

Use of Ultrasonic Baths for Analytical Applications: A New Approach for Optimisation Conditions

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Com o emprego de um método simples e rápido, são propostas algumas condições de otimização para a obtenção de máxima intensidade de cavitação em banhos de ultra-som. Os parâmetros estudados foram: volume de água dentro do banho, temperatura, concentração de detergente, posição vertical e horizontal dos tubos no banho, número de tubos dentro do banho, tempo de sonicação e substituição da água do banho. Os resultados obtidos para os banhos de ultra-som estudados (Neytech e Cole-Parmer) permitiram estabelecer as seguintes condições para máxima intensidade de cavitação: 1 L de água à temperatura ambiente; 0,2 % (v/v) de detergente; posição central e ao fundo do banho. Somente 1 tubo deve ser usado por vez dentro do banho durante a aplicação do ultra-som. A intensidade de cavitação foi linear com o tempo de sonicação até 10 minutos e a substituição de água durante a sonicação melhorou a reprodutibilidade. Esse sistema de troca contínua de água permite a sonicação de até 6 amostras consecutivamente sem mudanças no volume total de água.

Optimisation conditions for obtaining maximum cavitation intensity in ultrasonic baths are proposed using a simple and fast method. Parameters such as water volume, temperature, detergent concentration, horizontal and vertical positions, number of tubes in the bath, sonication time and bath water substitution were studied. The results obtained for both baths studied (Neytech and Cole-Parmer) lead to the following conditions for maximum cavitation intensity: 1 L of water at room temperature, 0.2 % (v/v) of detergent, central position on the bottom of the tank. Only one tube at a time should be used inside the bath during the ultrasound application. The cavitation intensity was linear with the sonication time up to 10 minutes and the water substitution during the sonication improved reproducibility. This system using continuous water change makes possible the sonication of 6 consecutive samples, without changes in the water volume.

Keywords: ultrasonic bath, analytical application, cavitation, iodine, hydrogen peroxide

Introduction

Ultrasound energy has been found to be an efficient way to improve the performance of several different applications of analytical chemistry, such as extractions of inorganic and organic compounds^{1,2}, slurry dispersion³, homogenisation⁴, and other applications⁵⁻⁸.

The sonochemical reaction is considered to originate from acoustic cavitation. This process can be characterised by the formation, growth and implosive collapse of gas vacuoles in a solution. The cavity growth depends on the intensity of sound⁹. The collapse may proceed as an adiabatic compression and generate high temperature and pressure¹⁰, while the implosion of cavities establishes an unusual environment for chemical reactions^{9,11}. The high

temperatures and pressures generated lead to formation of free radicals and other compounds; the sonication of pure water leads to the thermal dissociation of water vapour into H atoms and OH radicals, and the recombination of the latter tends to form hydrogen peroxide^{9,11,12}. In addition, when for example, an aqueous solution of potassium iodide is sonicated, iodine radicals are liberated⁴.

The principal instruments used in sonochemistry are ultrasonic baths and ultrasonic probes¹³. Ultrasound generators transform electrical energy into ultrasonic energy, which is a mechanical energy. The efficiency of the energy transformation depends not only on the equipment itself, but also on the ultrasound application conditions¹⁴. The effect of high-intensity ultrasound depends on many variables. Among the most important variables are the reaction medium characteristics (viscosity, surface tension, vapour pressure, nature and concentration of the dissolved

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gas, presence of solid particles, etc) treatment parameters (pressure and temperature), ultrasound generator performance (frequency, power input), size and geometry of the treatment vessel¹⁵.

The energy of ultrasound is not uniformly available from the ultrasonic bath. Only a small fraction of the total liquid volume in the immediate vicinity of the ultrasound source experiments the effects of cavitation. The intensity of ultrasound is continuously attenuated by the molecules present in the liquid due to various cohesive forces acting on the liquid¹⁶. The ultrasonic intensity profile in the baths depends entirely on the design and location of the transducers. For commercially available ultrasonic baths a variety of transducers with different configurations are used¹⁷.

The results of a sonochemical reaction largely depend on the placement of the reaction vessel in the bath. In order to study the effect of ultrasound on a reaction, a reproducible exposition to ultrasound waves is necessary. For this purpose it becomes essential to identify the optimum sonication conditions individually for each ultrasonic bath¹³.

