A New Approach for Removal of Caffeine from Coffee using Sunflower Oil

Md M Hossain and Wei E. Chong

***Abstract*— Conventional decaffeination processes are capable of removing caffeine present in the coffee, but it also removes the flavouring/aromatic components to some extent and in many cases use toxic solvents. In this article a simple extraction method is presented using sunflower oil, a much less toxic solvent with good process and environmental benefits. Equilibrium experiments were carried out to examine the distribution ratio of caffeine, first in the solvent only (physical extraction) and then with a carrier-solvent organic phase (reactive extraction). The effects of caffeine concentration, carrier concentration, pH and type of solvent on the distribution coefficient were determined. It was observed that the distribution coefficient in sunflower oil increases with the increase of caffeine concentration and pH values. The value of the distribution coefficient was not affected greatly with the addition of Amberlite – LA2 (an amine carrier) in the solvent. The use of pure solvents like oleic acid has proven to be less effective compared to sunflower oil although equilibrium experiment showed otherwise. The process was applied to a small pilot-scale hollow-fibre membrane (HFM) contactor with the aim to apply this new and sustainable approach to remove caffeine molecules without affecting the natural flavour and aroma in the coffee. In the HFM approach using a single stage it was possible to extract 50-55% of caffeine with the addition of Amberlite - LA2 as a carrier, compared to 45-50% in physical extraction. Thus the proposed approach with sunflower oil (considered to be a "green" solvent) in hollow fibre membrane module can be recommended as an alternative process as it is environmentally benign, operator friendly and provide good process performance.**

***Index Terms*—Caffeine, Extraction, Coffee, Distribution coefficient, Sunflower oil.**

I. Introduction

Coffee is the most popular beverage worldwide, second to oil in terms of world commodity trading (1). Two major species of coffee grown commercially are Robusta and Arabica (2). Arabica coffee contains half the caffeine of Robusta coffee, at about 1-2% on a dry weight basis (1, 2). The molecular formula of caffeine is shown in Figure 1.

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The high consumption of caffeine is argued to have created health hazards such as aggravating heart disease and high blood pressure

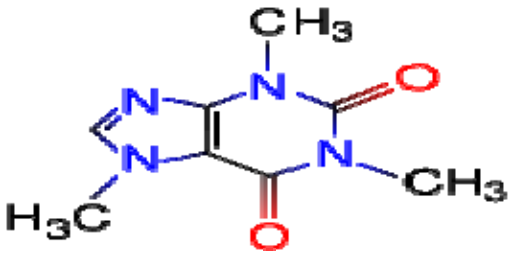

Figure 1: The molecular structure of caffeine.

(3). When one is very sensitive to caffeine's stimulant effects, decaffeinated coffee would be a better choice as it has lower caffeine level (3). The caffeine content of decaffeinated coffee is less than 0.3% on dry weight basis according to European Commission regulations (4).

The caffeine molecule is a bitter alkaloid which contributes to the bitterness of coffee (5). Removing this molecule will definitely alter those taste factors. Besides, other flavour or aroma components are also diminished or removed in the decaffeination process. This has resulted in the inferior taste of decaffeinated coffee compared to original coffee. Drinking decaffeinated coffee will be enjoyable if the caffeine is eliminated from it and the original bitter taste is preserved. Although improvements have been made to the decaffeination processes, the taste of decaffeinated coffee is still not fully preserved and not all the caffeine is successfully extracted (5). Furthermore, the toxic chemical used as the solvent in the extraction process may even leave traces in the decaffeinated coffee and thus may potentially be unsafe (5).

It is very complex to remove caffeine molecules from coffee beans as the coffee beans also contain other polyphenolic and aromatic compounds. The commercially available decaffeination processes (Table 1) are capable of removing caffeine to a great extent, but removes some of the flavouring and aromatic compounds giving a somewhat less natural taste. Some of the processes involve chemical solvents with bad environmental impact and poses health and safety problems. Furthermore, the decaffeinated coffee might contain traces of chemical solvents that might require additional steps (4). Therefore, there is a need to explore/develop a new decaffeination method which uses green solvent with less environmental impact and has the potential to remove only caffeine without extracting any flavouring and aromatic compounds.

