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# Tuning water chemistry for the recovery of greener products: pragmatic and sustainable approaches

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The environmental impact and denaturing propensity of organic solvents in the extraction of plant bioactives pose great challenges in extraction systems. As a result, proactive consideration of procedures and evidence for tuning water properties for better recovery and positive influence on the green synthesis of products become pivotal. The conventional maceration approach takes a longer duration (1–72 h) for product recovery while percolation, distillation, and Soxhlet extractions take about 1 to 6 h. An intensified modern hydro-extraction process was identified for tuning water properties with an appreciable yield similar to organic solvents within 10–15 min. The percentage yield of tuned hydro-solvents achieved close to 90% recovery of active metabolites. The additional advantage of using tuned water over organic solvents is in the preservation of the bio-activities and forestalling the possibility of contamination of the bio-matrices during extractions with an organic solvent. This advantage is based on the fast extraction rate and selectivity of the tuned solvent when compared to the traditional approach. This review uniquely approaches the study of biometabolite recovery through insights from the chemistry of water under different extraction techniques for the very first time. Current challenges and prospects from the study are further presented.

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## 1. Introduction

The early techniques for recovery of bioactive metabolites involve conventional cold or hot solvent extraction.<sup>1</sup> The choice is a function of the nature of the bioactive compound of interest.<sup>2</sup> The adverse effect of organic solvents (Table 1) which are mostly preferred extraction techniques has warranted the search for greener alternatives. One of the ways green extractions is described involves the isolation of medicinally active portions from a bio-material,<sup>3</sup> with the simultaneous use of eco-friendly solvents and optimal use of energy.<sup>4–9</sup> Prospecting for green solvents has brought water to the fore of extraction technology.<sup>10</sup> Water is affirmatively described as the “greenest solvent” imaginable, with its availability at the required purity, it is cost-effective, readily recycled, non-toxic, non-flammable,

and eco-friendly.<sup>10–13</sup> Based on the green chemistry precept, water is considered a green chemical per excellence.<sup>14–16</sup> Water is useful in the recovery of various phytochemicals including alcohols, sugars, proteins, and organic acids with natural water-soluble properties.<sup>12,16–21</sup> However, water as a solvent has some physical and chemical property disadvantages when compared to organic solvent.<sup>21–23</sup> The polar nature of water in its natural form reduces its efficacy and acceptability when compared with organic solvents for some kinds of extractions. Organic solvents are extensively desirable since they exhibit better recovery than water at ambient conditions.<sup>3</sup> Further setbacks experienced when using conventional hydro-extraction include time and energy consumption, thermal decomposition of thermo-sensitive metabolites and low recovery of hydro-solvent in its natural form.

There exists the need to investigate water properties that can be improved to complement its natural advantage and eradicate its attendant limitations as a solvent for extraction.<sup>5,8,10,28,29</sup> have indicated that improving traditional extraction must entail decreased energy input, sustainability and a non-toxic final product. Improving water to own variable chemistry will aid the extraction of a broad range of polar and non-polar biomolecules from sustainable natural products with non-toxic quality and eco-friendliness.<sup>10,21,29</sup> This approach will prevent the use of organic solvents, fossil energy, chemical waste and risks of extraction. It is known that water existing in its tunable form satisfies the conditions of green solvents.<sup>11–13</sup> Recently, the

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Table 1 Some selected organic solvents and their toxicological effects<sup>24–27</sup>

| Solvents                                                                                  | Toxicological effects                                                                                                                                                 |
|-------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Toluene                                                                                   | Appreciably fatal if it penetrates the airways or is swallowed. Has the potential of damaging the fetus. Prolonged exposure may warrant the damaging of organs        |
| Dichloromethane (DCM)                                                                     | Suspected of causing cancer                                                                                                                                           |
| Chloroform                                                                                | Suspected of causing cancer                                                                                                                                           |
| Dimethylformamide (DMF), dimethylacetamide (DMA) and <i>N</i> -methyl pyrrolidinone (NMP) | May damage fertility or affect the unborn child                                                                                                                       |
| 1,2,3-Trichloropropane and trichloroethylene and 1,2-dichloroethane                       | May reduce fertility or affect the unborn child                                                                                                                       |
| 2-Methoxyethanol, 2-ethoxyethanol and 2-ethoxyethyl acetate                               | May damage fertility or affect the unborn child                                                                                                                       |
| Benzene                                                                                   | Low flash point (−11 °C), carcinogenic. It has a high toxicological impact on man and its immediate environment, hence, strongly regulated in the US (HAP) and the EU |
| <i>n</i> -Hexane(s)                                                                       | Very low flash point (−23 °C), toxic, carcinogenic, pollutant                                                                                                         |
| Pyridine                                                                                  | Has reprotoxic and carcinogenic effects on long exposure                                                                                                              |
| <i>n</i> -Pentane                                                                         | Classified as a hazardous airborne                                                                                                                                    |

usage of water for extraction has been considered based on its negligible environmental impact.<sup>30,31</sup> To date, processes developed imply extraction with water could proffer net benefits concerning eco-friendliness, reduced process time, improved selectivity, preservation of heat-sensitive compounds and reduced energy input.<sup>7</sup>

