

Removal of organic contaminants from water or wastewater with liquefied gases

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Abstract: This study utilized liquefied gases (LG) as extractant to remove various organic contaminants including halogenated hydrocarbons and phenols as well as aromatic compounds from aqueous matrices. Orthogonal experiments were performed to optimize the operating conditions such as temperature, co-solvents and so on. Under favorable conditions, high removal efficiencies can be readily achieved for a great number of representative model organic contaminants, the removal efficiencies for most of the hydrophobic contaminants were greater than 90% in a single extraction stage. Tentative effort was also done for the removal of extracted contaminants from recycled liquefied gases.

Keywords: liquefied gases; butane; extraction; organic; contaminants; water

Over the last three decades, wastewater treatment technologies have been improved greatly, but, meanwhile, the situation of water pollution changes with times and presents a very complicated trend with the rapidly developing modern industries and expanded human activities. Moreover, owing to variation from one polluted case to another, no single technology is capable of the whole spectrum of wastewater treatment and management. This fact has also stimulated the approach on alternative and innovative technologies to meet the environmental requirement.

In order to effectively clean up wastewater in a timely and economical way, based on the criteria established for traditional solvent extraction, the concept emerged for a technology using liquid butane or similar type of highly volatile non-polar solvents as extractant. When gases such as propane, butane and carbon dioxide are liquefied, they have unique physicochemical properties that made them ideal and notably non-toxic for the removal of contaminants from environmental matrices (Titus, 1993; US EPA, 1992). Teo *et al.* (Teo, 1989) concluded from their pioneer experimental results that the butane extraction process is convincingly an extremely effective method for removing of toxic organic contaminants from water. Chriswell *et al.* (Chriswell, 1994) reported that high recoveries were obtained within 60 min when liquid butane and trimethylpentane were used to treat a high-humus soil and a sandy soil sample artificially contaminated with toluene or gasoline.

As well known, C₃ and C₄ are the main components in domestic liquid petroleum gas (LPG) which normally dominate a proportion of around 20% by volume. LPG is readily available from oil refineries of the petrochemical industry. Hence, it is expected that the cost can be greatly reduced if LPG can be an alternative to pure *n*-butane as extractant. A bench-scale test has demonstrated the potential for extraction and semi-solids can be achieved by a liquefied propane/butane mixture as the extraction solvent (US EPA, 1990). The solvent mixture comprised 70% propane and 30% butane. The system consistently achieved higher removals of total oil and grease to less than one percent residual of dry solids. The concentrations of individual components in treated matrices, including many aromatics and other polynuclear aromatics, met or better than the standards of existing demonstrated available technology.

Liquefied gases extraction is potentially capable of being developed into a successful commercial technology suitable for environmental cleanup (Yang, 2000). However, so far, there are very few references covering the systemic approach of this technique in detail. Actually, in recent years relatively few papers have been published in this area simply devoted to basic understanding of the nature of the LG extraction. The present study focused on an extensive basic R&D program hoping to gain performed toward

a further understanding of this emerging technology and was expected to provide the basis for the design of liquefied gases extraction process in the next phase of work.

1 Materials and methods

1.1 Reagents

Chemicals used in this study were all purchased from Aldrich Chemicals Co., USA and were highest purity available. Normal butane with purity greater than 99% was supplied by Messer Singapore Pte. Ltd. Domestic liquid petroleum gas came from Esso Sin-gas Ltd. The main components in LPG are determined to be propane, iso-butane and *n*-butane, and the proportion of the components varies with the condensation temperature of the experiment. *n*-butane is the main component of the LPG condensed at -1°C , which dominates nearly 100%. The weight percentage of propane increases when temperature drops. When LPG gas was condensed at -15°C , it contains more than 50 wt. % of propane.

Reagent grade water was prepared by passing doubly distilled water through an ultra-pure water system (Milli-Q plus 185, Millipore, USA). The reagent water contains no measurable organic background concentrations of any target analytes under the current experimental conditions. The stock aqueous solutions were prepared by spiking the appropriate amount of the pure chemicals into reagent water and were homogenized using an ultrasound bath.