This study is an effort in that direction to examine a simple and sustainable extraction method using a membrane module (a hollow-fibre membrane module, HFMM) to extract caffeine effectively and selectively using a less toxic and environmentally-friendly solvent, sunflower oil.

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In recent years, hollow-fibre liquid membrane-based processes are being examined widely and have demonstrated superior performance in removing organic and biomolecules (6-12). The major advantages of the membrane extraction process are: selectivity, improved productivity, smaller wastes, less energy requirement and availability of large-scale module (i.e. easy scale up methods).

In this paper the applicability of sunflower oil (a non-toxic, less costly, environmentally-friendly solvent system) with or without any specific carrier for extraction of caffeine is presented. The effects of solvent, carrier, caffeine concentration and pH on extraction were determined. The process was upgraded to a small pilot-scale module and the performance was evaluated.

A. *Decaffeination Methods*

Various decaffeination methods such as Swiss water process, Chemical solvent process, Supercritical carbon dioxide process are commercially used (Table I). The Swiss Water process used to be very popular as it does not require chemicals and retained more flavour components. This has been replaced by the chemical solvent process that requires the use of methylene chloride/ethyl acetate. These solvents are considered toxic and hazardous, their presence in the product and their effect on the environment and operators need to be monitored carefully. Supercritical carbon dioxide uses very high pressure may take the natural taste of the product by extracting the hydrophilic components of the coffee beans (5).

Table I: Summary of decaffeination methods

Decaffeination methods	Description	% Extraction
(1) Water	Non toxic, complex process, remove little flavoring components	94-96%
(2) Chemical Solvents: - Dichloromethane - Ethyl Acetate	Removes caffeine and little flavor compounds. Mildly toxic, removes some flavoring compounds.	96-98%
(3) Supercritical CO_2	Selectively removes caffeine and very little flavor compounds, expensive	96-98%
A hollow-fibre membrane approach using sunflower oil	Expected removal of only caffeine without extraction of any flavoring and aromatic compounds.	To be examined

B. *Liquid-Liquid Extraction with sunflower oil*

In physical extraction, no carrier is added, only solvent alone is used for extraction. Reactive extraction is carried out using a carrier molecule which forms a complex with the caffeine molecules. There is report available in the literature on the use of carrier in caffeine extraction. The choice is based on commercial availability and the properties of the carrier. Amines are generally used for extraction of many organic molecules because of their efficiency. However, primary amines are soluble in water and therefore, are not selected as carriers. A secondary amine was chosen as it performed well compared to other amines (preliminary results). The reactive extraction of caffeine is considered to be a reversible one with the caffeine (Caf^-) molecules forming a carrier-caffeine complex with the amine carrier (A) in the organic solvent as shown below [13].

$$Caf^-_{(aq)} + A_{(org)} \longleftrightarrow CafA_{(org)} \quad (1)$$

caffeine solute *amine carrier* *caffeine-carrier complex*

where $A_{(org)}$ and $Caf_{(aq)}$ represent the amine (carrier) and caffeine solute, respectively. CafA (org) represent the caffeine-carrier complex in the organic phase, being soluble only in the organic phase. The complex that forms (CafA) is transported into the organic phase, ultimately achieving extraction of the caffeine from the aqueous phase. The apparent distribution coefficient as defined below:

$$D_E = \frac{C_{Caffo}}{C_{Caffi}} \quad (2)$$

where C_{Caffo} and C_{Caffi} are the caffeine concentrations at the organic and the feed side of the aqueous-organic interface, respectively.

II. Materials and Methods

A. *Chemicals*

Caffeine from Sigma-Aldrich, USA, Amberlite LA-2 from Merck, Germany, Aliquat 336 from Acros Organics, USA, Oleic acid from Merck, Germany, Sunflower oil from Pams, New Zealand, green roasted coffee from Atomic Coffee Ltd., New Zealand, ethanol, phosphoric acid, from Merck, Germany.

B. *Hollow Fiber Membrane Module*

A microporous hollow fiber membrane contactor, 5PCM-218, was purchased from Hoechst Celanese Corporation, Charlotte, NC, USA. The contactor has a total of 10,000 polypropylene hollow fibers (Celgard X-30, 240 µm ID, 300 µm, OD, pore size 0.05 µm, porosity 40%) potted with polyethylene epoxy in a polypropylene case of 2.5 cm ID. The effective fiber length is 15cm and the total fiber surface area is 1.4m^2. A schematic of the experimental hollow-fibre membrane module set-up is shown in Figure 2.