## 2. Methods

This review is centered on the tunable chemistry of water. The search methodology adopted was according to Feli *et al.*<sup>32</sup> The study investigates the tunable properties of water with a positive influence on green synthesis. Data mining and processing of secondary information in literature engaged procedures as described in Fig. 1a and involve the review of 268 publications. About 125 articles reviewed comprehensively covered conventional and non-conventional techniques studied, 35 discussed the challenges of the green extraction techniques and 45 presented possibilities of tunable technology of water as an alternative extraction process.

Cumulatively, 183 articles were selected based on the extensive and quantifiable information and their systematic mode of data presentation on the alternative extraction processes. Various cogent keywords such as properties of water, tunable water, hydro extraction, merits of hydro solvent extraction and development of aqueous solvents and systems were typed and searched on notable databases such as Google scholar, science direct, pub med and web of science. Articles within the year of publication ranging from 1997 to 2021 were studied for review (Fig. 1b).

## 3. Hydro extraction and mechanism of tuned water

### 3.1 Water and extraction processes

The water molecule is very small with a hard-sphere diameter of 2.75 Å. The small size of the molecule is of vital importance in

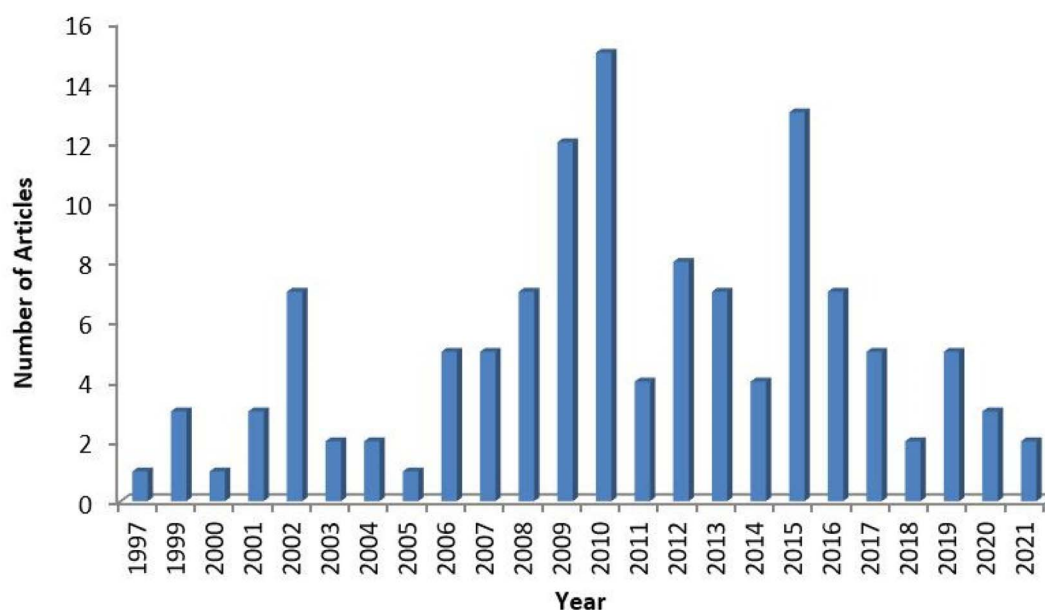
solute hydration. The dipole moment (1.85 D) of water molecules is a result of the two partial positive charges on the hydrogen [ $H^+$ ] atoms and the only single zone of negative charge on the oxygen [ $O^-$ ]. The contribution of the total electron density of the water molecule in the H–O–H plane makes it spherical one.<sup>33,34</sup> Also, one of the most essential parameters use in categorizing the polarity of the medium and the control exerted over the ionic dissociation of salts is the macroscopic dielectric constant of a solvent ( $\epsilon_r$ ). The high polarity of water can be attributed to dipole orientations of the hydrogen-bond network which gives it a dielectric constant value of 78.3. At higher temperatures and pressures, the polarity of water is significantly reduced as the hydrogen bond network is disintegrated.<sup>35,36</sup> Hence, using water as a solvent in extraction processes might be energy-demanding in those cases where water needs to be removed by evaporation. Furthermore, the energy demand to heat liquid water (25 °C to 250 °C, 5 MPa) is almost three times less than needed to vaporize the water to create steam (25 °C to 250 °C, 0.1 MPa).<sup>37</sup>