A great variety of techniques for the measurement of ultrasonic or cavitation intensity has been listed in the literature¹⁸, such as chemical reactions¹⁹, elastic sphere radiometry²⁰, aluminium foil erosion²¹, calorimetric and optical methods^{16,19,22}, thermoprobes²¹ and others^{18,23}.

In view to know the better conditions for maximum cavitation and its spatial distribution in ultrasonic baths in order to maximise the ultrasound effects for analytical applications, the aim of this work was proposed a simple spectrophotometric methodology to measure cavitation intensity in different conditions, using two chemical reactions: formation of I₂ (from KI solution) and H₂O₂ (from water).

Experimental

Instruments and apparatus

Two ultrasonic baths, a Neytech model 28H (USA) and a Cole-Parmer model R8860 were used at a frequency of 47±3 kHz. In order to monitor the reactions used to follow the sonochemical process an spectrophotometer (model 432 – Femto, São Paulo, Brazil) set at 352 nm or 426 nm for I₂ or H₂O₂ colour formation, respectively, was used. Hydrogen peroxide determination was also carried out using a monosegmented system described elsewhere²⁴.

Standards and reagents

All solutions were prepared with analytical reagent-grade chemicals (Merck, Darmstadt, Germany). Deionised

water was used throughout. To prepare the calibration curve for hydrogen peroxide monitoring, a concentrated H₂O₂ (30 % v/v) was used to prepare the working solutions (500 – 2000 µg L⁻¹) daily by serial dilutions with water. Also, 1 mol L⁻¹ NaOH, 5 × 10⁻⁴ mol L⁻¹ Tiron and 10 µg L⁻¹ Co [from Co(NO₃)₂·6H₂O] were prepared and used for the monosegmented system.

KI (0.29 mol L⁻¹) was prepared each two days by dissolving the respective mass with water and a 3.67 × 10⁻³ mol L⁻¹ (NH₄)₆Mo₇O₂₄ was prepared from a stock solution by serial dilutions with water. These solutions were prepared for monitoring the sonochemical process.

Procedure

In order to investigate the ultrasound pattern distribution inside the baths, first the positions of the tubes in two different baths (Neytech and Cole-Parmer) was fixed by using a piece of polyethylene foam where up to 9 tubes were supported (see Figure 1). In this way, different parameters were studied by using an univariate method, such as water volume in the baths (1 to 2 L and 0.4 to 1.3 L for Neytech and Cole-Parmer baths, respectively), water temperature (26 to 36°C), detergent concentration in water (0 to 0.4% v/v), tube height from the bottom of tank (0 to 2 cm), number of tubes in the bath (1 to 9), position of the tube(s), sonication time (1 to 10 min) and bath water substitution.

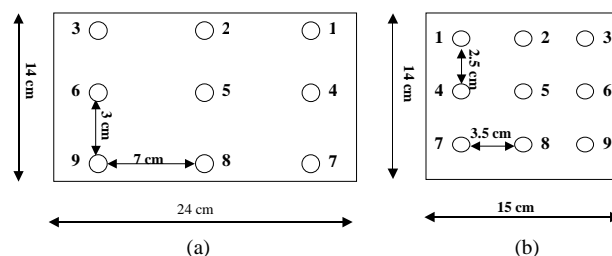


Figure 1. Tube positions inside the ultrasonic bath for ultrasound distribution studies for (a) Neytech bath and (b) Cole-Parmer bath. 1 – 9 correspond to different positions of the tubes.

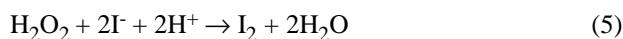
All parameters were evaluated by variation of the yellow colour, followed spectrophotometrically at 352 nm from I₂ reaction formation⁴ by sonication of a solution of 5 mL KI and 0.1 mL ammonium molybdate for 5 minutes. Each condition applied produced different I₂ concentrations. For confirmation, some tests were also used to determine the H₂O₂²⁵ formed from water sonication.

Results and Discussion

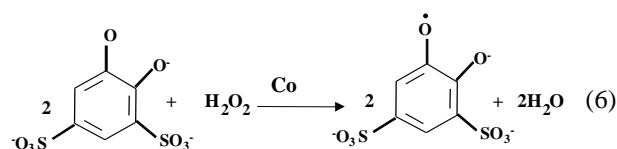
Reactions used

The I₂ formation can occur by two forms^{4,26}:

by forming radical like I^\bullet (reactions 1 and 2) and by redox reaction between I^- and H_2O_2 (reactions 3, 4 and 5).