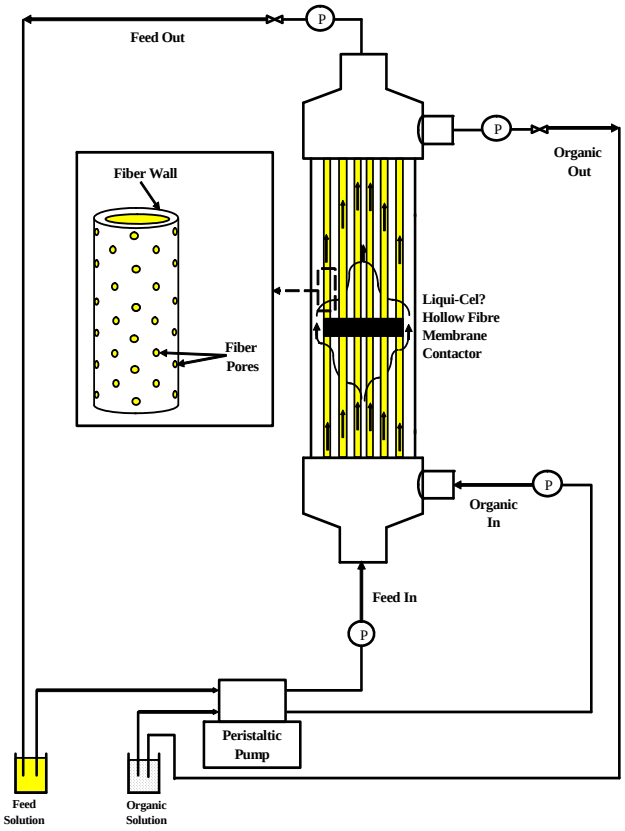

Figure 2: A schematic of the hollow-fibre membrane set-up.

C. *Equilibrium experiments*

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20 mg/ml caffeine solution was made by adding 2g of caffeine powder into 100ml hot boiling water, heated in on a heater. The pH value for this undiluted caffeine solution was measured using a pH meter (Cyberscan 510, Mettler Toledo, USA). 5ml of this aqueous caffeine solution made was pipetted into a centrifuge tube followed by addition of 5ml of sunflower oil (organic phase). The tube was then placed in the mixer at 500rpm for 20minutes to provide good mixing. It was then left for 2 hrs for settling of both phases.

Finally, the aqueous and organic phases were separated using centrifuge (Sigma Laboratory Centrifuge) under 4000rpm for 15minutes at 20 ^{0}C. After separation, 2ml of the aqueous phase was pipetted out into a 2ml centrifuge tube, ready for HPLC analysis.

To prepare the feed solutions at various pH concentrated phosphoric acid was diluted 1000 fold to prepare the diluted phosphoric acid. Then, a few drops of this diluted phosphoric acid were added in to the 5 ml caffeine solution to obtain pH values of 5, 4, 3 and 2. For the organic phase desired, concentrations of carrier (Amberlite LA-2/Aliquat 336) were added into the solvent (sunflower oil/ oleic acid) to make up 5 ml of the organic phase.

D. Analysis of the samples

HPLC analysis was used for the measurement of caffeine concentration. The HPLC system (Perkin Elmers, USA) contains a Berkin Coulter pump, autosampler and 32 Karat computer program as the data acquisition system. Quantitative determination was based on a DiamonsilTM C18 column (5 m, 200A, 4.6x250 mm). The column was operated at 40 ^{0}C at a flow rate of 0.5 ml/min with a mobile phase: solvent A (100% water) and solvent B (100%methanol) and the detection was at 280 nm.

E. Procedure for the hollow fibre membrane experiments

Initially, the organic phase was passed through shellside of the membrane in order to saturate the pores for a period of one hour using peristaltic pumps (Cole Parmer Instrument Company, USA.*)* The pump flow rate was initially high (approx. 400 ml/min) and then gradually decreased to approx. 30 mL/min. After an hour, distilled water was passed though the aqueous side (inside the fibers) followed by the feed solution containing caffeine. The desired flow rate was set, approx. 230 - 250 ml/min to circulate both the fluids through the module. The valves were used to maintain a positive differential pressure of approximately 30 kPa between the aqueous side and organic side, in order to retain the organic phase in the pores and on the shell-side. The membrane module was operated for 2 - 3 hrs and samples were taken every 10 minutes for analysis. Approximately 5 ml samples were taken out of the aqueous beaker. The operating conditions for the hollow-fibre experiments as a base case) are listed in Table II.