The chemical and physical properties of water are largely affected by temperature variation.<sup>38</sup> This possibility of change in the properties of water gives it variable characteristics which could be harnessed during the extraction of plant metabolites. One of the most dramatic changes for liquid water at saturation pressure is the static permittivity ( $\epsilon_r$ ), going from 78 at 25 °C to 14 at 350 °C.<sup>39</sup> Studies show that the property of water at near-critical conditions dissolves hydrophobic organic compounds.<sup>38,40</sup> At this point, inorganic solute such as NaCl becomes insoluble in water which is the attribute of organic solvents. The increasing temperature at a critical point diminishes electrostatic interactions within water molecules, as well as between water molecules and surrounding ions or molecules (*i.e.*, both  $\epsilon_r$  and  $\pi^*$  (polarizability) decrease with increasing temperature). At higher temperatures, there is an observed increase in the movement/rotation of water molecules. Hence, the use of liquid water at higher temperature and pressure allows the dissolving of less polar bioactive compounds. Inter-molecular interactions involving hydrogen bonding become





(a)



(b)

Fig. 1 Flow chart for the article selection process (a) and yearly distribution of articles used for extracting data (b).

less pronounced; thereby favoring dispersion forces (induced dipole-induced dipole forces). In other words, liquid water at elevated temperature (and pressure) becomes less polar of a solvent. Liquid water at temperatures of 200–275 °C and saturation pressure has  $\epsilon_r$  similar to that of methanol and ethanol at ambient conditions.<sup>41</sup> The notable properties of water include a strong hydrogen bond, which results in a very high specific heat capacity ( $C_p$ ,  $m$ , 75.3 J mol<sup>-1</sup> K<sup>-1</sup>, isobaric, molar, at 25 °C), high heat of vaporization ( $H_v$ , 40.7 kJ mol<sup>-1</sup> at

100 °C) and extremely high relative static permittivity ( $\epsilon_r$ , also referred to as the dielectric constant) of 76–80 at 20 °C. This implies that water creates electrostatic bonds with other molecules, thereby decreasing or eliminating intermolecular interaction between surrounding ions.<sup>42</sup> Water is non-toxic and non-flammable, it is cheap and readily available. Thus, it provides opportunities for clean processing and pollution prevention.





Fig. 2 Mechanism of movement of tuned water into the plant sample: Source: <https://www.berkem.com>.

### 3.2 Mechanisms of tuned water extraction

Generally, water can exist in three different states based on temperature change. These states include liquid water, solid

water (ice) and gaseous water (steam or vapour).<sup>43</sup> The physicochemical properties of water subjected to various tunable effects includes surface tension, dielectric constant and

Table 2 Convectional/traditional extraction methods

| Methods     | Process                                                                                                                                                                                                                                                                                              | Advantages                                                                                                                     | Disadvantages                                                                                     | References    |
|-------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|---------------|
| Squeezing   | The techniques involve the application of pressure on moistened plant samples <i>via</i> pestle, mortars, mullers, presses, <i>etc.</i> , on the plant samples to get the extrudate                                                                                                                  | Simple<br>Little or no solvent required<br>Requires no thermal degradation<br>Low extraction efficiency                        | Possibility of contamination of bio-actives                                                       | 59–61         |
| Maceration  | Powdered plant samples are added to the solvent already in a stoppered container with frequent agitation. The aqueous extracting solvent is then drained off followed by pressing and centrifugation to remove the remaining miscella from the plant material                                        | Can be used for a large amount of sample<br>A limited solvent is required<br>Long extraction time<br>Low extraction efficiency | Long extraction duration<br><br>Only useful for soluble or thermolabile bio-actives               | 39, 62 and 63 |
| Decoction   | The plant matrix comes in contact with the aqueous solvent at boiling point for a maximum duration of 30 min. The liquid is then filtered at end of the extraction. Then the liquid is filtered, and the squeezed liquid of the extracted matrix impregnated with the aqueous solvent is added to it | Use predominantly for phenolics<br>Requires moderate heat<br>Long extraction time<br><br>Low extraction efficiency             | Only useful for thermoresistant bioactive<br>Limited validity<br>Extracts have a short shelf life | 64–66         |
| Infusion    | Extraction in this regard involves soaking the solid plant powder in cold or boiling water for a short time                                                                                                                                                                                          | Long extraction time<br>Low extraction efficiency                                                                              | Easily altered extract<br>Limited validity                                                        | 4 and 67      |
| Percolation | The method makes use of narrow shaped percolator which holds the moistened plant samples. The plant material is then rinsed with the solvent several times until the active ingredient is extracted                                                                                                  | Easy to operate<br>Very fast                                                                                                   | Good grinding required<br>Requires preliminary humidification<br>Not exhaustive                   | 68–70         |



