

Pressurized Hot Water Extraction

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Abstract- Pressurized Hot Water Extraction (PHWE) is an extraction processes which has seen increasing use over the past years. It was introduced as a process to mainly extract thermally labile compounds from soil and plant samples, this process has gained popularity recently due to its eco-friendly nature. The process uses a relatively cheap solvent (water) under controlled temperature and pressure conditions to carry out the extraction process in plants, food materials as well as some chemical mixtures. It is known to be a relatively fast process as compared to the prevalent industrial extraction processes. Theoretically, this process can be used for extraction in a wide range of substances if the key parameters such as temperature, pressure, flow rate and additives are controlled. It is also considered to be an important process in drug discovery in the field of medicine. Studies are in progress to scale-up this process for industrial applications to extract major components of mixtures in an eco-friendly and cost effective way. The primary parameter in PHWE, temperature, has been studied in this paper. This paper explores the economic aspects and feasibility of this process in industry by comparing it with existent extraction processes such as ultrasonic extraction, microwave extraction, supercritical carbon dioxide extraction etc.

Keywords: Temperature, Microwave extraction, Ultrasonic Extraction, Supercritical CO₂ Extraction

I. INTRODUCTION

Pressurised hot water extraction, utilizes pressurised hot water i.e water ranging in the temperature of 100°C to critical temperature T_c . This process uses water or even steam too. It is an effective extraction technique that allows for selective extraction of components by simple manipulations of temperature and pressure. It is especially useful for thermally labile compounds or those that are susceptible to thermal degradation. The extracts and efficiency of the extraction can be studied by chromatography like high performance liquid chromatography under UV detector or even gas chromatography-mass spectrometry.

Pressurised hot water is useful in a number of ways. It provides better diffusion rates and also reaction and extraction rates. It has lower surface tension and better solubility of less polar compounds. It can be used for gasification of biomass, solid waste management.

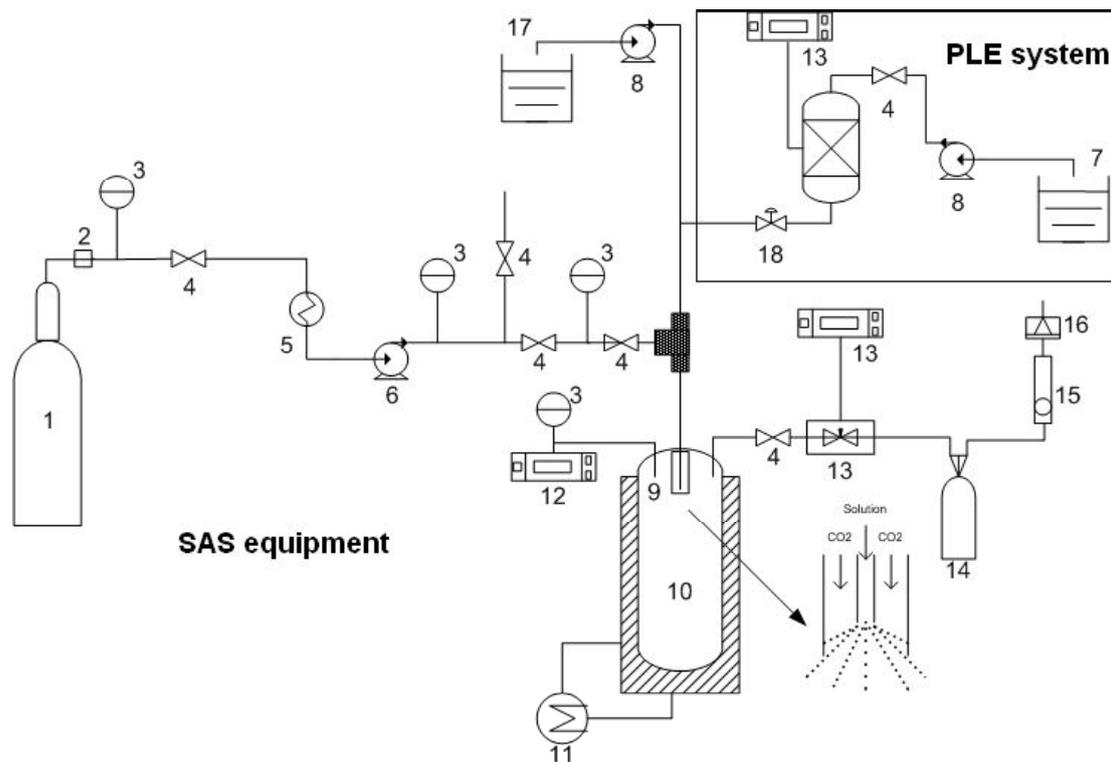
However at higher temperature and pressure, water can prove to be more corrosive. Hence suitable material of construction should be utilised when dealing with it.