The percentage of caffeine, E (%), in the organic phase, was calculated from the concentration change using the following expression:

$$E(\%)=\frac{(C_{Cafi(aq)}-C_{Caff(aq)})}{C_{Cafi(aq)}}x100, \quad (3)$$

where $C_{Cafi(aq)}$ and $C_{Caff(aq)}$ are the initial and final concentrations of the feed, respectively.

Results and Discussion

F. Equilibrium Experiments

1) Effect of caffeine concentration

The effect of feed concentration (0.005 – 0.020 g/ml) on the physical extraction (solvent only) on caffeine is shown in Figure 3. The distribution coefficient increased with increasing caffeine concentration. A relatively linear relationship was resulted, similar to those in the literature (6). The results were reproducible, i.e. % error in the distribution coefficient was ca. 4%.

Table II: Experimental conditions for hollow-fibre experiments

Feed Solution	
Concentration of Caffeine (mg/ml)	20
Volume (ml)	400-500
pH (-)	6.7-6.9
Flow rate (L/h)	12-13
Temperature (K)	293
Organic Solution	
Concentration of carrier in sunflower oil (%v/v)	0.5-1
Volume (ml)	400-500
Flow rate (L/h)	9-10
Temperature (K)	293

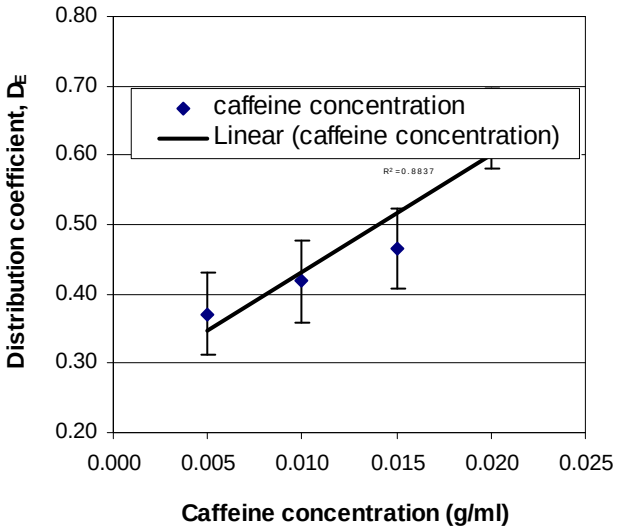

Figure 3: Distribution coefficient against caffeine concentration.

2) Effect of carrier concentration (Amberlite LA-/ Aliquat 336)

The effect of the organic phase concentration was examined using the carriers, Amberlite LA-2 and Aliquat 336 separately dissolved in sunflower oil and performing equilibrium experiments. The results are presented in Figure 4. The values of the distribution coefficient decreased from 0.47 (at 1% Amberlite LA-2) to 0.35 (at 10% Amberlite), suggesting better removal at very low concentration of the carrier. The value of distribution coefficient remained constant approx. at 0.35 with the Aliquat 336 concentration in the same range (results not shown). By comparison, Amberlite LA-2 yielded greater distribution coefficient (0.47 compared to 0.35) than Aliquat 336. This may be due to the higher solubility of the caffeine complex formed with Amberlite LA-2.

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3) Effect of solvent (sunflower oil and oleic acid)

Two solvents, sunflower oil and oleic acid were used as organic phase with the purpose of comparing their distribution coefficients (results not shown). The use of oleic acid (a component of sunflower oil, it contains 15-40% oleic acid) gave a higher DE = 0.6 compared to that in sunflower oil (DE = 0.35). Oleic acid was able to achieve better distribution coefficient partly it is in the pure form and able to react with caffeine molecules more than the other fatty acid components of sunflower oil. However, the breakthrough pressure and viscosity of sunflower oil is higher (14) and it is cheaper, non-toxic, much less corrosive and operator-friendly. Therefore most of the equilibrium and hollow-fiber experiments were conducted with sunflower oil instead of oleic acid.