In the determination of the H_2O_2 formed (reactions 3 and 4), an indirect method was used²⁵. This reaction is based on catalytic effect of cobalt in the oxidation of Tiron by hydrogen peroxide. Reaction 6 is shown below:



Effects of the water volume in the baths

Cavitation intensity in organic liquids is lower than water and this intensity change between different solvents used. Liquids of cyclic structure (such as styrene, toluene, and xylene) tend to cavitate most intensity. On the other hand, liquids presenting carboxylic acids and aliphatic amines tend to cavitate weakly²⁷. Although the I_2 method never was used to this purpose, seems to be that it can be used to measure cavitation intensity in some organic solvents or mixing these solvents with water. However, cavitation intensity may be lower when compared when only water is used²⁷, as well as longer times of sonication can be required.

Because this work was proposed for analytical applications and most of these applications were made in aqueous solution, only water was investigated. In this way, different levels of water were used due to the different capacities related to each bath. However, the best results were obtained with 1 L of water for both baths. The results are presented in Table 1 and the measurements were obtained by applying the iodine method. In this sense, higher absorbances mean a more intense cavitation process. In addition, with 1 L of water low Relative Standard Deviation - RSD (*ca.* 5 and 12% for the Neytech and Cole-Parmer baths, respectively) for the measurements were obtained with the spectrophotometric method.

It is interesting to note that since the Neytech bath has two ceramics (piezo electric) and Cole-Parmer bath has

Table 1. Effects of the water volume inside the ultrasonic baths on the absorbances for the I_2 method.

Cole-Parmer bath			Neytech bath		
Vol. (L)	A ^a	%RSD	Vol. (L)	A ^a	%RSD
0.4	0.064	17.43	1.00	1.162	4.96
0.6	0.031	22.89	1.25	0.005	16.09
0.8	0.173	11.61	1.50	0.038	23.91
1.0	0.507	11.99	1.75	0.085	14.76
1.2	0.386	10.53	2.00	0.299	14.29
1.3	0.228	10.12			

^aMean absorbance obtained with $n = 5$.

only one for producing the ultrasound, the maximum I_2 quantities formed for the Neytech bath are nearly the double those obtained for Cole-Parmer bath. Ultrasonic baths are usually designed to produce a standing-wave pattern within the cleaning liquid, with maximum ultrasound intensity generated at the antinodes in the pattern²⁸. This pattern can be seen by visual inspection of the cleaning liquid surface; such inspection also reveals that the pattern shifts across the surface with time and therefore is not a true standing-wave pattern²⁸. According some authors^{18,20,4}, if the water level is significantly lower than half of the ultrasound wavelength (λ) in water, the ultrasound intensity diminishes with an increase in the distance from the source. When the water level was $\geq \lambda/2$, intensity profiles of standing-waves were observed. At a water level of *ca.* $n \times \lambda/2$ resonating standing-waves are achieved. The λ could be calculated with the frequency of the bath and the sound velocity in the media. However, the velocity of an ultrasonic wave in liquids is dependent on the temperature and densities²⁹. In this case, it is difficult to calculate λ exactly because the room temperature of water varied during the day and the frequency supplied by manufacturer has a variation of $\pm 6\%$. In this sense, the better way to obtain the maximum cavitation conditions for analytical applications is experimental.

Effects of the water temperature

Since a temperature control does not exist in the Cole-Parmer R8860 ultrasonic bath model, this test was only performed with the Neytech bath. The temperature range (26 - 36 °C) was chosen because in different ultrasound applications an environmental temperature (26 °C) is used while some authors suggest that the effect of high temperatures (above 40 °C) decreases the ultrasound intensity^{14,19,30}. According to Table 2, although a higher RSD was obtained with environmental temperature (26 °C), the absorbances achieved for the temperatures studied were not different at the 95% confidence interval. In this way, for simplicity, the temperature of 26 °C was chosen for other experiments.

Table 2. Effects of the water temperature on the absorbances for the I₂ method for Neytech bath.