II. PROCESS DESCRIPTION

Pressurized Hot Water Extraction first appeared in the early works of Hawthorne and his co-workers for the extraction of polar and non-polar compounds from soil samples in 1994. Over the years, the process has undergone many alterations and is morphed according to the sample matrix subjected to PHWE. In general, the process follows a 4-step mechanism:

1. The first step is desorption of solutes from the various active sites in the sample matrix under the pressurized and elevated temperature conditions.
2. The second step may involve the diffusion of extraction fluid into the matrix.
3. The third step involves the solutes partitioning themselves from the sample matrix and entering the extraction fluid phase.
4. The fourth step involves removal of these solutes from the system by the use of chromatographic elution.

This is brought about by a simple mechanism as follows:



Scheme of the home-built equipment, designed to carry out the organic solvent extraction with particle formation on-line (OEPO) 1. Sample Storage; 2. Filter; 3. Manometers; 4. Blocking Valves; 5. Thermostatic bath; 6. Pump; 7. Extracting solvent (Water) reservoir; 8. HPLC pumps; 9. Thermocouple; 10. Precipitation vessel; 11. Heating bath; 12. Temperature controllers; 13. Micrometric valve with a heating system; 14. Glass flask; 15. Glass float rotameter; 16. Flow totalizer; 17. Carrier or surfactant solution reservoir; 18. Back Pressure regulator

The solvent is pumped by a HPLC pump into the extraction cell, which is placed in an electrical heating jacket at a desired temperature, until the required pressure is obtained. The sample from which solute is to be extracted is placed in an extraction cell containing a sintered metal filter at the bottom and upper parts. The cell containing the sample is heated, filled with extraction solvent (water) and then pressurized. The sample is placed in the heating system for adequate time to ensure that the extraction cell would be at the desired temperature during the filling and pressurization procedure. After pressurization, the sample with pressurized solvent is kept statically at the desired pressure for the desired time (static extraction time). Once adequate residence time is provided, the back pressure regulator (BPR) valve is carefully opened, keeping the pressure at an appropriate level for the desired flow, to rinse the extraction cell with fresh extracting solvent for a predetermined time, known as dynamic extraction time. After pressurized hot water extraction (PHWE), the extracts are rapidly cooled in ice water using glass flasks to prevent extract degradation.

III. COMPARISON OF PHWE WITH OTHER EXTRACTION METHODS

3.1 COMPARISON OF PHWE WITH MICROWAVE EXTRACTION

3.1.1. Introduction:

Microwave extraction is a process of removal of polynuclear aromatic hydrocarbons using solvents such as chloroform, n-hexane, acetone, methanol, dichloromethane etc which are subjected to microwave irradiation for short periods of time. The temperature-pressure controlled microwave process is used mainly in laboratories and small scale extractions of hydrocarbons from plant samples.

3.1.2. Procedure:

In MAE, the source of energy is microwaves. They are used to provide the necessary energy to the solvent molecules, which in turn bring about the extraction. The extraction process takes place in three different steps: an equilibrium phase where the phenomena of solubilization and partition occur, in which the substrate is removed from the surface of the particle at a relatively constant velocity. This is followed by an intermediary transition phase where diffusion into the outer bulk occurs. In the last phase, the solute must overcome the forces that bind it to the sample matrix and it must enter the solvent bulk to complete the process. MAE does not include a filtration step or a process to remove the extracted solute from the system, thus, a secondary "cleanup" process is often necessary. In PHWE, however, the cleanup process is present within the main process itself.