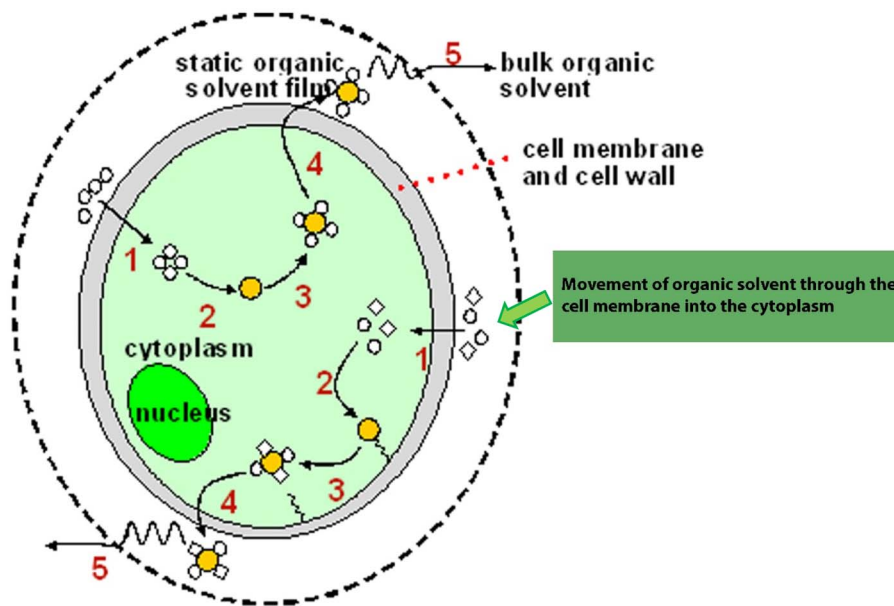


Fig. 3 Schematic representation of extraction processes of bioactives in cell. Source: Halim *et al.*<sup>58</sup>

viscosity. These properties are tuned under external influences such as temperature, pressure, ultrasound, and the incorporation of some other bio-based solubilizing compounds and hydrotropes. Mottaleb and Sarker<sup>44</sup> affirmed that at high temperature and pressure, the viscosity of solvent is lowered, surface tension reduces and the rate of the penetration of hydro-solvent into the pores of the sample matrix may increase (Fig. 2).<sup>44</sup> In addition to this, at room temperature and atmospheric pressure, water is a highly polar solvent with a high dielectric constant based on the presence of hydrogen-bonded structure.<sup>42</sup> Dielectric constant points to the strength of the polarity of water. When heat and pressure are applied to water, a drastic change is observed in the properties of the water as the hydrogen-bonded lattice is disrupted with increasing thermal motion and a fall in the value of the dielectric constant with the resultant lesser polarity of water.<sup>45,46</sup> Hence, water begins to exhibit similar properties of organic solvents with no environmental concerns.<sup>47–49</sup> The tuning effect also speeds up the rate of molecular diffusion and interaction of the liquid phase (hydro-solvents) with the material. The ease of diffusion and penetration of matrices observed in the tuned hydro-solvent is an appreciable attribute predominantly known in many extraction systems that use organic solvent.<sup>50</sup>

Brignole,<sup>51</sup> Smith,<sup>46</sup> and Carr *et al.*<sup>41</sup> in their studies revealed that under conditions of high temperature (250 °C) and sufficient pressure (25 bar) water remains in its liquid state. Though the dielectric constant of water is 80 at 25 °C; however, at elevated temperature, the dielectric constant drops to 25, which falls between those of methanol ( $\epsilon = 33$ ) and ethanol ( $\epsilon = 24$ ) at 25 °C. Under such conditions, water exhibits properties that mimic some organic solvents, dissolving compounds with low polarity.<sup>33,36,42,52–56</sup> In addition, it has been reported that intensified techniques are faster when compared to the conventional extraction technique.<sup>57</sup>

## 4. Extraction processes

### 4.1 Conventional extraction processes

There are diverse traditional extraction methods such as described in Table 2. However, these methods are generally challenged with contamination of extracted bio-actives resulting from prolonged exposure to organic solvents and other disadvantages. Solvents may penetrate through the cell, move into the cytoplasm containing neutral lipids, and form a solvent–lipid interaction by van der Waals forces. During this process, lipids may be extracted from the cell matrix which may contaminate extracellular metabolites of interest and bioactivities (Fig. 3).