1.2 Instruments

The basic laboratory scale processing unit was designed and constructed in-house. The apparatus comprises a thick-wall Pyrex glass extractor unit with an inner diameter of 80 mm, a height of 160 mm and a wall thickness of 8 mm. Four internal vertical stationary baffles were evenly spaced on the inner wall to provide turbulence mixing in order to prevent the vortex formation in order to enhance the extraction rate.

The 1028S iso-temperature refrigerated circulators from Fisher Scientific, Inc. of USA was used to control the operating temperature. Laboratory stirrer was supplied by Kika Works (Asia) Sdn. Bhd., Malaysia. A 12-channel scanning thermocouple thermometer was obtained from Colo-Parmer Instrument Co. USA.

1.3 Test procedures

The schematic setup of LG extraction system is depicted in Fig. 1. Freshly prepared aqueous solution spiked with model organic contaminants and liquid extractant were transferred to the extractor for a predetermined volumetric ratio. The operating temperature was maintained at 25°C by the thermostated water-bath. Liquefied gases were supplied by means of condensation or by placing the tank in reverse direction for direct liquid transfer, the latter needs special stand to support the tank for safety. It must be emphasized that direct feeding of liquid LPG is not a problem for commercial-scale operation, where extractant can be pumped and metered from storage tank. The two-phase solution was agitated at a given speed. Each experiment lasted till extraction equilibrium was achieved, usually less than 30 min, and periodically samples

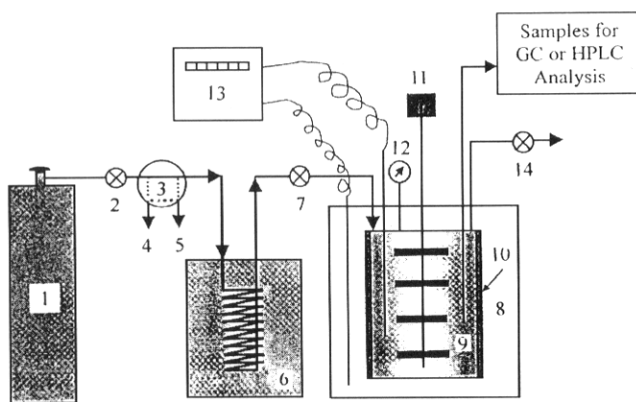


Fig. 1 Schematic diagram of LG extraction process

1. butane tank; 2, 7, 14. valve; 3. four-port valve; 4, 5. vent; 6. LPG refrigerator; 8. water bath; 9. extractor; 10. internal vertical stationary baffles; 11. stirrer; 12. pressure gauge; 13. scanning thermocouple thermometer

were taken every 0.5 min for the initial 2.0 min of the experiment, thereafter every 5.0 min per sampling. Concentration of solute in aqueous phase was determined by appropriate analytical techniques such as HPLC or GC, and removal efficiencies were derived and calculated.

2 Results and discussions

2.1 Optimization of experimental conditions

In order to achieve satisfactory extraction result, operation conditions need to be optimized. Trichloroethylene, nitrobenzene and *m*-cresol were chosen as model organic compounds, since their removal efficiencies span over a wide range, and are considered to be good representatives. Many variables shown in

Table 1 List of potential factors for liquefied gases extraction

Factor designator	Variable	Level I	Level II
A	Solvent: feed ratio ($V_0 : V_w$) ¹	1:5	1:2
B	Concentration of solution	Higher	Lower
C	Type of cosolvent	<i>n</i> -butyl acetate	Tributylamine
D	Ratio of butane and cosolvent	9:1	3:1
E	Temperature, °C	25	10
F	Stirring speed, r/min	300	800
G	Extraction time, min	30	10

¹ V_0 represents the volume of organic extractant; V_w represents the volume of aqueous solution spiked model organic pollutants

Table 1 were thought to be influential factors of butane stripping process. Orthogonal table was designed for the initial investigation. A factorial scheme for seven factors with two levels was considered for the experimental design. Let A, B, C, D, E, F and G represent the main levels for each of the factors, and a, b, c, d, e, f and g for the secondary levels of each factor. A set of experimental parameters will then be completely specified by selecting either a lower or upper case letter for each of the factors (Graham, 1993). Such a set is given in the orthogonal Table 2.

