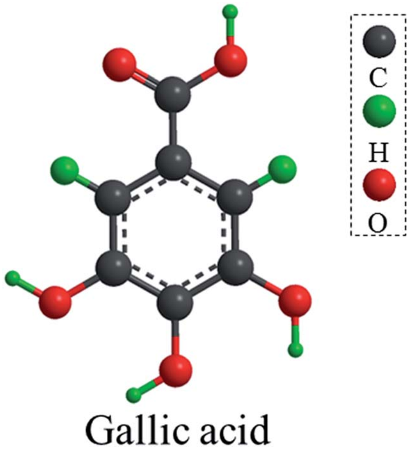
Liquid–liquid extraction is a popular method used for separation and generally uses esters, alcohols, alkylamines and trialkylphosphine oxides as the extraction solvents.[14,15] For instance, Jiang *et al.*[7] investigated the treatment of wastewater containing 6000 mg L^{-1} phenol using an extraction method, which showed highly effective performance with above 99% of the phenol being removed. Similarly, Liu *et al.*[16] used cumene as an extractant, which showed excellent performance for removing phenol. Zidi *et al.*[17] also noted that 90% of phenol was extracted using tributyl phosphate (TBP) as the extractant. TBP is one of the neutral organophosphorus extractants containing a phosphoryl group, which is a stronger Lewis base than carbonyl.[18,19] When compared to other solvents, TBP shows good extraction performance[20] due to its low solubility (450 mg L^{-1}) in water,[19] low cost, easy to implement and high flash point, which lowers the flammability potential.[21] TBP has been widely applied in the extraction of organic chemicals, such as phenol,[22,23] benzoic acid[24] and carboxylic acid,[25] and a higher degree of extraction can be obtained for hydrophobic chemicals.[21] However, for phenolic-type compounds with a carboxyl group also bound to the benzene ring (*e.g.* GA, Table 1), investigations on their extraction using TBP are rare. The extraction efficiency is generally low when applying TBP alone due to its viscous property. To achieve a good extraction efficiency, some organic diluents, for example *n*-octanol, 4-methyl-2-pentanone (MIBK), *n*-hexane and kerosene, are generally used along with TBP.[26,27] Wu *et al.*[6] illustrated TBP in kerosene is feasible to extract GA with a 93.7% extraction rate. Extraction solvents coupling TBP with one diluent have been widely investigated when extracting other organic pollutants,[7,21,23,24,27–29] while research on TBP combined with two different diluents in the extraction of organic pollutants, especially of GA, is rare. A diluent alone always has some disadvantages that may impact the extraction efficiency, but in the presence of another diluent, the disadvantages that both diluents have may make up for each other, eventually leading to a high extraction efficiency.[26] For example, MIBK has relatively high water solubility (Table 2) and along with *n*-hexane are common diluents, which can improve the physical properties of mixed solvents combined with the TBP extractant, which may lead to the better phase distribution of TBP between aqueous and organic phases, and eventually, better extraction performance.[30] Thus, a feasibility study for the

Table 2 The main properties of the solvents

Solvent	Density[a] (g cm^{-3})	Boiling point[a] (°C)	Melting point[a] (°C)	Water solubility at 20 °C (mg L^{-1})
TBP	0.98	289	−80	450[b]
MIBK	0.80	117–118	−84.7	19 000[a]
n-Hexane	0.70	69	−95	9.5[a]
n-Octanol	0.83	194–195	−15.5	0.30[b]
n-Hexanol	0.82	157	−0.44	5900[b]

[a] Data was obtained from the National Center for Biotechnology Information (NCBI). PubChem compound database: http://www.ncbi.nlm.nih.gov/pccompound. [b] Ref. 19.

Table 1 The main properties and the molecular structure of GA

Property	Description[a]	Molecular structure
Stability	Stable (but may discolour upon exposure to light), hygroscopic and incompatible with strong oxidizing agents, strong bases, acid chlorides and acid anhydrides	
Appearance	Colorless or slightly yellow crystalline needles or prisms	
Safety	Inhalation of dust may irritate nose and throat. Contact with eyes or skin causes irritation	
Melting point	222–240 °C	
Density	1.69 g cm^{-3}	
Water solubility	11 900 mg L^{-1} (20 °C)	
Molar mass	266.32 g mol^{-1}	

[a] Data was obtained from the National Center for Biotechnology Information (NCBI). PubChem compound database: http://www.ncbi.nlm.nih.gov/pccompound.

application of TBP combined with two diluents in the extraction treatment of GA and investigating the effect of different operating variables on its application is of great interest.

In this study, both model and actual GA processing wastewater were investigated. For model wastewater, two kinds of mixed extraction solvent, TBP combined with MIBK and *n*-hexane, and TBP combined with *n*-octanol were investigated. As a comparison, the physical extractant *n*-hexanol alone was also investigated. The effects of some important variables, such as the component proportion in the mixed extraction solvent, stirring speed, extraction time, pH, phase ratio (extraction solvent/GA solution), temperature and salt on the extraction rate were examined. A Box–Behnken design was applied to determine the optimum conditions for GA extraction and also to explain the relationship between GA extraction rate and three pertinent parameters (*i.e.* pH, temperature and phase ratio). Stripping of the GA-accumulated organic phase was also implemented to recover the GA and reuse the extractants for the most effective extraction solvent. The FT-IR spectra of the organic phase manifested the different mechanisms of the three kinds of extractants. Finally, the extraction of GA from actual wastewater was conducted using the most effective extraction solvent based on the optimized operation conditions obtained through Box–Behnken design and stripping.

2 Materials and methods

2.1 Materials and reagents

Tributyl phosphate (TBP) (purity > 98.5%), *n*-hexanol (purity > 98%), 4-methyl-2-pentanone (MIBK) (purity > 99%), *n*-octanol (purity > 99%) and *n*-hexane (purity > 97%) were the product of Sinopharm Chemical Reagent Co. Ltd. (China). NaOH, concentrated sulfuric acid and GA were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. (China). All the chemicals used in this work were of analytical grade and used without further treatment. Deionized water produced by UPT-II-40 (Ulupure, Chengdu, China) was used throughout the experiments. The actual GA processing wastewater, mainly containing GA, tannic acid and a large amount of pigment, was obtained from a company in Guizhou province, China. The GA concentration in the actual wastewater was approximately 24 000 mg L^{-1}. The main properties of the solvents in this research are shown in Table 2.

2.2 Procedures

2.2.1 Univariate crossover extraction experiment for model GA wastewater. Model GA wastewater with an initial concentration of 6000 mg L^{-1} was prepared by dissolving GA into deionized water, due to its approximate water solubility of 11 000 mg L^{-1}. However, the initial concentration of GA was varied from 1000 mg L^{-1} to 10 000 mg L^{-1}, when investigating the effect of the different initial concentration of GA. TBP was mixed with *n*-hexane and MIBK or *n*-octanol and *n*-hexane to form the two integrated extraction solvents, namely TBP/MIBK/*n*-hexane and TBP/*n*-octanol/*n*-hexane, respectively. *n*-Hexanol was used as the physical extractant for comparison.

A typical set of extraction experiments was designed and carried out as follows: all the extractive experiments were conducted in a 150 mL flask. The extraction solvent and GA aqueous solution were added to each flask after adjusting the pH of the aqueous solution with sulfuric acid or NaOH solution. The flask containing the mixture was then placed in a stirred thermostatted batch system (putian SHA-A, China) shaken for 15 min at the desired temperature. Then, the agitated mixtures were transferred to a 150 mL separation funnel and left to equilibrate for 10 min followed by separation of the two phases. The aqueous phase was subsequently analyzed for further quantification.

2.2.2 FT-IR spectra used for extraction mechanism. In order to characterize the organic phases before and after extraction, Fourier transform infrared (FTIR) spectroscopy was used. FT-IR spectroscopy is a chemical microenvironment sensitive and functional group characteristic technique. The FTIR spectra were recorded on a Nicolet 6700 IR spectrometer with a demountable KBr slice. All spectra were recorded at a resolution of 4 cm^{-1} with 32 scans and the infrared spectrum was taken in the range of 4000–400 cm^{-1}.

2.2.3 Box–Behnken design optimization experiment. According to the results of the univariate crossover experiment, a Box–Behnken design was employed to optimize the significant factors (*i.e.* pH, temperature and phase ratio) and the results were analyzed using the response surface method.[5,29] Then, extraction experiments of model wastewater using three extraction solvents were conducted based on the optimized operation conditions.

2.2.4 Stripping for model wastewater. For the most effective extraction solvent in this study (*i.e.* TBP/MIBK/*n*-hexane) according to results of the univariate crossover experiment, the upper organic phase was stripped to recover GA and the organic extractant solution reused in the next cycle. After extracting GA, the upper organic phase was transferred to another 150 mL separation funnel and then, an equal volume of 0.2 mol L^{-1} of NaOH solution was added and mixed. The funnel was then held stationary for 30 min to reach equilibrium. Finally, the GA concentration in the aqueous phase was measured. To achieve the complete recovery of GA, a multi-stage stripping process was also implemented. The effect of NaOH concentration on the stripping and extractive capacity of reused extractant was also investigated.