### 4.2 Intensified modern hydro-extraction processes

The intensified modern extraction processes include microwave-assisted, supercritical or pressurized liquid water, ultrasound-enhanced, water–oil-based solvents and enhanced hydrotropic extraction which is summarized in Table 3. These extraction systems make use of water as their solvent for extraction under critically controlled conditions and is commonly called “green solvent”.<sup>9,11,12,71</sup> The extraction principles alongside the representations of conventional and intensified processes are presented in Table 3 and Fig. 4 respectively.

## 5. Results and discussion

### 5.1 Effect of extraction techniques on yield of biometabolites

From Tables 4 and 5, the extracted bio-actives can be categorized into phenolics and polyphenolics, essential oils, alkaloids and carotenoids, terpenes, carbohydrates, proteins pigments and vitamins.



Table 3 Non-conventional/intensified water extraction techniques

| Techniques                                                                | Mechanism                                                                                                                                                                                                                                                                                                                                                 | Advantage (s)                                                                                                        | Limitations                                                      | References   |
|---------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|--------------|
| Enhanced hydro-accelerated extraction                                     | Water is subjected to elevated temperatures above the boiling point and pressures while maintaining its liquid state ( <i>i.e.</i> , liquid water). The tuned aqueous solvent accelerates selective desorption of the analytes thus, giving room for selective extraction by solubilizing the analytes from plant samples                                 | High solvent strength<br>Fast extraction rate<br>No phase change of liquids                                          | Expensive<br>Requires extraction clean up                        | 73 and 74    |
| Microwave-enhanced hydro-extraction/microwave-assisted hydro distillation | The dielectric of water is tuned under non-ionizing electromagnetic fields in the frequency range from 300 MHz to 300 GHz. The supplied electromagnetic energy is converted to heat following ionic conduction and dipole rotation mechanisms of the hydro-solvent. This leads to the separation of solutes from active sites of the sample matrix        | High selectivity<br>Lower extraction time<br>Enhanced bio-active recovery                                            | Formation of free radicals<br>Possibility of thermal degradation | 75–78        |
| Pressurized or subcritical hydro-extraction                               | Water is tuned at critical pressure (1–22.1 MPa) and critical temperature (between 100–374 °C) while maintaining its liquid state. Under this condition, properties such as dielectric constant and viscosity are tuned which consequently decreases the surface tension of the water and increases its diffusivity                                       | Possibility of dielectric variation over a wide range<br>Efficient mass transfer and diffusion. Fast extraction rate | Expensive                                                        | 57, 79–84    |
| Aqueous ultrasonic hydro-extraction                                       | The properties of water are tuned under ultrasound from 20 kHz to 2000 kHz. The ultrasound enhances the propagation of mechanical waves, formed compressions and rarefactions, respectively. Thus, in contact with a bio-matrix, the cell of the material is damaged by the principle of acoustic cavitation favouring the release of bioactive compounds | High extraction efficiency and faster extraction rate                                                                | —                                                                | 4, 77, 85–89 |
| Enhanced hydrotropic extraction                                           | The solubility of water is enhanced by the incorporation of hydrotropes. These compounds consist of a hydrophilic part and a hydrophobic part in the similitude of surfactants. However, they act as coupling agents to tune the                                                                                                                          | Simplicity<br>Cost-effective<br>Eco-friendly nature<br>High solubilization and selectivity capacity                  |                                                                  | 90–94        |



Table 3 (Contd.)

| Techniques                         | Mechanism                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Advantage (s)                                                                                                                                                                        | Limitations | References |
|------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|------------|
| Water-oil biosurfactant extraction | polar property of water and aid its extraction<br>This involves the dispersion of thermodynamically stable micelles in water. These micelles consist of the polar head which attracts the aqueous core (water) and the non-polar part of the hydrocarbon chain is attracted by the organic phase which points outside. The coupling is known as water-oil surfactant. During the extraction, water and hydrophilic plant metabolites are solubilized inside the cores | High selectivity<br>Bioactivities protection<br>Shorter phase separation time<br>Thermodynamically stable, low costs, energy savings, ease of operation at a continuous steady-state |             | 95–100     |