Temperature (°C)	A ^a	%RSD
26	1.144	5.33
31	1.255	1.84
36	1.202	1.37

^aMean absorbance obtained with n = 5.

Effects of the detergent concentration in water

At higher viscosities the cavitation process is more difficult to be induced (greater power input is required) and the number of cavitating bubbles per unit volume is reduced^{15,17}. With the use of a detergent, the surface tension is decreased, facilitating ultrasound propagation³¹ and producing better cavitation. Since it is necessary for the rarefaction pressure to overcome the cohesive forces in the liquid in order to be able to generate a bubble any increase in viscosity or surface tension will naturally lead to an increase in the amount of energy needed to separate the liquid¹⁷. This is confirmed according Table 3 where, with the use of a detergent at 0.2 or 0.4 % v/v, an increase of *ca.* 33 and 26%, respectively in the absorbances were obtained, related to those obtained without detergent. In this way, the detergent concentration was fixed in 0.2 % v/v.

Table 3. Effects of the detergent concentration on the absorbances for the I₂ method for Neytech bath.

Detergent (%v/v)	A ^a	%RSD
0	1.007	5.64
0.2	1.336	1.91
0.4	1.265	1.34

^aMean absorbance obtained with n = 5.

Effects of tube height

In order to verify the vertical distribution of the ultrasound, a study was performed using the Neytech bath. In this study the tube height was varied from 0, 1 or 2 cm from the bottom of the tank. Pugin has shown that the ultrasonic intensity within a bath varies with distance from the transducers²¹. As can be seen in the Table 4, when the tubes were positioned at 1 or 2 cm from the bottom of the tank, lower results were obtained, related to the bottom position. This can be explained due to the distance of these tubes from the ultrasound source. On the other hand, when the tube was positioned in the bottom position, an increase in the absorbance up to 10 times was achieved. In this way, the tubes were always located in this position.

Effects of the number of tubes in the bath

A great amount of tubes inside the bath provokes ultrasound wave reflections, reducing the efficiency of the

Table 4. Effects of tubes height on the absorbances for the I₂ method by using the Neytech bath.

Height (cm)	A ^a	%RSD
0	1.267	4.55
1	1.071	5.50
2	0.119	15.57

^aMean absorbance obtained with n = 5.

sonication process. For this study, up to 9 tubes were placed in the positions specified in Figure 1. According to Tables 5 and 6, a decrease in the absorbance was obtained (*ca.* 5 and 12 times in the absorbance for Cole-Parmer and Neytech baths, respectively) with an increase in the number of the tubes inside the bath. Also, it is interesting to note that, for the Cole-Parmer bath, depending on the tube distribution, the optimum position for cavitation is modified (see Table 5, rows 4 and 6). These results also show that, for analytical applications, only one tube and the same position should be used in order to obtain precise results.

Horizontal distribution of the ultrasound

The study was realised in two water volumes: 1 L (maximum cavitation intensity in the central point) and maximum capacity of the bath (2 and 1.3 L for Neytech and Cole-Parmer baths, respectively). The ultrasound distribution in the baths can be seen in Figure 2 and 3 for Neytech and Cole-Parmer baths, respectively. Although these two baths present the same best cavitation position (point 5, Figure 1a and 1b) when used with 1 L of water, the shape of the ultrasound distribution in the Cole-Parmer bath seems to be more uniform, related to the Neytech bath. For baths fitted with a single transducer (Cole-Parmer bath), the maximum ultrasonic intensity is found above the transducer; for baths equipped with two transducers (Neytech bath) the maximum intensity is found midway between the two acoustic wave generators²¹. Position 5 is located above the transducer in the Cole-Parmer bath and between the two transducers in the Neytech bath. The spatial distribution of the ultrasonic intensity is significantly affected by a variety of factors, including water volume in the bath, operating voltage of the transducer(s), and shape and position of the flask in the bath²⁸, as can be observed by comparing the Figure 2(a) and 2(b) or 3(a) and 3(b). The change in the water volume in the bath completely modifies the horizontal distribution of the cavitation. When the total volume was used, the Cole-Parmer bath presented two points of maximum cavitation intensity (positions 5 and 6, Figure 1b) and the Neytech bath presented maximum cavitation at a different position (8, Figure 1a). The susceptibility of the ultrasonic field within the bath to these various external factors leads to considerable difficulties

Table 5. Effects of the number of tubes in the Cole-Parmer bath.