2.2.5 Extraction and stripping for actual wastewater. To maintain the same GA initial concentration with that in our prior univariate crossover experiments (*i.e.* 6000 mg L^{-1}), actual wastewater was diluted four times before the extraction experiments. The actual wastewater was extracted through one-stage and four-stage processes using TBP/MIBK/*n*-hexane based on the optimized operation conditions obtained by Box–Behnken design. After extraction, the upper organic phase was also stripped to recover the GA.

2.3 Analysis

2.3.1 GA concentration. A UV visible spectrophotometer (Shimadzu UV-2550, Japan) was used to measure the GA

Table 3 The experimental parameters and level coding of the Box–Behnken design (BBD)

Parameters	Range and levels −1	0	+1
pH, X_1	0.5	1.75	3
Temperature, X_2 (°C)	30	40	50
Phase ratio, X_3	0.2	0.6	1

concentration in the aqueous phase at the related wavelength of 272 nm. Then, the extraction rate (E) was determined based on:

$$E\ (\%) = (C_0V_0 - C_rV_r)/C_0V_0 \times 100\% \quad (1)$$

$$\text{Distribution rate} = (C_0V_0 - C_rV_r)/C_rV_r \quad (2)$$

where C_0 and C_r represent the GA concentration in the aqueous solution before and after the extraction process, respectively. V_0 is the volume of GA aqueous solution before extraction and V_r is volume after the extraction process. The GA concentration in the organic phase was calculated through material balance calculations.

2.3.2 Response surface method (RSM). Three parameters, pH, X_1 (0.5–3), temperature, X_2 (30–50 °C) and phase ratio, X_3 (0.2–1.0) were obtained and the corresponding value ranges were selected based on the results of the previous univariate analysis. These three parameters demonstrated the largest effect on the extraction rate in the previous univariate crossover experiment and were further optimized by RSM. The statistical software Design Expert 8.0.5 was used for analysis. Box–Behnken design (BBD), which is a standard of RSM, was developed with three parameters at three levels (Table 3). The extraction rate was used as the response variable. The response was fitted using a poly-nominal regression equation to obtain an empirical model for the best response with three independent parameters. The mathematical form is described as follows:

$$Y = \beta_0 + \sum\beta_iX_i + \sum\beta_{ii}X_i^2 + \sum\beta_{ij}X_iX_j \quad (3)$$

where Y is the response, β_0, β_i, β_{ii} and β_{ij} are the coefficients of the intercept, linear, square and interaction effects, respectively. The optimum response (Y_{opt}) and corresponding process parameters were also determined. The analysis was conducted through a 3D response surface method (RSM) and the model was estimated using variance (ANOVA) tests. The quality of the polynomial model was analyzed by correlation coefficient (R^2) and its statistical significance was evaluated using an F-test (F: degree of freedom). The model terms were expressed based on the P-value (P: probability).

3 Results and discussion

3.1 The effect of various parameters on GA extraction

3.1.1 The component proportion in the mixed extraction solvent. As shown in Fig. 1, TBP exhibited high extractive activity. When compared between both the mixed extraction solvents, the extraction rate of GA was higher in the presence of MIBK than in the presence of *n*-octanol, showing that MIBK as a diluent has a greater positive effect on the extraction behavior. For example, when the volume ratio was 1 : 4 : 1, the extraction rate containing the diluent MIBK or *n*-octanol was 84.9% and 73.7%, respectively. For both the mixed extraction solvents, when the proportion ratio between the other two components remained constant, the extraction rate increased as the proportion of TBP increased, decreased slightly with an increase in the proportion of MIBK or *n*-octanol, but decreased sharply as the proportion of *n*-hexane increased.

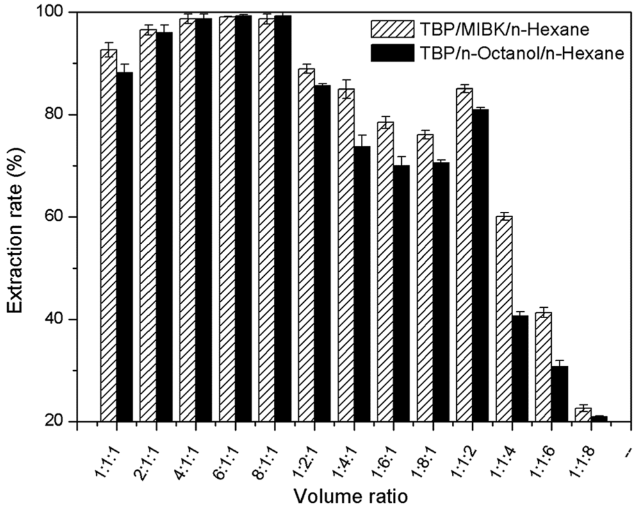


Fig. 1 The effect of the component proportion in TBP/MIBK/*n*-hexane and TBP/*n*-octanol/*n*-hexane on the GA extraction rate (initial concentration of GA = 6000 mg L^{-1}, extraction time = 20 min, pH = 1.5, stirring speed = 200 rpm, phase ratio = 1, T = 30 °C, extraction times = 1).

It is obvious that the extraction rate reached nearly 99.9% when the relative proportion of the three components for both extraction solvents was 6 : 1 : 1 or 8 : 1 : 1, respectively. However, during the experiment, because a third phase (emulsion phase) was generated at the interface between the aqueous phase and the organic phase, complete stratification between the organic phase (extraction solvent) and aqueous phase (GA solution) was noticed and required a long time to separate when the TBP proportion was higher than 30%, resulting in low time-related efficiency for the extraction despite the high extraction rate. Thus, in the actual application of these mixed extraction solvents, the proportion of TBP was more appropriate below 30%.

In the experiment, it was observed that the emulsification phenomenon significantly improved in the presence of *n*-hexane, which demonstrated the great demulsifying ability of *n*-hexane. However, the sharp decrease in the extraction rate as the *n*-hexane proportion was increased demonstrated that a high proportion of *n*-hexane in the mixed extraction solvent had a negative impact on the extraction process; taking the extractant of TBP/MIBK/*n*-hexane, for example, as the volume rate was changed from 1 : 1 : 1 to 1 : 1 : 8, the extraction rate decreased from 92.6% to 22.6%, respectively. This was probably due to the highly hydrophobic nature of *n*-hexane, which may increase the hydrophobicity of the mixed extraction solvent in the presence of a high proportion of *n*-hexane that prevents the efficient distribution of GA, which is a polar organic acid, into the hydrophobic extraction solvent and consequently leads to a significant decrease in the extraction rate.[28] Meanwhile, in the mixed extraction solvent, as the proportion of the TBP extractant decreases as the proportion of *n*-hexane as the diluent increased, this may also result in a decrease in the GA extraction rate. In addition, mixtures of polar and non-polar diluents can significantly reduce the separation time and emulsion formation, this similar result was consistant with Morales *et al.*[30] Thus, to obtain both a high extraction rate and high extraction efficiency, the proportion of TBP and *n*-hexane should be controlled at an appropriately low level. Overall, based on results shown in Fig. 1, for both mixed extraction solvents, the volume proportion of three components was selected to be 1 : 2 : 1 for the subsequent experiments investigating the effect of other parameters on the extraction of GA.

3.1.2 Extraction time. As shown in Fig. 2, the extraction rate increased significantly before 50 s of extraction time, the highest extraction rate for TBP/MIBK/*n*-hexane, TBP/*n*-octanol/*n*-hexane and *n*-hexanol were 85.3%, 84.1% and 75.8%, respectively and then remained constant from 50 to 300 s. For all three extraction solvents, the effect of the extraction time on the extraction rate retained a similar trend, showing the different properties of the extractants had little influence in this case. These results indicated that the extraction proceeded rapidly and the time required to achieve the extraction equilibrium was less than 60 s (in order to make sure of an established equilibrium) and the mixed solvents could remove GA efficiently. Therefore, 60 s was used in the subsequent univariate analyses of the rest.