**a Essential oils.** Table 4 presents the extraction conditions and yield of selected compounds from the plant using conventional and intensified techniques. With regards to time and temperature, the data presented showed that tuned solvents and intensified techniques have lower extraction time. It was observed that essential oil extracted from lavender flowers *via* microwave-enhanced extraction and the traditional method gives the yield of 8.86% and 8.75% at 10 and 90 min, respectively. Essential oil from *Thymus vulgaris* was extracted in 75 min using the intensified approach as against 240 min in the traditional method. The faster extraction rate observed for microwave extraction may be attributed to the transformation of the hydro-solvent used into an organic mimic at elevated temperature during extraction. This makes it easy for cell wall disruption and easy extraction of the plant's product.<sup>101–103,166–170</sup>

Generally, from Table 4, the extraction technique with the higher time frame is maceration, although at a lower temperature. However, when compared with extraction of essential oil *via* pressurized hydro extraction, pressurized technique operates at a lesser time frame for the extraction of oil from *M. chamomilla* and *Thymus vulgaris* with yield of 120% and 150% respectively. Similarly, in Table 5 the use of hydro-solvent *via* steam distillation compared to the pressurized technology has a faster oil extraction rate with a yield of 12% at 40 min and >12% at 5 min respectively.

Although the extraction process in traditional maceration took place at low temperature but disadvantaged with longer extraction time when compared to intensified methods of pressurized hydro-extraction, microwave-enhanced hydro solvent and ultrasound-assisted hydro extraction with lower recovery duration. The longer extraction durations in conventional extractions make extracted bio-products susceptible to deterioration and reduced pharmacological activity.<sup>104</sup> Furthermore, it is imperative to add that extracts of organic solvent exhibit toxicological impact in the environment.<sup>105,106</sup>

**b Phenols and polyphenols.** The vital study of the green extraction of phenols and polyphenolics as compared to the conventional organic solvent techniques is based on the significant anti-oxidizing activity potential of these bio-actives in pharmacognosy.<sup>106–108</sup> From Table 5, the use of tune hydro-solvent and technology shows a higher extraction performance of 29.8 for *M. charantia* compared to a low value of extract from Soxhlet (0.4%). Furthermore, the extraction of *Phyllanthus amarus* is reported as 52.97 mg g<sup>−1</sup> compared to 17.67 mg g<sup>−1</sup> from conventional reflux at a higher time frame of 30 min. The use of tuned ultrasonic hydro-solvent in an ultrasound-assisted extraction system results in fast extraction time of 10 and 15 min respectively for the extraction of pectin from jack fruit and polyphenols, amino acid and caffeine from green tea which helps to conserve its pharmacological attributes.<sup>107–109</sup> Hydro-solvent tuned under the influence of this green technology especially the ultrasound exhibits no environmental concern as compared to the toxic organic solvents which can contaminate the activity and quality of the extracts.<sup>102,103,107,110</sup>

**c Alkaloids, volatile oils and terpenes.** From Table 5 the yield with pressurized hydro-solvent for stevioside, rebaudioside A extraction was higher (91.8%) with a lesser extraction time of 15 min when compared to the use of traditional reflux method of extraction (84%, 1–1.5 h). Furthermore, extraction of borneol, terpinen-4-ol, carvacrol from *Origanum onites* and volatile oil from *Cuminum cyminum* L. equally exhibited greater yield of 5.05% and 16.2% at a lesser time using tuned solvent when compared to the lower yield of 3.16% for both conventional Soxhlet extraction, hydro and steam distillation at longer extraction duration of 12 h. The extraction of anthocyanins phenolics from dried red grape skin with intensified pressurized solvent is approximately 4 times higher (45%) when compared with the traditional method (10.5%).