In this work, the experimental results collected are the removal efficiencies because they vary with the experimental conditions and can reflect the overall extraction performance. The data for the eight experimental designs are shown in Table 2. To determine the effect of the variability in the experimental system caused by factor the two averages are examined according to the results. The differences and squares of the differences are then computed from the averages. It can then be quickly determined by inspection the

Table 2 Orthogonal table showing eight experiments and results of seven factors

Factor level	Experiment number							
	1	2	3	4	5	6	7	8
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	e	E	e	E
F or f	F	f	f	F	F	f	f	F
G or g	G	g	g	G	g	G	G	g
Trichloroethylene	98.5 ¹ (0.6) ²	97.0 (1.2)	98.2 (1.0)	97.1 (1.3)	98.5 (0.8)	99.7 (0.6)	99.9 (1.4)	98.9 (0.9)
Nitrobenzene	90.9 (1.0)	83.5 (1.0)	94.4 (0.2)	84.2 (0.7)	90.7 (0.3)	94.5 (0.9)	95.9 (0.3)	93.2 (0.2)
<i>m</i> -cresol	58.8 (3.1)	46.7 (1.7)	80.7 (1.7)	67.9 (0.3)	90.9 (2.0)	81.1 (4.5)	76.1 (1.8)	61.2 (0.4)
Letter designator	s	t	u	v	w	x	y	z

1. removal efficiency, %; 2. standard deviation, %

data which factors actually affect the experimental results in a significant way. In view of the information summarized in Table 3, the optimized conditions are higher ratio of butane to water, moderate stirring speed, presence of *n*-butyl acetate as cosolvent, and larger ratio of cosolvent to butane in the case where the hydrophilic substances (e. g. phenols) are the main concern for the desirable treatment.

As can be seen, overall, the largest differences are the differences between variable A and C for nearly all model analytes. This observation illustrated that the significant factors for extraction include the ratio of two phases, type of cosolvent, and the volume ratio of butane and cosolvent. It is apparent from the results that greater ratio of $V_0 : V_w$ and lower ratio

of butane to cosolvent will benefit the extraction results. It is obvious that the removal efficiency is related to the distribution constant and the ratio between the volume of extractant and aqueous phase. Therefore, it is well understood that using more organic extractant can definitely increase the removal efficiency, meanwhile it will increase the operating costs associated with more solvent needed in the scale-up system. A volume ratio of *n*-butane to aqueous phase at 1 : 5 was used for the study, which will allow greater concentration of analytes to be used in aqueous phase and consequently leads to greater accuracy for the analytical determination.

Table 3 Optimization and importance sequence of factors for LG extraction

Chemical	Optimized condition						Sequence of importance	
Trichloroethylene	a	b	C	d	E	f	G	A > E > G > C > F > D > B
Nitrobenzene	a	b	C	d	E	f	G	A > E > C > F > B > G > D
<i>m</i> -cresol	a	b	C	d	E	f	G	D > A > C > B > F > G > E
Overall	a	b	C	d	E	f	G	A, C > E, D, B, F, G

It appears that *n*-butyl acetate is better than amine as a cosolvent for the extraction of hydrophilic organic compounds from water. Trichloroethylene can be effectively removed when *n*-butane is used as

the sole extractant. It was also shown from the results that concentration of solute has no significant effect on the extraction. Generally, when a substance is added to a two-phase liquid mixture, it is distributed with different equilibrium concentrations in the two phases. The concentrations of solutes in the two phases change with the amount of analytes added. However, if the amount of solute added is sufficiently small, it is found that the distribution constant, which is defined as the ratio of the concentrations of the solute in the two phases, is relatively independent of concentration. As the extraction equilibrium can be achieved within short time for most of organic pollutants, stirring speed and extraction time have no or little effect and commonly should not be considered as major factors. On the other hand, very vigorous agitation should be avoided since this tends to produce troublesome emulsions in some cases.