3.1.3 pH. Previous studies have claimed that the extraction performance was significantly affected by the pH (ref. 6, 7 and 22) and it was also confirmed by the results shown in Fig. 3. As shown in Fig. 3, the range of pH was varied from 0.5 to 10 and the extraction rate decreased slightly as the pH was increased below 3. When the pH was higher than 3, the extraction rate evidently declined upon a further increase in the pH until the pH reached 7 and then increased slightly in the range of pH > 7. GA strongly relies on the pH value of the aqueous solution and this behavior resembled the charge characteristic of the GA solution at different pH values. The GA dissociation constants, pK_{a1}, pK_{a2}, pK_{a3} and pK_{a4} in an aqueous phase were 4.16, 8.55, 11.44 and 12.80,[6] respectively, which ionized in the aqueous phase *via* a multistage ionization process:

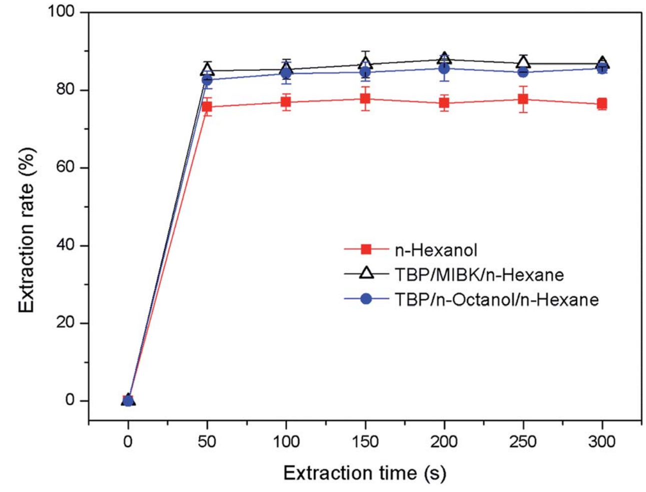


Fig. 2 The effect of extraction time on the GA extraction rate (initial concentration of GA = 6000 mg L^{-1}, the component proportion in the mixed extraction solvent = 1 : 2 : 1, pH = 1.5, stirring speed = 200 rpm, phase ratio = 1, T = 30 °C, extraction times = 1).

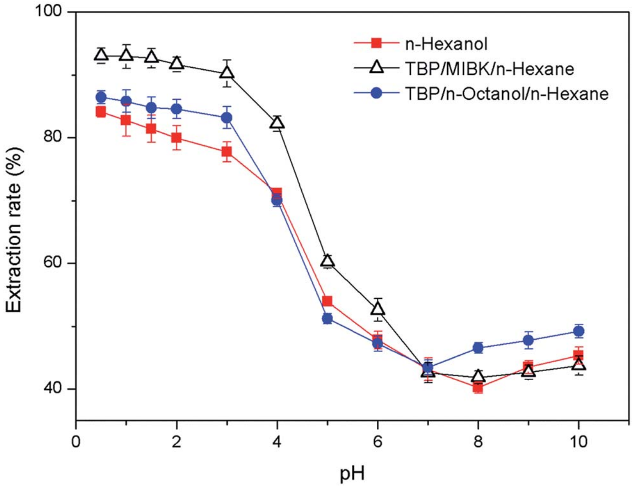


Fig. 3 The extraction rates at different pH (initial concentration of GA = 6000 mg L^{-1}, the component proportion in the mixed extraction solvent = 1 : 2 : 1, extraction time = 60 s, stirring speed = 200 rpm, phase ratio = 1, T = 30 °C, extraction times = 1).

$$GA \rightleftharpoons GA^{-} + GA^{2-} + GA^{3-} + GA^{4-} + nH^{+}$$

The highest pH investigated in the study was 10 ($<pK_{a3}$), therefore the GA molecule can only undergo at most a two-stage ionization, resulting in GA existing at most in the form of GA, GA^{-} and GA^{2-} throughout our experiments. When the pH was lower than 3, which was below pK_{a1}, GA had little ionization and existed exclusively in the GA form in the aqueous phase. Thus, the majority of GA was validly extractive from the aqueous solution and the pH exhibited a small influence on the extraction rate (Fig. 3). When compared between three extraction solvents, the extraction rate at the same pH followed the order of TBP/MIBK/*n*-hexane > TBP/*n*-octanol/*n*-hexane > *n*-hexanol when the pH was below 3. These results may also be explained by the variation of the molar fraction of undissociated GA; TBP combined with GA can forming very weak hydrogen bonds with hydroxyl groups and the different diluents had different abilities to TBP.[15,22] As the pH gradually increased beyond pK_{a1} or pK_{a2}, however, more and more GA molecules dissociate into GA^{-} or GA^{2-}, the ionic form, leading to less GA molecules that can readily distribute into the extraction solvent and consequently, a decrease in the extraction rate.[6,22] The slight increase in extraction rate at pH > 7 was probably caused by the fact that GA was not stable under alkaline conditions and easily degraded.[31] The decreased amount of GA that was due to degradation under alkaline conditions would introduce an error in the calculation of the extraction rate when applying eqn (1) and consequently, resulted in the calculated extraction rate being higher than the actual value. As the original pH of the model wastewater before adjustment was about 1.5 at which the extraction rate already exhibited a high value (Fig. 3), further experiments were conducted under the acidic conditions of pH 1.5 for investigating the other factors.

3.1.4 Stirring speed. As shown in Fig. 4, for the three extraction solvents, there was a sharp increase in the GA extraction rate with a stirring speed from 0 to 50 rpm. Then, the extraction rate increased slowly upon increasing the stirring speed to 100 rpm and stabilized when the stirring speed continued increasing; the extraction rate for the extractant of TBP/MIBK/*n*-hexane, TBP/*n*-octanol/*n*-hexane and *n*-hexanol reached up to 88.1%, 84.6% and 76.8%, respectively. A lower

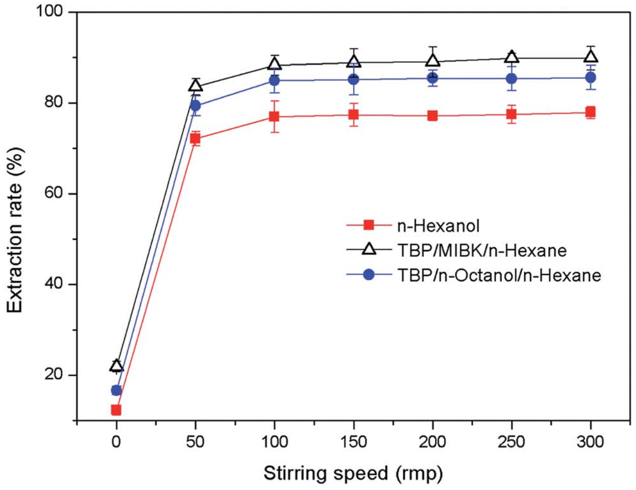


Fig. 4 The effect of the stirring speed on the GA extraction rate (initial concentration of GA = 6000 mg L^{-1}, component proportion in the mixed extraction solvent = 1 : 2 : 1, extraction time = 60 s, pH = 1.5, phase ratio = 1, T = 30 °C, extraction stage = 1).

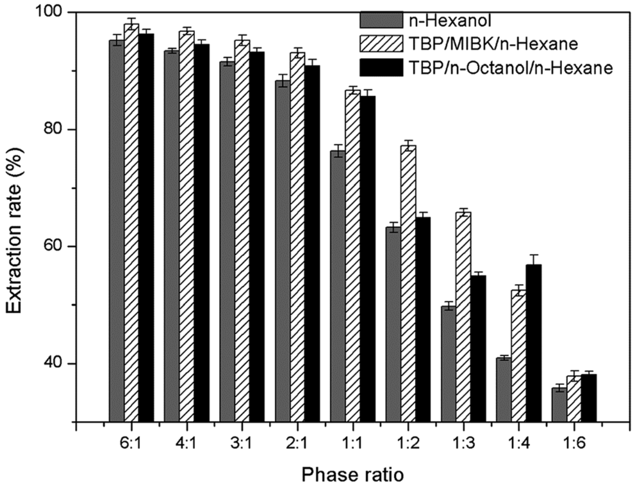


Fig. 5 The effect of the phase ratio on the GA extraction rate (initial concentration of GA = 6000 mg L^{-1}, the component proportion in the mixed extraction solvent = 1 : 2 : 1, extraction time = 60 s, pH = 1.5, stirring speed = 150 rpm, T = 30 °C, extraction times = 1).