Fig. 4 Comparative mechanism of conventional (A) and selected intensified methods (B and C).<sup>72</sup>

Similarly, from Table 5, the extraction of capsaicinoids from *Capsicum annuum* using Soxhlet was reported to have 5.243 mg g<sup>-1</sup> of bio-actives at 300 min while the green technology using

pressurized hydro-solvent had improved performance compared to the conventional technology at 20 min. These appreciable attributes are connected to the mimicking ability of the tuned

Table 4 Some selected extraction of plant metabolites using different approaches

| Methods                           | Sample                                          | Desired product                      | Experiment temp. (°C) | Optimum time (min)    | Yields                    | Sources     |
|-----------------------------------|-------------------------------------------------|--------------------------------------|-----------------------|-----------------------|---------------------------|-------------|
| Maceration                        | <i>Brassica oleracea</i> var. <i>italica</i>    | Essential oil                        | 4                     | 1440                  | 82.2 mg GAE/100 g DW      | 122 and 123 |
|                                   | <i>Solanum scabrum</i> leaves                   | Essential oil                        | —                     | 4320                  | 34.2 g GAE/100 g          | 124         |
|                                   | <i>Lepidium sativum</i>                         | Essential oil                        | 50                    | 1440                  | 25 mg RuE/g DW            | 125         |
|                                   | <i>Artocarpus heterophyllus</i> wastes          |                                      | 25                    | 4320                  | 871.4 mg QuE/g DW         | 126         |
|                                   | <i>Quercus robur</i> L.                         | Phenolic compounds                   | 40                    | —                     | 412 mg CE/g bark          | 127         |
| Percolation                       | <i>Artocarpus heterophyllus</i> wastes          | Essential oil                        | 25                    | 60                    | 511.6 mg QuE/g DW         | 128         |
| Infusion                          | Moroccan <i>Acacia mollissima</i> bark          | Phenolic compounds                   | 20                    | 120                   | 258.4 mg GAE/g bark       | 129         |
| Soxhlet                           | <i>Artocarpus heterophyllus</i> wastes          | Essential oil                        | 10                    | 300                   | 381.4 mg QuE/g DW         | 128         |
|                                   | <i>Vernonia cinerea</i> leaves                  | Essential oil                        | —                     | 120                   | 26.22 mg QuE/g DW         | 130         |
|                                   | <i>Pinus radiata</i> bark                       | Essential oil                        | 82                    | 60, 120, 180, and 360 | 622.40 mg GAE/g           | 131         |
|                                   | <i>Morus nigra</i> (dried)                      | Essential oil                        | 50                    | 180                   | 58.94% of flavonoid yield | 132         |
| Steam distillation                | Lavandula flowers                               | Essential oil                        | 100                   | 90                    | 8.75%                     | 133         |
| Hydro distillation                | <i>Thymus vulgaris</i>                          | Essential oil                        | —                     | 240                   | —                         | 134         |
|                                   | <i>Pinus pinaster</i>                           | Polyphenols                          | 100                   | 180                   | 14.3 mg GAE/g bark        | 135         |
| Pressurized hydro-extraction      | <i>Gossypium herbaceum</i> seed                 | Oil                                  | 180–280               | 270                   | 30%                       | 136         |
|                                   | <i>Solanum tuberosum</i> peel                   | Glucose                              | 140–240               | 240                   | 15%                       | 137         |
|                                   | <i>Pinus densiflora</i>                         | Organic acid product                 | —                     | 270                   | 10%                       | 123         |
|                                   | <i>M. chamomilla</i>                            | Essential oils                       | 100–175               | 150                   | 120%                      | 138         |
|                                   | <i>Zea mays</i> stalk                           | Fermentable hexose                   | 180–392               | 280                   | 27%                       | 139         |
|                                   | <i>Triticum aestivum</i> L. straw               | Fermentable hexose                   | —                     | 280                   | 54%                       | 139         |
|                                   | Cellulose                                       | Oligosaccharides                     | —                     | 380                   | 16%                       | 140         |
|                                   | <i>Triticum aestivum</i> L. straw               | Reducing sugars                      | 170–210               | 190                   | 30%                       | 136         |
|                                   | Fish proteins                                   | Amino acid                           | 180–320               | 260                   | 30%                       | 141         |
|                                   | <i>Thymus vulgaris</i>                          | Essential oils                       | 100–175               | 150                   | 150%                      | 138         |
|                                   | Gramineae <i>Saccharum officinarum</i> L. waste | Reducing sugars                      | 200–240               | 240                   | 2%                        | 142         |
|                                   | Defatted rice bran                              | Sugars and proteins                  | 200–260               | 200                   | 5%                        | 143         |
|                                   | <i>Simmondsia chinensis</i> seed                | Oil                                  | 180–260               | 240                   | 30%                       | 144         |
|                                   | Rosmarinic acid                                 | Terpenes                             | 60–100                | —                     | 25%                       | 145         |
| Microwave enhanced hydro solvent  | Lavandula flowers                               | Essential oil                        | 100                   | 10                    | 8.86%                     | 133         |
|                                   | <i>Thymus vulgaris</i>                          | Essential oil                        | —                     | 75                    | —                         | 134         |
| Ultrasound-assisted hydro solvent | <i>Artocarpus heterophyllus</i>                 | Pectin                               | 90                    | 10                    | —                         | 146         |
|                                   | <i>Camellia sinensis</i> leaves                 | Polyphenols, amino acid and caffeine | 65                    | 15                    | —                         | 147         |
| Solid-liquid extraction           | <i>Pinus</i> nuts                               | Inositol                             | 60                    | 120                   | 3.7 mg g <sup>-1</sup>    | 148         |