3.1.3. Speed of extraction:

Microwave-assisted extraction is generally used in study laboratories and it finds very few industrial applications. Given the low quantity of samples, the extraction time varies from a few minutes to about 2 hours. This reduces the possibility of thermal degradation and keeps the solute integrity intact. An increase in extraction time increases yield, but beyond a certain point, it is found that the increase is miniscule. Thus, it is not advisable to use MAE for industrial processes which have to handle high sample quantities. Sometimes, the process is carried out in stages, this increases solvent requirement and microwave energy systems required.

PHWE is not generally used for low scale laboratory applications, but in the removal of sulphonamides and carbamates from samples of milk and certain animal tissue, it is found to require barely 4-5 minutes. In the extraction of anthocyanins and phenolics from fruit skins, it is found that PHWE completes the process in less than one minute (40sec) while MAE is found to require at least 300 -400 seconds. Conversely, a typical Microwave extraction of benzopyrene from a mixture of 16 polynuclear aromatic hydrocarbons is completed by irradiating a solvent mixture of n-hexane-acetone(3:2 v/v) in under 20 minutes at 413K, while the same extraction with PHWE would take close to an hour.

3.1.4. Comparison:

PHWE requires less time as compared to traditional Soxhlet extraction, but Microwave extraction requires even lesser time. Example: A typical Microwave extraction of benzopyrene from a mixture of 16 polynuclear aromatic hydrocarbons is completed by irradiating a solvent mixture of n-hexane-acetone(3:2 v/v) in under 20 minutes at 413K, while the same extraction with PHWE would take close to an hour. However, PHWE has a much lower installation and equipment cost, and it can be applied to a large scale industry, while the application of Microwave extraction to large industries is both harmful and expensive.

3.2 COMPARISON OF PHWE WITH SUPERCRITICAL CO₂ EXTRACTION

3.2.1. Introduction:

Supercritical carbon dioxide extraction is the use of CO₂ at supercritical temperature and pressure as an extractant for removal of cannabinoids, flavouring agents etc in industry. Carbon dioxide, when subjected to temperature and pressure above its critical temperature(304.25K) and critical pressure(72.9 atm or 7.39 MPa) behaves as a supercritical fluid. This relatively low critical temperature allows for safe extraction of certain chemicals and medicinal compounds from plant leaves and seeds without denaturing of the samples.

3.2.2. Procedure:

Supercritical carbon dioxide extraction uses carbon dioxide above supercritical pressure and temperature to act as an extractant. The system must contain a pump for the CO₂, a pressure cell to contain the sample, a means of maintaining pressure in the system and a collecting vessel. The gas is pumped to a heating zone, where it is heated to supercritical conditions. It then passes into the extraction vessel, where it rapidly diffuses into the solid matrix and dissolves the

material to be extracted. The dissolved material is swept from the extraction cell into a separator at lower pressure, and the extracted material settles out. The CO₂ can then be cooled, re-compressed and recycled, or discharged to atmosphere.

PHWE follows a similar procedure, with certain alterations. The detailed procedure has already been provided in the earlier section. The residence time provided in PHWE is higher than that in SCO₂E, because the water requires more time to overcome the various resistances. Also, it is easier to keep supercritical carbon dioxide in continuous flow condition. This residence time usually means that PHWE requires more time to achieve the necessary extraction.

3.2.3. Speed of extraction:

Carbon Dioxide: Diffusivities are much faster in supercritical fluids than in liquids, and therefore extraction can occur faster. Also, there is no surface tension and viscosities are much lower than in liquids, so the carbon dioxide can penetrate into small pores within the matrix inaccessible to liquids. Both the higher diffusivity and lower viscosity significantly increase the speed of the extraction: An extraction using an organic liquid may take several hours, whereas supercritical carbon dioxide extraction can be completed in 10 to 60 minutes.

PHWE: The time required for completion of process is dependent on the nature of compounds to be extracted and the extent of extraction required. On an average, the process completion time varies from 30 minutes to about 2-3 hours. For the same sample, it is estimated that carbon dioxide would require lesser time, on account of the residence time needed for PHWE.

3.2.4. Comparison:

Achieving desired high pressures above 72.9atm increases production cost significantly, and its use is limited to food industry, on account of its unimpressive efficiency to be used in high capacity industrial chemical processes, while PHWE can be applied to high capacity process vessels and covers a wide array of extractable compounds.