2.2 Removal of organic contaminants in water with *n*-butane and LPG

The experiments were performed for a wide range of model organic contaminants spiked into water. The model contaminants covered various classes of organic species such as halogenated compounds and phenolic compounds, which frequently appear as water contaminants. *n*-butane and domestic LPG were used as extractants to remove these organic contaminants at the optimized operating conditions listed in Table 4. The experiments were all conducted in triplicate.

Table 5 lists the removal efficiencies of model organic contaminants spiked in reagent water with a single stage extraction. As can be seen, removal efficiencies range from a few percent up to 100 percent for the studied contaminants. The results demonstrated that high removal

Table 4 Experimental conditions of LG extraction

Aqueous feed	300 ml	Operating temp.	25 °C
<i>n</i> -butane or LPG	60 ml	Stirring speed	400 r/min
Condensation temp.	- 5 °C ¹	Pressure	300 - 600 kPa ¹ 700 - 1500 kPa ²
	- 15 °C ²		
Solute concn.	10 - 1000 ppm	Extraction time	30 min

¹ *n*-butane as extractant; ² domestic LPG as extractant

efficiencies were achieved for all hydrophobic halogenated hydrocarbons and aromatic compounds in a single stage extraction. Lower efficiencies were achieved for phenolic compounds with the exception for *o*-nitrophenol which was about 80%. *n*-butane and LPG are likely unfavorable extractants for the removal of polar phenolic and water-miscible compounds in water. Though the quality of treated water can not meet the sanitation standard with single batch extraction. However, multiple stage extraction in the continuous treatment facility will surely satisfy the demand.

Commercial liquid petroleum gas was used as a possible alternative of solvent extraction. The advantages are lower in cost and abundantly availability. Overall, the values of removal efficiencies for LPG extraction are slightly less than that for butane extraction. One possible reason is the solubility

parameter of LPG mixture is less than that of pure *n*-butane. In the case of using commercial LPG as a substitute of *n*-butane for extraction of contaminants in water, the major challenge is that the operating pressure will inevitably increase because the vapor pressure of propane and butane mixture is higher than that of *n*-butane alone. The overall vapor pressure depends on the composition of LPG. Obviously, with higher propane and iso-butane content in the liquefied gas, the higher vapor pressure will be. Normally, the operating pressure using LPG as extractant remains within the range of 700–1500 kPa compared to that using *n*-butane at 300–600 kPa at room temperature. Therefore, stricter handling procedures are essential for the safe operation.

In addition, liquid petroleum gas for domestic usage is often spiked with odorants (e.g. ppb concentration of thio-compounds) which are used as indicator in order to arouse the attention of user in case of gas leakage. These odorants could possibly introduce new contamination in treated water.

However, this will not happen

for the scale-up operation as LPG used for the extraction will be the undoped LPG stock.

2.3 Removal of extracted contaminants in recycled extractants

Recycle of the extractant is another important step in industrial solvent extraction process, which can be accomplished in several ways, for instance, by backextraction or fractional distillation (Ritcey, 1992). This approach presented a tentative effort on the reclamation of *n*-butane for reuse and recycle. Normal butane has a much lower boiling point (-0.5°C) with higher volatility than the majority of contaminants of concern. The pressure on the separated solvent-organics mixture can be reduced to such as by depressurization to extract the solvent vapor and eventually separate it from the extracted organic contaminants. The butane vapour is then recovered and compressed to the liquid butane for reuse or recycle. The isolated or concentrated organic contaminants are collected for disposal or further treatment.