Position	9 ^a	7	5 ^b	5 ^b	4	3 ^b	3 ^b	2	1 ^c
1	0.031 ^d			0.067					0.154
2	0.052		0.037				0.025		0.025
3	0.029	0.022		0.060					0.022
4	0.064	0.016	0.018		0.034	0.036			0.325
5	0.186	0.185	0.084	0.264	0.032	0.661	0.632	0.730	0.869
6	0.165	0.130	0.228		0.023	0.135		0.022	0.035
7	0.028	0.022		0.040					0.040
8	0.050	0.102	0.271		0.151		0.271		0.270
9	0.030	0.138		0.095					0.024

^a Number of tubes inside the bath simultaneously; ^b Three or five tubes in different positions; ^c One tube sonicated each time; ^d Mean absorbance obtained with n = 3.

Table 6. Effects of the number of tubes in the Neytech bath.

Position	9 ^a	7	5 ^b	5 ^b	4	3 ^b	3 ^b	2	1 ^c
1	0.058 ^d			0.040					0.063
2	0.024		0.023			0.007			0.033
3	0.018	0.032		0.024					0.020
4	0.041	0.026	0.037		0.039		0.080		0.018
5	0.020	0.189	0.670	0.448	0.792	0.958	1.030	1.171	1.280
6	0.033	0.021	0.023		0.045		0.013	0.015	0.034
7	0.050	0.035		0.040					0.024
8	0.030	0.019	0.048		0.027	0.007			0.039
9	0.015	0.027		0.020					0.032

^a Number of tubes inside the bath simultaneously; ^b Three or five tubes in different positions; ^c One tube sonicated each time; ^d Mean absorbance obtained with n = 3.

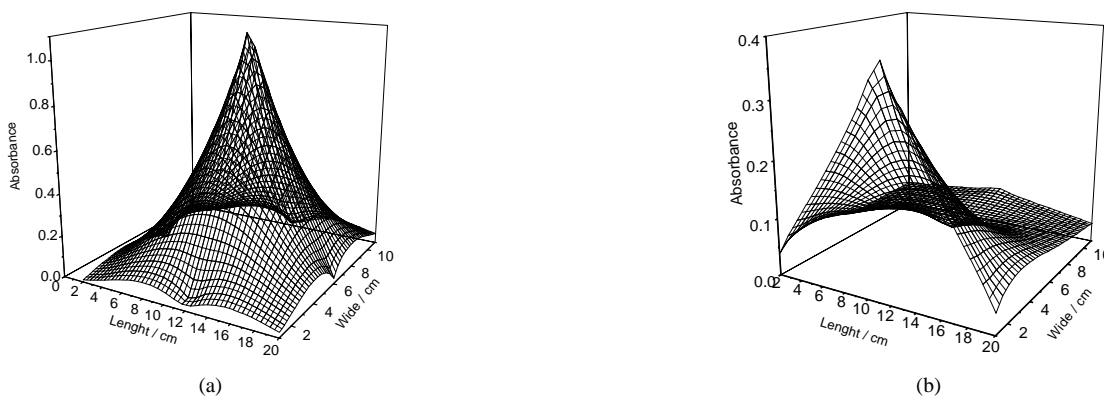


Figure 2. Spatial distribution of the ultrasonic field in the Neytech bath: (a) using 1 L of water in the bath and (b) using the total volume (2 L) of water in the bath.