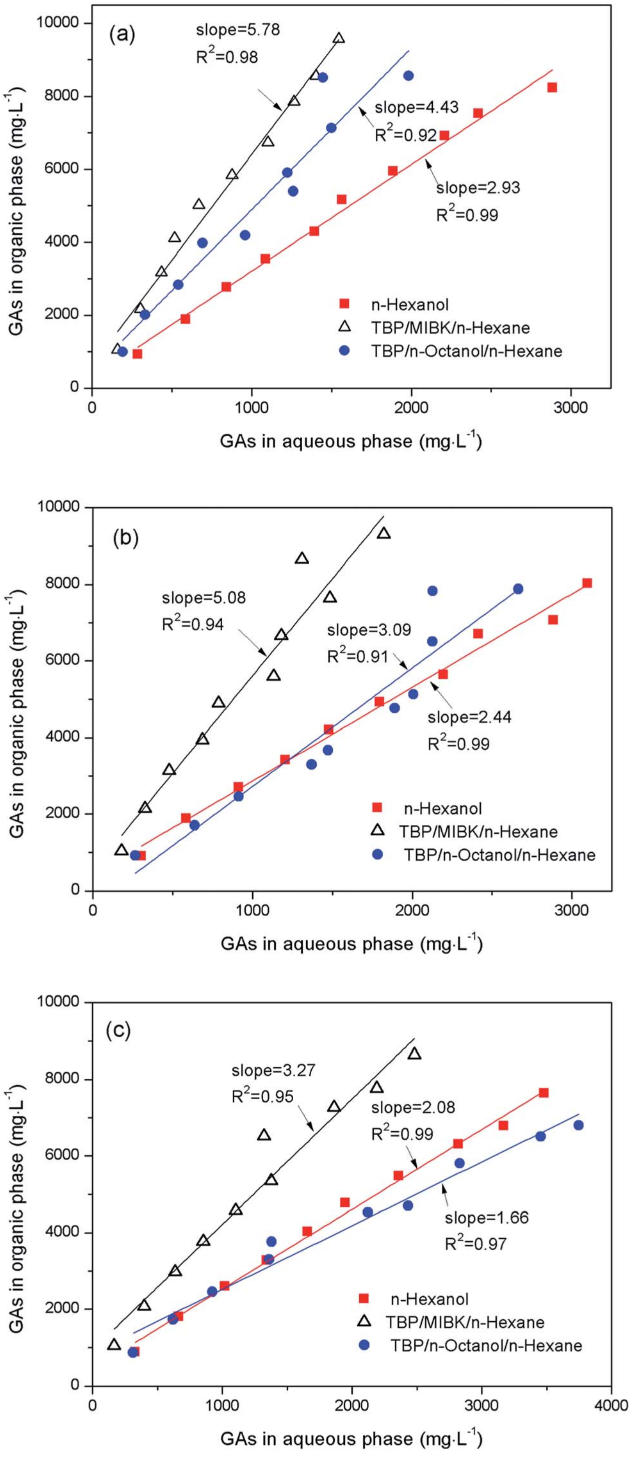


Fig. 6 The extraction isotherms obtained for GA at (a) 30 °C, (b) 40 °C and (c) 50 °C (initial concentration of GA = 6000 mg L^{-1}, the component proportion in the mixed extraction solvent = 1 : 2 : 1, extraction time = 60 s, pH = 1.5, stirring speed = 150 rpm, phase ratio = 1, extraction times = 1).

Table 4 The effect of different salts on the GA extraction rate using the three kinds of extraction solvents. Note, the concentration of all the salts was 1 mol L^{-1}, initial concentration of GA = 6000 mg L^{-1}

	n-Hexanol	TBP/MIBK/*n*-hexane	TBP/*n*-octanol/*n*-hexane
Salt	Extraction rate (%)	Extraction rate (%)	Extraction rate (%)
NaCl	82.1	93.5	89.8
$NaSO_4$	80.7	91.9	86.1
KCl	79.1	90.5	85.3
KNO_3	77.9	90.4	85.3
$CaCl_2$	87.2	94.7	91.4
$NaNO_3$	77.8	91.0	85.7
$MgCl_2$	91.8	96.6	94.9
Control	77.1	90.3	85.3

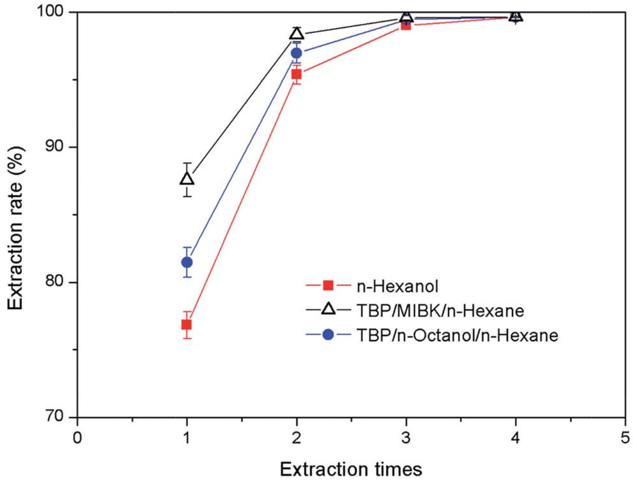


Fig. 7 The effect of extraction stage on the GA extraction rate (initial concentration of GA = 6000 mg L^{-1}, the component proportion in the mixed extraction solvent = 1 : 2 : 1, extraction time = 60 s, pH = 1.5, stirring speed = 150 rpm, phase ratio = 1, *T* = 30 °C).

stirring speed often leads to a lower speed of mass transfer, since the extraction of GA was also a distribution process of GA between an organic phase and aqueous phase, which is largely affected by the degree of mixing of both phases. Fig. 4 demonstrated that thoroughly mixing the extractant and GA solution can be obtained at relatively low stirring speed (*e.g.* 100 rpm). When comparing between the three extraction solvents, the extraction rate at a same stirring speed follows in the order of TBP/MIBK/*n*-hexane ≈ TBP/*n*-octanol/*n*-hexane > *n*-hexanol (Fig. 4), showing that the TBP extractant has stronger extraction ability than *n*-hexanol. For a high value of the extraction rate, 150 rpm was chosen as the stirring speed for mixing in the other experiments.

3.1.5 Phase ratio. As shown in Fig. 5, the extraction rate for TBP/*n*-octanol/*n*-hexane in the phase ratios of 6 : 1, 1 : 1 and 1 : 6 were 96.2%, 83.9% and 38.1%, respectively. The extraction rate decreased slightly as the phase ratio between the extraction solvent and GA aqueous solution decreased from 6 : 1 to 1 : 1 and then sharply decreased with the phase ratio continuing decreasing to 1 : 6. This demonstrated that a high extraction rate benefits from a large volume of extraction solvent. This is because a larger volume of extraction solvent has the capability to extract a greater amount of GA. However, at a phase ratio of 1 : 1, the extraction rate was already high enough and changed little, as the phase ratio became larger than 1 : 1, the extraction rate was not increased significantly but the volume of extractants increased largely, which had disadvantages to industrial applications and cost saving. Thus, 1 : 1 was the chosen as the operation volume ratio between the extraction solvent and GA aqueous solution in the following investigations. When comparing between the three extraction solvents at the same phase ratio, it was shown that the extraction rate follows the order: TBP/MIBK/*n*-hexane ≈ TBP/*n*-octanol/*n*-hexane > *n*-hexanol (Fig. 5), which is consistent with the trends found for the effects of the previously investigated factors, showing that the TBP extractant has a stronger extraction ability than *n*-hexanol.

3.1.6 The initial concentration of GA and temperature. As shown in Fig. 6, after extraction, when the extraction

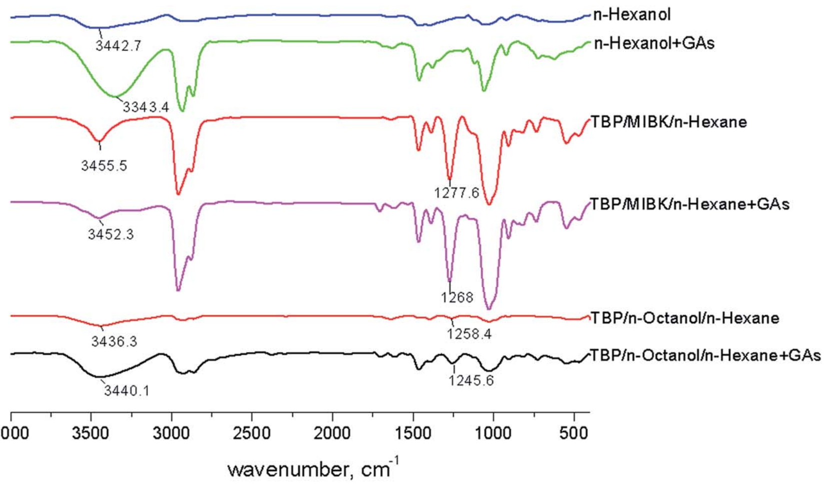


Fig. 8 The IR spectra of the extractants and extracted complex.