In the laboratory, the contaminated butane, which contains the extracted organic contaminants and/or co-solvents, was separated through a consecutive series of columns filled with compacted stainless steel fibre (some cases need multiple columns), and subsequently treated with activated carbon column followed by a drying column. Butane from the column overhead was liquefied again for reuse or recycling in a

continuous unit. A given volume of liquefied butane was slowly released to let butane gas pass through a column of water or other appropriate solvents. The recycled butane vapor was sampled and dissolved in a suitable solvent and the solution was analyzed by HPLC or GC for the possible trace or ultratrace residual of the contaminants.

Table 6 illustrated that it is easy and feasible to separate

Table 5 Removal of organic contaminants in water by a single stage LG extraction

Chemical	R^1 , %	R^2 , %	Chemical	R^1 , %	R^2 , %
Chloroform	88.4	90.3	Benzene	94.8	90.3
Bromodichloromethane	93.5	91.7	Toluene	99.1	99.0
Bromoform	91.5	88.5	<i>o</i> -xylene	99.7	99.7
Carbon tetrachloride	97.8	97.5	Nitrobenzene	88.4	80.8
1,2-dichloroethane	92.2	81.1	Chlorobenzene	99.3	98.9
1,1,1-trichloroethane	97.6	96.7	Phenol	2.6	2.5
Trichloroethylene	98.8	97.9	<i>o</i> -nitrophenol	80.7	79.9
1,2,3-trichloropropane	92.4	90.6	<i>o</i> -chlorophenol	46.8	45.4

¹ *n*-butane as extractant; ² LPG as extractant

Table 6 Reduction of pollutant concentration in *n*-butane after the multi-column fractionation and purification assembly

Chemical	C_F^1 , g/L	R^2 , %	Chemical	C_F^1 , g/L	R^2 , %
Chloroform	1.19	97.5	Toluene	2.49	99.7
1,2-dichloroethane	2.67	74.4	Nitrobenzene	0.99	100
1,2-dichloropropane	3.33	97.7	Chlorobenzene	2.24	99.9
1,1,1-trichloroethane	0.33	82.5	<i>o</i> -dichlorobenzene	0.78	96.0
Trichloroethylene	2.27	95.4	Phenol	0.12	100
Tetrachloroethylene	0.54	96.8	<i>m</i> -cresol	0.14	100
Carbon tetrachloride	0.98	99.6	<i>o</i> -nitrophenol	0.19	100
Benzene	4.78	99.6	<i>o</i> -chlorophenol	0.19	100

¹ feed concentration in extractant; ² percent reduction, %

extracted contaminants from butane by fractionation distillation. The removal efficiencies for most organic contaminants can approach near 100%. Some higher volatile organics can not be totally removed by such mean. However, the concentrations of residual contaminants in the quality of recycled butane are low enough and they will not affect the performance of later butane extraction process.

2.4 Special concerns for LG extraction

The experimental results have made LG extraction an attractive technology. However, as for other waste treatment technologies, many problems remain to be solved such as the feed of liquefied gases, the removal of highly hydrophilic compounds and the wastewater with higher concentration of surfactant, and others. Moreover, LG extraction is not a destructive method, it just simply concentrates pollutants so that they can be recycled for use or destroyed by other effective means. When contaminants are not recycled, they must be combined with other technologies to destroy the separated or concentrated contaminants. Meanwhile, liquefied petroleum gases have the potential for explosion and fire hazard due to their flammability. It will therefore require more careful handling and in the overall engineering design and operation of the system. Use of explosion-proof electrical equipment and stringent safety precautions are musts during the operation. Up to now many mature technologies have been available to solve these problems. Despite these drawbacks, undoubtedly, LG extraction is capable of being developed into a successful marketable technology for environmental clean-up.

3 Conclusions

This study investigated the possible application of liquid butane and liquid petroleum gas as an extractant. Laboratory experimental results showed its great potential for extraction for a broad range of organics from water and/or wastewater. The method can offer high removal efficiencies in a single extraction stage for the studied model contaminants except for phenolic substances and water-miscible compounds. Investigation will be furthered on the removal of these hydrophilic compounds with the aid of cosolvent. The work tentatively carried out to test the feasibility of the reusing of extractants and the experimental approaches in this laboratory bench-scale study have proven it to be successful.

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