3.3. COMPARISON OF PHWE WITH ULTRASONIC EXTRACTION:

3.3.1. Introduction:

Ultrasonic extraction is the removal and recovery of organic analytes from a permeable solid matrix by means of a solvent which is energized by sound energy at frequencies in excess of those audible to the human ear. Energy may be introduced into the sample by means of an ultrasonic probe which is inserted into the sample or an ultrasonic bath into which the sample plus solvent is immersed. The ultrasonic energy may be strong enough to disrupt and pulverize the matrix, thus increasing the extractability of the analyte. This process is mainly used for small scale, laboratory studies of bacteria, and is often combined with other forms of energy:

1. thermo-sonication, i.e. heat and ultrasound
2. mano-sonication, i.e. pressure and ultrasound
3. mano-thermo-sonication, i.e. pressure, heat and ultrasound

3.3.2. Procedure:

The sample is placed in a ultrasonic cleaning vessel containing a dilute sodium hydroxide solution (sonicating liquid). It is then boiled for 20-80 minutes depending upon the necessity of extraction. After this, sound waves at a specific frequencies are passed through the vessel. When sonicating liquids at high intensities, the sound waves that propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles, with rates depending on the frequency. During the low-pressure cycle, high-intensity ultrasonic waves create small vacuum bubbles or voids in the liquid. When the bubbles attain a volume at which they can no longer absorb energy, they collapse violently during a high-pressure cycle. This phenomenon is termed cavitation. During the implosion very high temperatures (approx. 5,000K) and pressures (approx. 2,000atm) are reached locally. The implosion of the cavitation bubble also results in liquid jets of up to 280m/s velocity. The resulting shear forces break the cell envelope mechanically and improve material transfer. This process of implosion of cavitation bubble are used to bring about the extraction of chemicals from certain surfaces or mixtures.

Ultrasonic Extraction, in principle, only replaces the heat energy with sound energy, and makes the process eco-friendly. However, this process cannot be applied on a large scale because generating such a high amount of sound energy and effectively delivering it to the extraction system without dissipation of the energy is highly complex. Thus, PHWE emerges as the better choice for large scale applications.

3.3.3. Speed of extraction:

Use of sound energy to provide necessary energy to sonicating liquids is an extremely slow process. The typical activation time is 20-100 minutes. This is followed by a residence time at which high temperature and atmospheric pressure has to be maintained to allow the solute to diffuse into the sonicating liquid bulk. Also, in spite of being eco-friendly, this process is extremely time consuming for relatively high quantities of samples. Thus, it is only suitable for laboratory studies. An increase in ultrasonic wave frequency can cause increase in yield and decrease in time required, although it is not very substantial.

3.3.4 Comparison:

Ultrasonic Extraction, in principle, only replaces the heat energy with sound energy, and makes the process eco-friendly. However, this process cannot be applied on a large scale because generating such a high amount of sound energy and effectively delivering it to the extraction system without dissipation of the energy is highly complex and very costly. Thus, only small scale applications are recommended. Also, the process requires a solvent to which the energy must be supplied. Since this process is used for biological purposes such as study of microorganisms, the solvents must be inert and may have certain special requirements. Thus, PHWE can be applied to a broader industry and is much more cost effective as compared to Ultrasonic Extraction.

3.4 TABULATED COMPARISON

QUANTITY	PHWE	MAE	SCO ₂ E	USE
Temperature (°C)	100-374	25-70	31.1<	50-80
Pressure (atm)	10-200atm	1-100atm	73atm<	1atm
Solvent	Water	Organic	CO ₂	Organic
No. of Stages	1	1-5	1(recycled)	1
Extraction Time	3min-150min	15min-120min	10min-60min	20-100min
Major Applications	Plant samples, medicinal compounds	Essential oils, thermolabile compounds	Cannabinoids, decaffeination of coffee beans	Lipids, proteins, anthocyanins, steroids

IV.CONCLUSION

As we continue to come face-to-face with technological advancements and global economic development our attention from the environment should not get diverted. We must aim towards establishing techniques and processes that increase profitability yet contribute towards environmental sustainability. PHWE is increasingly becoming an important process in green chemical technology. At present, it has limited applications but with more and more countries investing in green technology, the improvements could be manifold.

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