Table 5 The Box–Behnken design (BBD) and its results

	Coded values			*n*-Hexanol			TBP/MIBK/*n*-hexane			TBP/*n*-octanol/*n*-hexane		
Run	X_1	X_2	X_3	Y_{exp}	Y_{pred}	Residual	Y_{exp}	Y_{pred}	Residual	Y_{exp}	Y_{pred}	Residual
1	−1	0	1	75.1	74.7	0.39	89.0	88.7	0.33	76.2	76.3	−0.15
2	0	−1	−1	38.8	39.0	−0.23	40.2	39.9	0.03	46.9	47.0	−0.13
3	−1	1	0	59.3	59.9	−0.63	76.0	76.0	−0.01	68.5	68.4	0.02
4	0	−1	1	77.3	77.3	0.03	87.7	87.2	0.53	85.6	84.8	0.84
5	1	0	1	72.6	73.2	−0.66	80.7	81.2	−0.54	73.2	74.0	−0.82
6	0	1	−1	35.5	35.6	−0.03	39.4	39.9	−0.53	37.1	38.0	−0.84
7	1	−1	0	63.6	63.0	0.63	76.0	76.0	0.01	73.7	73.7	−0.02
8	0	0	0	65.0	65.4	−0.32	72.1	72.6	−0.55	61.7	61.5	0.19
9	0	0	0	65.0	65.7	−0.37	72.0	72.6	−0.64	60.8	61.5	−0.68
10	0	1	1	70.1	69.9	0.23	78.91	79.23	−0.32	75.2	75.1	0.13
11	1	1	0	60.6	60.2	0.42	77.1	76.3	−0.86	64.0	63.3	0.69
12	−1	−1	0	67.6	68.0	−0.42	83.4	84.2	−0.86	76.1	76.8	−0.69
13	1	0	−1	35.6	36.0	−0.40	41.0	41.4	−0.33	34.9	34.7	0.15
14	−1	0	−1	40.0	39.3	0.66	42.5	41.9	0.05	41.5	40.7	0.82
15	0	0	0	66.0	65.4	0.65	73.2	72.6	0.57	62.4	61.5	0.85
16	0	0	0	65.2	65.4	−0.15	72.7	72.6	0.07	61.2	61.5	−0.31
17	0	0	0	65.5	65.4	0.18	73.1	72.6	0.53	61.5	61.5	−0.07

equilibrium was reached, the GA concentration in the organic phase (abscissa) and aqueous phase (vertical axis) were analysed and the initial concentration of GA was obtained. For the three extraction solvents at 30 °C, 40 °C and 50 °C, the correlation coefficient (R^2) of isotherm fitting lines were all beyond 0.9, demonstrating that the initial concentration of GA had little impact on the extraction rate and the features of the different initial concentrations on the extraction were similar. This was consistent with the results of Liu *et al.*[16] Moreover, this phenomenal proved that the extraction method was suitable for a wide range of concentrations. In addition, for the extractants TBP/MIBK/*n*-hexane; TBP/*n*-octanol/*n*-hexane and *n*-hexanol, the distribution rate was 5.78, 4.43 and 2.93 in 30 °C, 5.08, 3.09 and 2.44 at 40 °C, and 3.27, 1.66 and 2.08 at 50 °C, respectively. Thus, for each extraction solvent, the distribution rate of GA between the organic phase and aqueous phase (namely the slope of the isotherm fitting line) decreased as the temperature increased from 30 °C to 50 °C. For *n*-hexanol, the decrease upon increasing temperature was not obvious. However, for both mixed extraction solvents, an obvious decrease was observed, indicating that the mixed extractants were sensitive to temperature and raising the temperature has a negative influence on interaction between the components of mixed extractants. The other reason was probably the weak intermolecular hydrogen bonds are much stronger at low temperature[15] and raising the temperature leads to a sharp decrease in the GA extraction rate with the extractants TBP/MIBK/*n*-hexane and TBP/*n*-octanol/*n*-hexane. So, when the temperature increased, the slope for the

Table 6 Analysis of variance (ANOVA) for the GA extraction rate with *n*-hexanol[a]

Source	SS[b]	DF[b]	MS[b]	F^b	P^b ($\times 10^{-2}$)	CE[b]
Model[b]	3045	9	338	750	<0.01	
pH, X_1	11.4	1	11.4	25.2	0.15	−1.19
Temperature, X_2	58.2	1	58.2	129	<0.01	−2.70
Phase ratio, X_3	2636	1	2636	5851	<0.01	18.2
X_1X_2	7.02	1	7.02	15.6	0.55	1.32
X_1X_3	0.78	1	0.78	1.74	22.9	0.44
X_2X_3	3.84	1	3.84	8.53	2.23	−0.98
X_1^2	5.03	1	5.03	11.2	1.24	−1.09
X_2^2	9.41	1	9.41	20.9	0. 26	−1.50
X_3^2	300	1	300	666	<0.01	−8.44
Residual	3.15	7	0.45			
Lack of fit	2.44	3	0.81	4.53	8.91	
Pure error	0.72	4	0.18			
Cor. total	3048	16				

[a] S.D. = 0.67; C.V. = 1.12%; *R*-Sq = 0.9990; *R*-Sq(Adj) = 0.9976; *R*-Sq(Pred) = 0.9868; adeq. precision = 81.0. [b] SS: sum of square; DF: degree of freedom of the different sources; MS: mean of square; *F*: degree of freedom; *P*: probability; CE: coefficient estimate.

Table 7 Analysis of variance (ANOVA) for the GA extraction rate with TBP/MIBK/*n*-hexane[a]

Source	SS[b]	DF[b]	MS[b]	F^b	P^b ($\times 10^{-2}$)	CE[b]
Model[b]	4060	9	512	821	<0.01	
pH, X_1	32.1	1	32.1	51.5	0.02	−2.00
Temperature, X_2	31.5	1	31.5	50.6	0.02	−1.99
Phase ratio, X_3	3747	1	3747	6010	<0.01	21.6
X_1X_2	17.9	1	17.9	28.6	0.11	2.11
X_1X_3	12.0	1	12.0	19.2	0.32	−1.73
X_2X_3	15.6	1	15.6	25.1	0.15	−1.98
X_1^2	55.6	1	55.6	89.2	<0.01	3.63
X_2^2	15.2	1	15.2	24.3	0.17	1.90
X_3^2	706	1	706	1132	<0.01	−12.7
Residual	4.36	7	0.62			
Lack of fit	3.04	3	1.01	3.07	15.4	
Pure error	1.32	4	0.33			
Cor. total	4611	16				

[a] S.D. = 0.79; C.V. = 1.14%; *R*-Sq = 0.9991; *R*-Sq(Adj) = 0.9978; *R*-Sq(Pred) = 0.9890; adeq. precision = 80.5. [b] SS: sum of square; DF: degree of freedom of the different sources; MS: mean of square; *F*: degree of freedom; *P*: probability; CE: coefficient estimate.

Table 8 Analysis of variance (ANOVA) for the GA extraction rate with TBP/*n*-octanol/*n*-hexane[a]

Source	SS[b]	DF[b]	MS[b]	F^b	P^b ($\times 10^{-2}$)	CE[b]
Model[b]	3436	9	381.81	524.51	<0.01	
pH, X_1	34.6	1	34.61	47.55	0.02	−2.08
Temperature, X_2	176	1	176	242	<0.01	−4.69
Phase ratio, X_3	2804	1	2804	3851	<0.01	18.7
X_1X_2	1.00	1	1.00	1.37	28.0	−0.50
X_1X_3	3.39	1	3.39	4.65	6.79	0.92
X_2X_3	0.09	1	0.09	0.12	73.6	−0.15
X_1^2	19.1	1	19.1	26.2	0.14	2.13
X_2^2	201	1	201	276	<0.01	6.91
X_3^2	219	1	217	300	<0.01	−7.21
Residual	5.10	7	0.73			
Lack of fit	3.77	3	1.26	3.81	11.5	
Pure error	1.32	4	0.33			
Cor. total	3441	16				

[a] S.D. = 0.85; C.V. = 1.37%; *R*-Sq = 0.9985; *R*-Sq(Adj) = 0.9966; *R*-Sq(Pred) = 0.9819; adeq. precision = 76.5. [b] SS: sum of square; DF: degree of freedom of the different sources; MS: mean of square; *F*: degree of freedom; *P*: probability; CE: coefficient estimate.

extractants TBP/MIBK/*n*-hexane (5.78 to 3.27) and TBP/*n*-octanol/*n*-hexane (4.43 to 1.66) decreased sharply, but the slope for the extractant *n*-hexanol (2.93 to 2.08) decreased slowly, leading to a cross at high temperature (*e.g.* 40 °C and 50 °C). This is consistent with the results of Lee *et al.*[32] Thus, the extraction procedure was preferably conducted at 30 °C or room temperature to obtain a high extraction rate in this study.

3.1.7 Salts. In the actual production, the wastewater generally contains a variety of different salts. The effect of some typical kinds of salt ions was also investigated in this study. As presented in Table 4, for the three extraction solvents, a slight increase in the extraction rate of GA occurred in the presence of salt ions when compared to the control. This can result from the reduced mutual solubility between these solvents and water in the presence of salts and was also attributed to the hydrophobic nature of these extractants (such as TBP and *n*-hexanol). The reduced solubility of the extractants in water can make the organic layer rich in the extraction solvent phase, which is favorable for an improvement in the extraction rate. Meanwhile, the hydrophobicity of the extractants is also advantageous for a high extraction efficiency as there will be less co-extraction of water in the solvent phase.[33] Nevertheless, due to the slight increase in the extraction rate in the presence of salt on the whole, the effect of salt was not needed to be considered in the experiments.