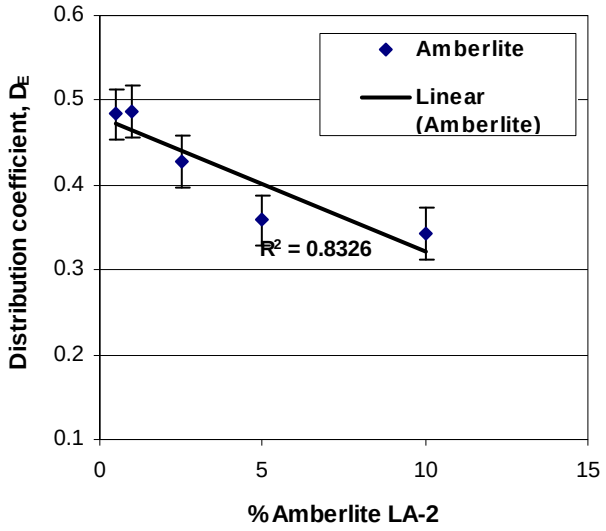

Figure 4: Distribution coefficient against Amberlite LA-2 concentration

4) Effect of pH

The distribution coefficient at the natural pH (6.7) is about 0.25. From the observation of Figure 4, the distribution coefficient decreased with decreasing pH (decreasing acidity). The best extraction was achieved at pH approx. 6.6, close to the natural pH of pure caffeine solution. Therefore, it is suggested that the natural pH can be used (i.e. no additional chemicals are required to change the pH) for better removal of caffeine from the aqueous solution. The results were reproducible and the relationship of the distribution coefficient with pH was found to be linear.

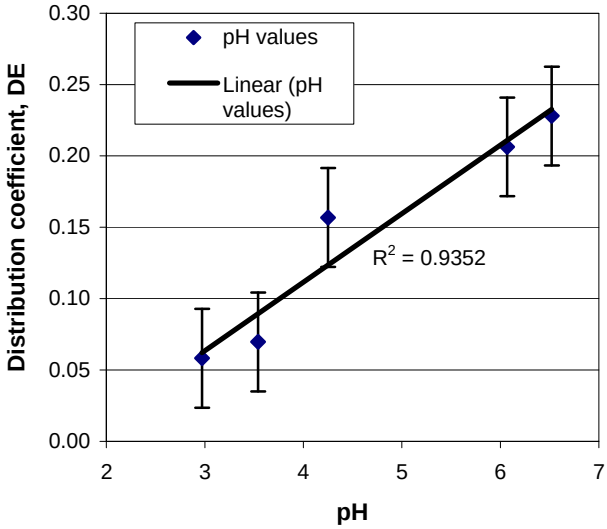

Figure 5: Distribution coefficient against pH values of caffeine solution.

G. Hollow Fibre Membrane (HFM) Experiments

With the intention to study the percentage extraction of caffeine, 0.5-1% Amberlite LA-2 and 0.5-1% Aliquat 336 were added into sunflower oil. The extraction of caffeine at its natural pH was performed in the hollow fibre module, operating in a recirculating mode. For comparison the results of pure sunflower oil are also presented. The extraction percentage with the experimental run time in the hollow-fibre is shown in Figure 6.

The addition of carrier in sunflower oil shows some increase in the extraction percentages. The highest extraction with 0.5% and 1% Amberlite-LA2 were 69% and 78%, respectively after 45 minutes. The extraction percentage eventually stabilizes at a lower value of 55%, at about 10% higher than those obtained with physical extraction (sunflower oil only). The highest extraction rate with Aliquat 336 occurred slightly earlier than those for Amberlite LA-2.

The extraction percentage with oleic acid was lower than those obtained with sunflower oil (Figure 7). The average percentages were less than 40% for both the carriers. More importantly the extraction with oleic acid was unstable with possible leakage of the solvent. This could be due to lower viscosity and smaller breakthrough pressure of the oleic acid-carrier system. From the comparative values for the organic systems the Aliquat 336-sunflower system can be recommended for further study, i.e. the effect of adding more stages on extraction percentages and stability.