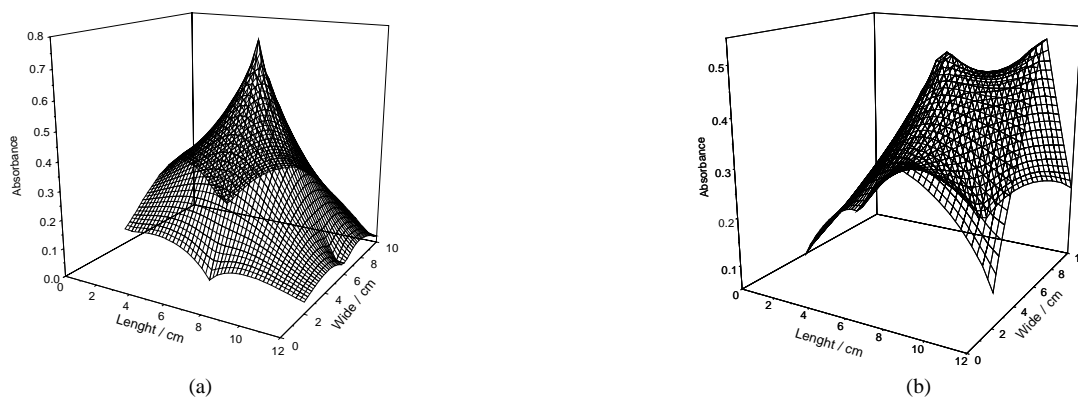


Figure 3. Spatial distribution of the ultrasonic field in the Cole-Parmer bath: (a) using 1 L of water in the bath and (b) using the total volume (1.3 L) of water in the bath.

in quantifying the amount of power dissipated, and the cavitation generated, within a reaction vessel placed in the bath. This also leads to problems with reproducibility; reaction vessels of similar shape need to be placed in the same position in the bath for each experiment if reproducible and consistent results are required²⁸.

For the Neytech bath with 1 L water, the ultrasound distribution was obtained by the I₂ method and confirmed by the amount of H₂O₂ formed (950 µg L⁻¹ at the point 5) during the cavitation process.

Sonication time vs. cavitation intensity

In order to verify the efficiency of the sonication time, different sonication times were applied (1-10 min) at the tube positioned at point 5 (see Figure 1). Longer times were not tested since higher absorbances (> 1.8 A) for the I₂ method were produced, compromising the measurements and giving higher RSD (more than 50%). Comparing both baths, slight differences were observed, presenting a linear correlation coefficient for I₂ results of 0.990 and 0.998 for Neytech and Cole-Parmer baths, respectively.

Effects of substitution of water in the baths

Ultrasonic baths are warmed up during use, particularly over an extended period of time. This leads to inconsistent results when working at room temperature or below²⁸. This can be resolved by using a thermostated bath or by substitution of the bath water.

As can be seen in Table 7, a great difference exists in the results when water was continuously changed during the sonication process. The water was pumped at 18.2 mL min⁻¹, being inserted at position 9 and discarded at position 1 (see Figure 1a). With this simple system, up to 6 samples were sonicated consecutively with a RSD of only 5.3%. Instead, when the water was not changed a RSD of 45% was obtained with a gradual decrease in the absorbances (from 1.156 to 0.277 A for 5 consecutive sonications).

Table 7. Effects of water substitution on the absorbance for the I₂ method by using the Neytech bath.

Samples	without water substitution		with water substitution	
	A ^a	%RSD	A ^a	%RSD
1	1.156	10.45	1.057	8.42
2	0.932	21.43	1.131	5.08
3	0.879	30.83	1.149	4.21
4	0.568	42.38	1.097	3.11
5	0.277	13.16	1.054	4.07
6			0.993	4.20
Mean	0.762		1.080	
%RSD	44.99		5.31	

^aMean absorbance obtained with n = 3.

Conclusions

The proposed method offers advantages to other methods presented in the literature which use thermoprobes, aluminium foil erosion, calorimetric or optical probes. In the present method, the system proposed can simulate the real conditions for analytical application. Its optimisation was carried out with the same flask which for example, it can be also used for extraction procedures. In addition, this method requires only a spectrophotometer, making possible its use in any laboratory in an easy way.

Characterisation of the ultrasonic bath is very important for sonochemical reactions. The conditions of maximum cavitation intensity can be different for each ultrasonic bath and, due to this behaviour, it is very difficult to compare the results obtained with different ultrasonic baths even using the same conditions. In analytical chemistry, when reproducible and accurate results are required, the experimental conditions (such as water volume, temperature, detergent concentration, vertical and horizontal positions, number of tubes, sonication time) must be studied, established and rigorously reproduced for each experiment. An innovative way to study these conditions was employed in the present work by spectrophotometrically following the I₂ formation from free radical of iodine (I[•]) obtained after sonication of a KI solution.

In this way, the use of ultrasonic energy in analytical chemistry can be an alternative related to other energy forms, since some applications (such as extractions, homogenisation, lixiviation and others) can be easily performed, with simplicity and low cost.

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