3.1.8 Extraction stage. As shown in Fig. 7, the extraction rate of GA using the three solvents, TBP/MIBK/*n*-hexane, TBP/*n*-octanol/*n*-hexane and *n*-hexanol was 88.2%, 82.5% and 76.7%, respectively, through a one-stage extraction process based on the various influencing parameters determined

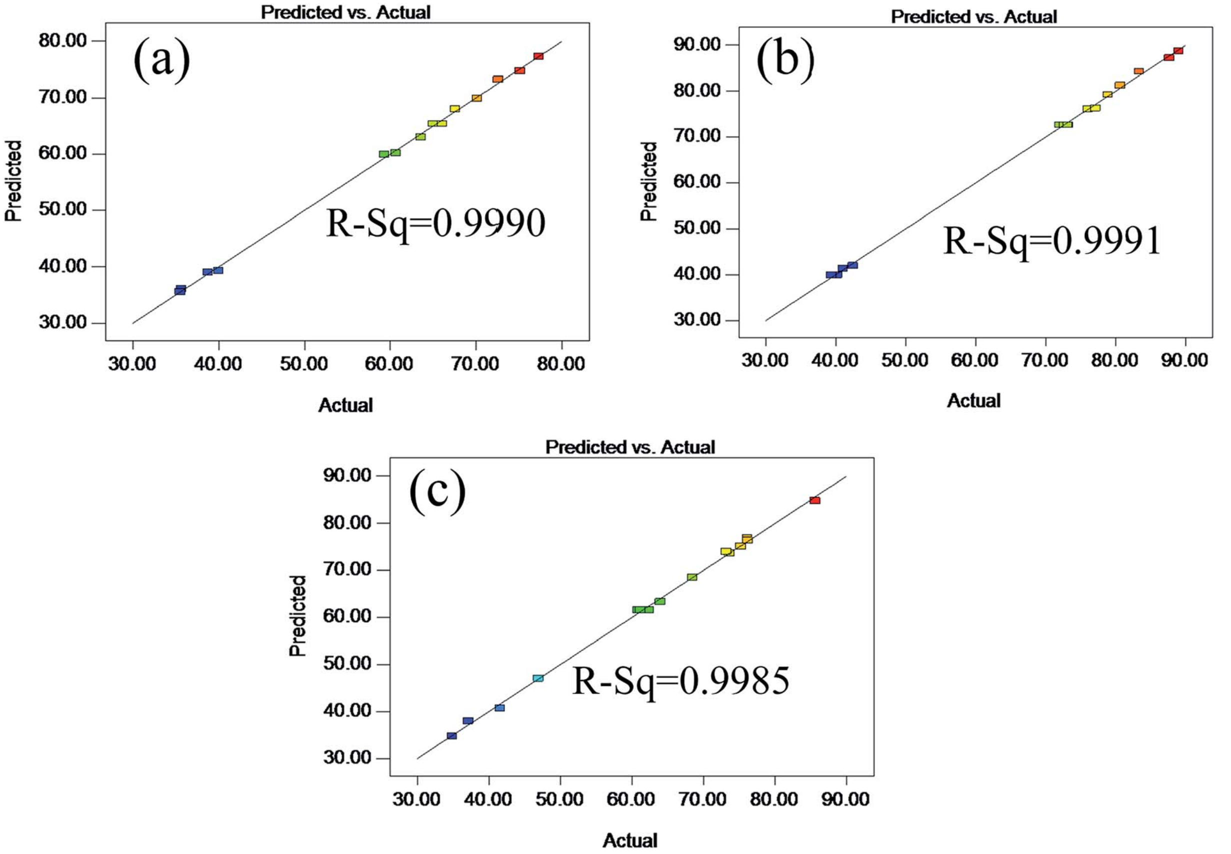


Fig. 9 A comparison of the experimental results with those calculated *via* the BBD resulted equation using (a) *n*-hexanol, (b) TBP/MIBK/*n*-hexane and (c) TBP/*n*-octanol/*n*-hexane.

as mentioned above. After increasing the stage to four, the extraction rate of these solvents all reached nearly around 99.6%. Hence, the deep removal of GA could be realized successfully through a four-stage extraction in this case, which is similar to the investigation reported by Wu *et al.*,[6] who obtained a 93.7% extraction rate using a six-stage extraction process. It can be inferred that the deep removal of GA from actual wastewater can be obtained through an appropriate multi-stage extraction process with a consideration of the efficiency and cost.

3.2 Extraction mechanism

As shown in Fig. 8, the IR spectra of *n*-hexanol after extracting GA differ obviously from *n*-hexanol in the 3500–2500 cm^{-1} range, due to the introduction of hydroxyl and carboxyl groups when extracting GA, whereas there is little difference in the 2500–400 cm^{-1} range, showing the physical nature of *n*-hexanol when extracting GA. In contrast, for TBP/MIBK/*n*-hexane or TBP/*n*-octanol/*n*-hexane, the IR spectra in the 3500–2500 cm^{-1} range differ slightly before extracting GA from that observed after extraction. This can be explained by the existence of the carbonyl group in numerous MIBK (50% of total extraction solvent volume) or hydroxyl groups in *n*-octanol (also 50% of total extraction solvent volume), respectively. Among the 2500–400 cm^{-1} range, the band from 1210 to 1320 cm^{-1} was assigned to the stretching vibration of P=O in TBP.[34] For TBP/MIBK/*n*-hexane and TBP/*n*-octanol/*n*-hexane, the characteristic peak for P=O shifted from 1277.6 to 1268.0 cm^{-1} and from 1258.4 to 1245.6 cm^{-1}, respectively, after extracting GA. This result manifested that weak intermolecular hydrogen bonding P=O···HO was probably formed and contributed to the extraction of GA by TBP.[35,36]

3.3 Optimization by Box–Behnken design

The pH (X_1), temperature (X_2) and phase ratio (X_3), determined by the previous univariate analysis, were chosen in the Box–Behnken design (BBD) with three parameters and three levels. In the study, 51 experimental observations were taken randomly for the optimization of the GA extraction rate using the three extraction solvents. The experimental parameters and levels are listed in Table 3. The results of the response surface method (RSM) were used to perform the analysis of variance (ANOVA) using Expert Design 8.0.6 software and the experimental results were analyzed to obtain an empirical model for the best response. The final quadratic poly-nominal regression equation was fitted as follows:

GA extraction rate (Y)

$$Y_1 = 65.36 - 1.19X_1 - 2.70X_2 + 18.15X_3 + 1.32X_1X_2 + 0.44X_1X_3 - 0.98X_2X_3 - 1.09{X_1}^2 - 1.50{X_2}^2 - 8.44{X_3}^2$$

$$Y_2 = 72.60 - 2.00X_1 - 1.99X_2 + 21.64X_3 + 2.11X_1X_2 - 1.73X_1X_3 - 1.98X_2X_3 + 3.63{X_1}^2 + 1.90{X_2}^2 - 12.95{X_3}^2$$