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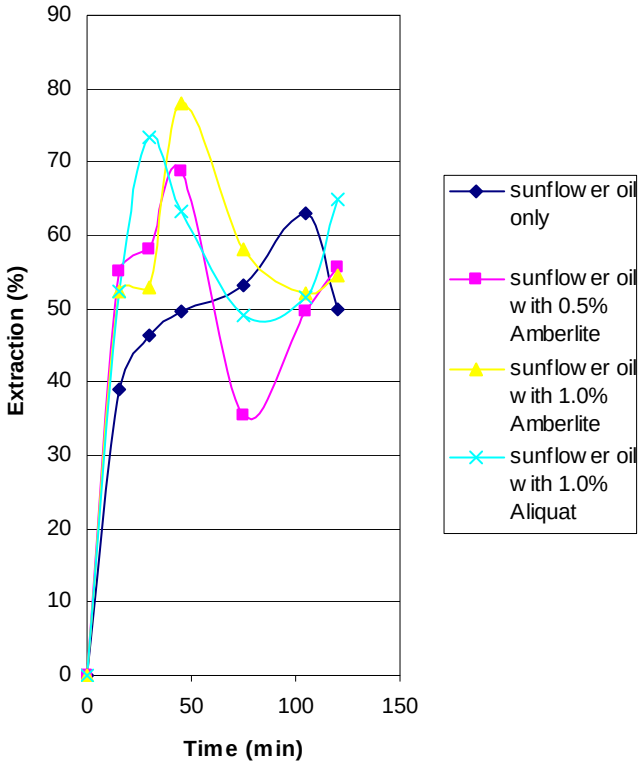

Figure 6: Extraction (%) of caffeine with sunflower oil (with or without carrier).

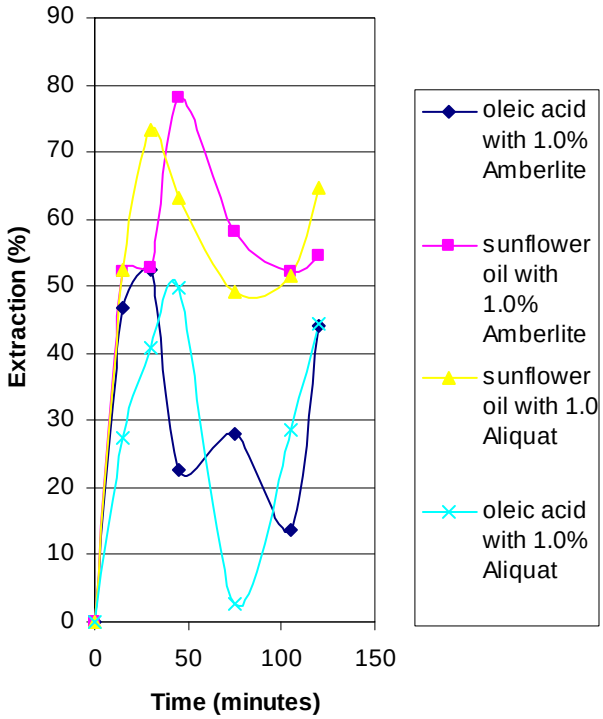

Figure 7: Extraction (%) of caffeine with oleic acid and sunflower oil (1% carrier- Aliquat 336 and Amberlite LA-2).

III. Conclusion

- The removal of caffeine from an aqueous phase into sunflower oil, a non-toxic and environmentally-friendly solvent, was successfully achieved**.** The distribution coefficient in sunflower oil increased with the increase of the following variables: initial caffeine concentration and feed solution pH. The best value was obtained at around pH 6.6, the natural pH of aqueous caffeine solution.
- The percentage removal of caffeine is dependant on type of operation, either physical or reactive extraction. In the physical process the removal is approx. 45% and this can be increased to approx. 55% by the addition of a small amount of Amberlite LA-2, an ionic carrier in sunflower oil, the aqueous phase being at its natural conditions.
- This extraction was achieved in the pilot-scale hollow fibre module using a process flow rate of 12 L/h and with only 1% Amberlite LA-2 in sunflower oil under normal room temperature and pressure.
- Finally, hollow-fibre membrane pilot scale experiments demonstrate the potential of this simple new process to remove caffeine from coffee using a less toxic and more operator-friendly solvent and with potential economic, environmental and process benefits.

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