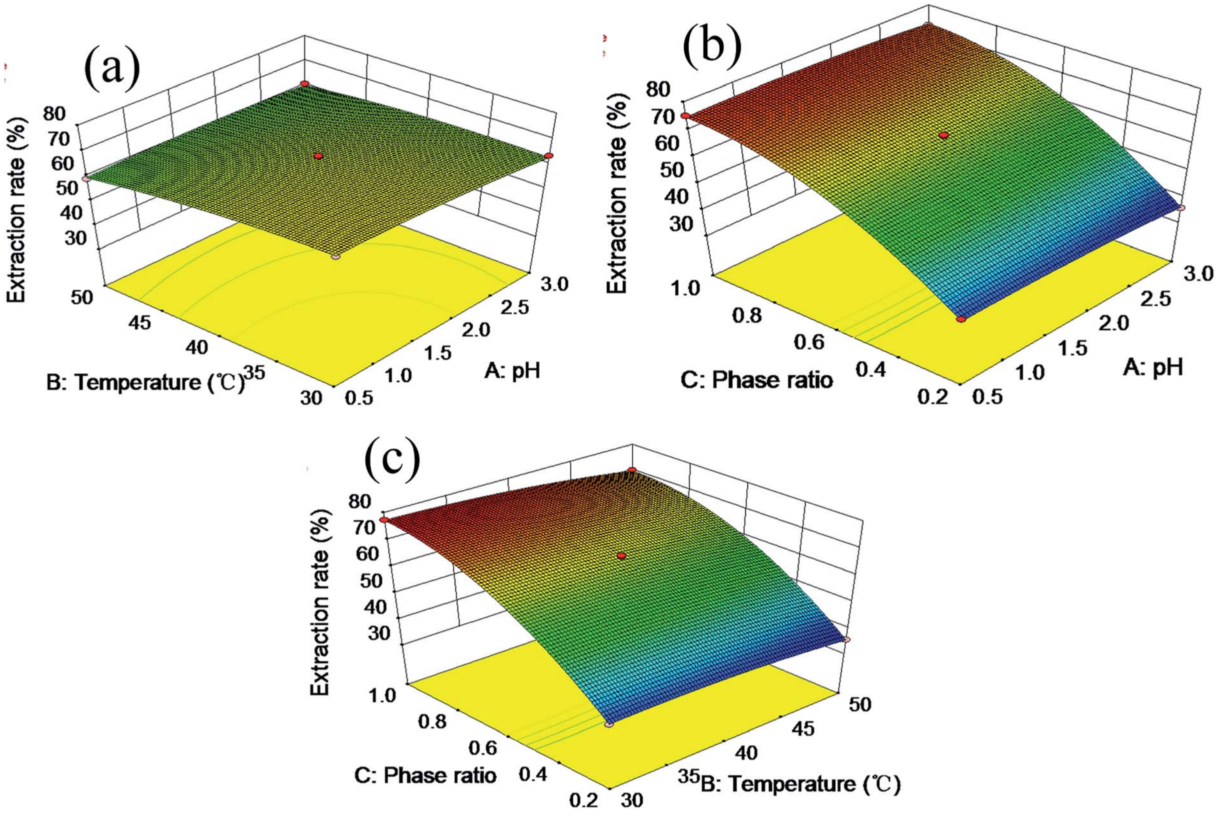


Fig. 10 3D surface plots of *n*-hexanol for GA extraction rate as a function of (a) pH and temperature, (b) pH and phase ratio, and (c) phase ratio and temperature.

$$Y_3 = 61.52 - 2.08X_1 - 4.69X_2 + 18.27X_3 - 0.50X_1X_2 + 0.92X_1X_3 - 0.15X_2X_3 + 2.13{X_1}^2 + 6.91{X_2}^2 - 7.21{X_3}^2$$

Y_1 – *n*-hexanol; Y_2 – TBP/MIBK/*n*-hexane; Y_3 – TBP/*n*-octanol/*n*-hexane.

The ANOVA results shown in Table 5 illustrate the reliability of the quadratic model was extremely significant. The regression effect of the response surface regression equation was good and highly reliable, with insignificant fitting values (Tables 6, 7 and 8). There was only a 0.01% chance that a "Model *F*-value" this large could occur due to noise. This indicates that the assumed second order polynomial was highly significant. The values obtained for "Prob. > *F*" were less than 0.0500 and indicate the model terms are significant.[37] In this case, X_1, X_2, X_3, X_1X_2, X_2X_3, ${X_1}^2$, ${X_2}^2$ and ${X_3}^2$ in Table 6, X_1, X_2, X_3, X_1X_2, X_1X_3, X_2X_3, ${X_1}^2$, ${X_2}^2$ and ${X_3}^2$ in Table 7 and X_1, X_2, X_3, ${X_1}^2$, ${X_2}^2$, ${X_3}^2$ in Table 8 are significant model terms. Taking the solvent TBP/MIBK/*n*-hexane for example, the results showed the phase ratio was the most influential parameter among the three factors, which achieved an *F*-value of 6010 (Table 7). The model *F*-value of 821 and an adequate precision of 80.5 implies the model was significant. Higher R^2 (*R*-Sq) values (0.9991) suggest that the predicted polynomial model was reasonably well-fitted with the data. Meanwhile, the model is considered reproducible if the C.V. for the model was less than 10%, thus a C.V. of 1.14% indicated that this model was highly accurate and credible. A predicted R^2 (Pred *R*-Sq) value of 0.9890 was in line with the adjusted R^2 (Adj *R*-Sq) value of 0.9978. A comparison between the experimental and predicted values obtained for GA extraction rate are shown graphically with 45°-line values in Fig. 9 and demonstrate excellent agreement between the experimental values and predicted values. Similar results were also found for the fitted data obtained for the other two extraction solvents.

The importance of each of the three independent elements (pH, temperature and phase ratio) was settled by illustrating the response surfaces as three-dimensional (3D) plots (Fig. 10, 11 and 12). The phase ratio remained constant at 0.6 in Fig. 10a, 11a and 12a, meanwhile the temperature and pH remained constant at 40 °C and 1.75 in Fig. 10b, c, 11b, c, 12b and c. Fig. 10a revealed that the GA extraction rate was slightly affected by pH and temperature, which was consistent with the results of the previous univariate crossover experiments (Fig. 3 and 6). The results also indicated that lower pH was beneficial for the extraction of GA. The GA extraction rate was highest when the pH and temperature were kept at 0.5–1.0 and 30–35 °C, respectively. As the phase ratio has a larger effect on the GA extraction rate when the pH was unchanged, the interaction between these variables had an effect on the GA extraction rate, though the overall change was not significant. In addition, in Fig. 10b, alteration of the phase ratio obviously affected the GA extraction rate, while changing the pH was less important. Fig. 10c shows the influence of temperature and the phase ratio on the GA

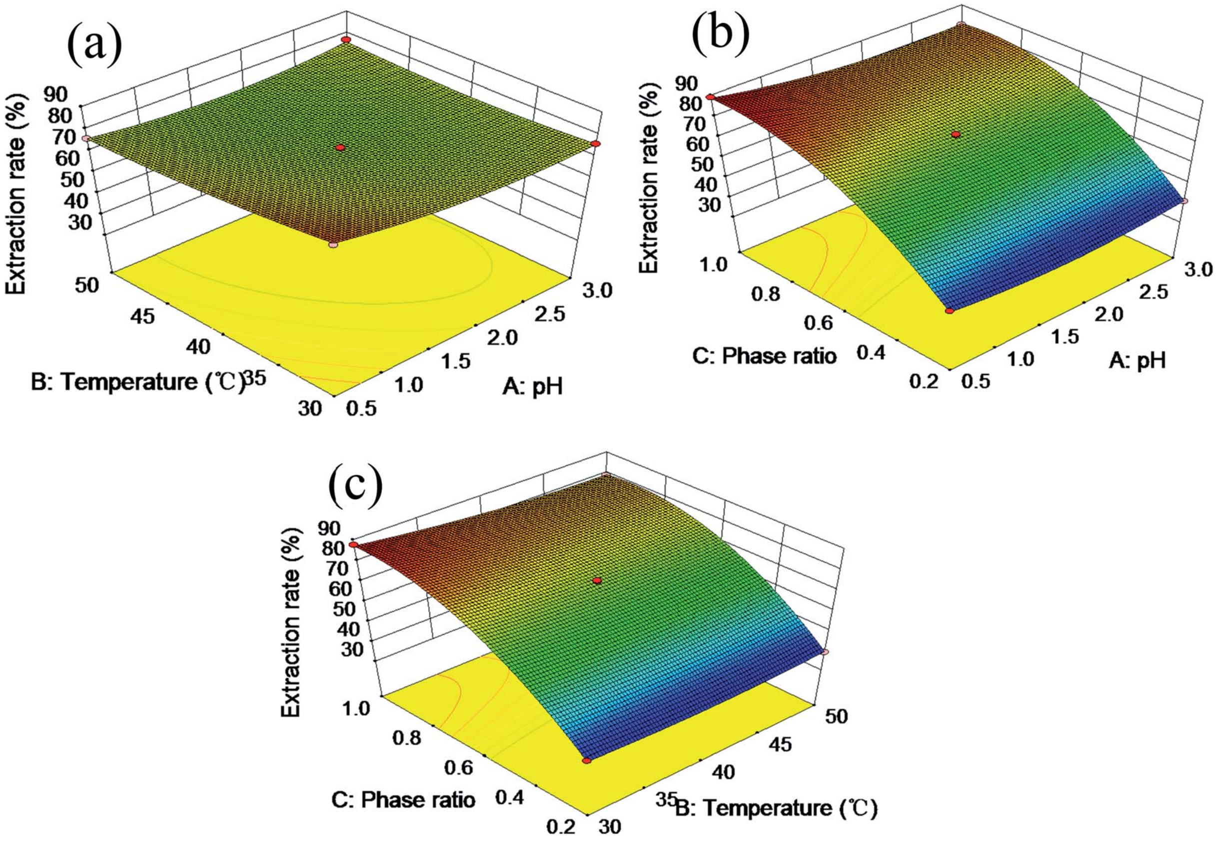


Fig. 11 3D surface plots of TBP/MIBK/*n*-hexane for GA extraction rate as a function of (a) pH and temperature, (b) pH and phase ratio, and (c) phase ratio and temperature.

extraction rate at pH of 1.75. Apparently, the phase ratio is more important than temperature. As presented in Fig. 11 and 12, when compared with Fig. 10, the other two extraction solvents have similar regularity. On the whole, the degree of importance for these parameters on the GA extraction rate was of the order: phase ratio > pH > temperature at the selected range.

A response optimization technique was applied to produce a combination of input variables that corporately optimizes the response. The maximum extraction rate was estimated to be 78.2%, 96.6% and 87.6% for *n*-hexanol, TBP/MIBK/*n*-hexane, and TBP/*n*-octanol/*n*-hexane under the optimized parameters (*i.e.* pH, temperature and phase ratio at 0.5, 30 °C and 1.0, respectively). An extra experiment was performed under these optimum conditions. The experimental extraction rate for *n*-hexanol, TBP/MIBK/*n*-hexane, and TBP/*n*-octanol/*n*-hexane (78.1%, 95.5% and 86.8%, respectively) matched with the predicted results excellently and also verified the results of the response surface optimization. Moreover, for *n*-hexanol, TBP/MIBK/*n*-hexane and TBP/*n*-octanol/*n*-hexane, the experimental extraction rates under the optimum conditions were also larger than those found under the optimum conditions determined in the previous univariate crossover experiments (78.1%, 95.5% and 86.8% *vs.* 76.7%, 88.2% and 82.5%, respectively). Therefore, RSM could be applied for the optimization of the GA extraction experiment conditions to obtain the highest extraction rate and efficiency after comprehensive consideration of the influencing factors (Table 9).

Table 9 The optimum values of the process independent variables resulting in the maximum GA extraction rate for the three extraction solvents predicted by RSM

Extractant	X_1 (pH)	X_2 (temperature)	X_3 (phase ratio)	Extraction rate (%)
n-Hexanol	0.56	30	1.00	78.2
TBP/MIBK/*n*-hexane	0.50	30	0.99	96.6
TBP/*n*-octanol/*n*-hexane	0.50	30	1.00	87.6

3.4 Stripping to recover GA and reuse of the extractants

In the process of stripping, when the solvent rich in GA was extracted by an alkali solution, the GA will reversibly enter into the aqueous phase in the form of its salt, meanwhile the organic solvent may be recovered.[15] As shown in results of the stripping experiment for TBP/MIBK/*n*-hexane, around 72% of GA was stripped after a one-stage process and more than 94.4% of GA was stripped through four stages, showing the possibility of the

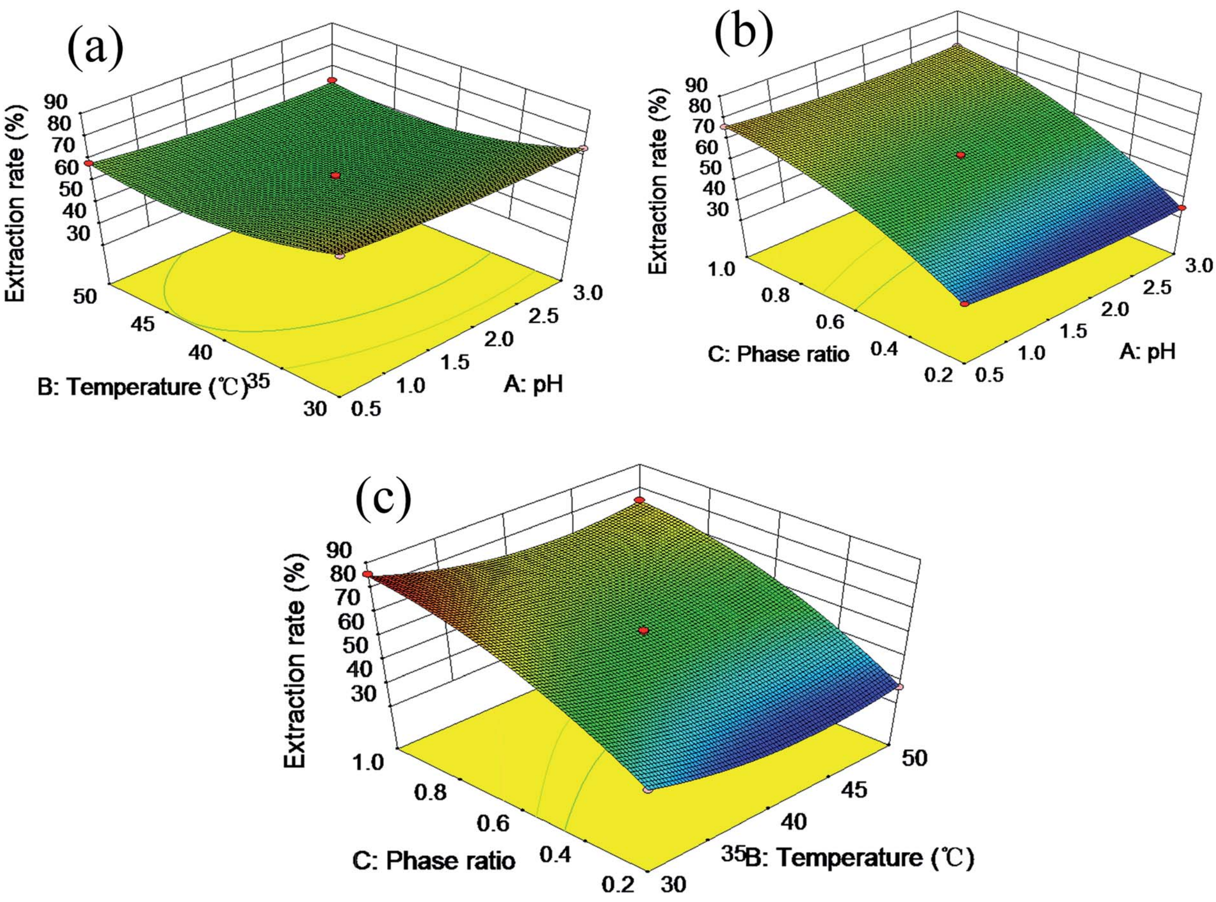


Fig. 12 3D surface plots of TBP/*n*-octanol/*n*-hexane for GA extraction rate as a function of (a) pH and temperature, (b) pH and phase ratio, and (c) phase ratio and temperature.

near complete recovery of GA through a multi-stage stripping procedure. The recovered solvents were used circularly and the separated GA was regenerated. In addition, increasing the NaOH concentration had no obvious improvement on the stripping effectiveness and the extractive capacity of these reused extractants did not change significantly after four-stages of stripping in this case (data not shown), which is similar to results reported in the literature.[16,22]

3.5 Extraction and stripping of actual wastewater

The one-stage extraction rate of GA actual wastewater using TBP/MIBK/*n*-hexane extraction solvent based on the optimized operation conditions reached 88.9% and further increased to 92.5% through a four-stage process. After stripping, more than 88.7% of GA was recovered through a four-stage process. The obtained sodium salt solution of GA by stripping was highly concentrated, which could be acidified and crystallized to generate pure GA directly, or be used as raw material during the hydrolysis step of the industrial production process of GA. The results indicate that using the mixed extractants solvent TBP/MIBK/*n*-hexane in liquid–liquid extraction is feasible to remove and recover GA from its processing wastewater.

4 Conclusions

The liquid–liquid extraction method was proven to be effective for the removal and recovery of gallic acid (GA) from GA processing wastewater. TBP combined with two diluents was a feasible and an effective extraction solvent. After univariate crossover experiments it was found that when using the TBP/MIBK/*n*-hexane system the maximum one-stage extraction rate was 88.2% and a 99.6% extraction rate was achieved after four-stage extraction process. The extractions conditions were set as follows: the component proportion in the mixed solvents (TBP/MIBK/*n*-hexane or TBP/*n*-octanol/*n*-hexane) $= 1:2:1$, pH $= 1.5$, phase ratio between extraction solvent and aqueous GA solution $= 1:1$, stirring speed $= 150$ rpm, extraction time $= 60$ s and temperature $= 30$ °C (room temperature).

The FT-IR spectra used to characterize the extracted organic phases proved the physical process of *n*-hexanol and showed that intermolecular hydrogen bonds were probably formed, which contributed to the extraction of GA by TBP.

In the previous univariate crossover experiments, the pH, temperature and phase ratio were found to be the three most influential operating parameters. The results were further optimized by Box–Behnken experiment design and the optimal conditions were determined to be pH $= 0.5$, temperature $= 30$ °C and phase ratio $= 1:1$, under which the extraction rate was maximized at 95.5% for the TBP/MIBK/*n*-hexane system, which agreed with the predicted values pretty well.

For model GA wastewater, around 72% of GA was stripped after a one-stage process and more than 94.4% through a four-stage process when using the TBP/MIBK/*n*-hexane system.

For actual GA processing wastewater, the one-stage extraction rate obtained for the TBP/MIBK/*n*-hexane system reached 88.9% and further increased to 92.5% through four stages. In addition, more than 88.7% of GA was recovered through the four-stage stripping process.

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