hydro-solvent and its ease of disrupting the cell wall of the plant leading to diffusion, transportation and effective mass transfer of the bio-actives at low time duration.<sup>111–114</sup> Other bio-actives such as carbohydrates, proteins, vitamins and pigments exhibit similar extraction performance. Apart from the eco-friendliness, Cao *et al.*<sup>115</sup> also showed that the use of pressurized extraction protocol results in significant reduction of extraction time while simultaneously increasing the yield to about four times when compared with the traditional method.<sup>116</sup>

The extraction capacity of tuned water does not only stand out with greater and greener potential, but it also influences vital properties of other green solvents such as ethanol and

methanol.<sup>117</sup> Although high selectivity of organic solvents is the reason behind their choice during extraction over water. For instance, water in its natural state, as studied by Carrero-Carralero *et al.*<sup>118</sup> is less selective when compared to alcohol.<sup>119</sup> However, the use of intensified technology can effectively alter the polarity, penetration and selectivity of water as solvent for the extraction of both hydrophilic and hydrophobic plant bio-actives.<sup>120</sup> Water tuning *via* ultrasound technology at known frequencies and amplitude generates cavitation bubbles at a non-stable point resulting in the release of high temperature and pressure *via* imploding. This improves the penetration of the tune hydro-solvent beyond the plant cell



Table 5 Comparative extraction of some plant's bio-actives using pressurized hydro-solvent and conventional techniques

| Analytes                             | Matrix and yield                                     | Reference methods and conditions                                                                    | Temp. (°C)         | Pressure  | Mode    | Flow rate (ml min <sup>-1</sup> ) | Extraction time (min) | References  |
|--------------------------------------|------------------------------------------------------|-----------------------------------------------------------------------------------------------------|--------------------|-----------|---------|-----------------------------------|-----------------------|-------------|
| Stevioside, rebaudioside A           | <i>Stevia rebaudiana</i> , 91.8%                     | Reflux 60 °C, 1–1.5 h, 84.3%                                                                        | 100                | 11–13 bar | Dynamic | 1.5                               | 15                    | 149 and 150 |
| Gastrodin, vanillyl alcohol          | <i>Gastrodia elata</i> , 8.6%                        | Reflux with 95% methanol, 2 h and 70 °C and 0.075% Soxhlet extraction, 180 °C, 30 ml methanol, 0.4% | 100                | 8–10 bar  | Dynamic | 1.5                               | 20                    | 151         |
| Phenolics and polyphenolic compounds | <i>Momordica charantia</i> , 29.8%                   | Hydrodistillation ethanol : water 3 : 1 w/w, 0.55 g GAE/g extract                                   | 150–200            | 10 Mpa    | Dynamic | 2.0                               | 320                   | 152         |
|                                      | <i>Pinus radiata</i> bark                            | Heat reflux with water, 11.7 GAE/g extract                                                          | 120                | 1.01 bar  | Nil     | Nil                               |                       | 153         |
|                                      | <i>Quercus petraea</i>                               | Hydrosolvent extraction with water and ethanol, 5.0–13.4 mg GAE/g DW                                | 100                | 1.01 bar  | Nil     | Nil                               | 120                   | 154         |
|                                      | <i>Quercus robur</i> L. and <i>Quercus petraea</i>   | Reflux, 17.67 mg g <sup>-1</sup>                                                                    |                    | 1.01 bar  | Nil     | Nil                               | 360                   | 154         |
|                                      | <i>Phyllanthus amarus</i> , 52.97 mg g <sup>-1</sup> |                                                                                                     | 192.4 85           | 110 bar   | Static  | 1.0                               | 15 30                 | 155         |
| Essential oil                        | <i>Fructus amomi</i> , >12%                          | Steam distillation, 40 min, 12%                                                                     | 150                | 60 bar    | Dynamic | 1.0                               | 5                     | 156         |
| Borneol, terpinen-4-ol, carvacrol    | <i>Origanum Onites</i> , 5.05%                       | Steam distillation, Soxhlet extraction, 50 ml <i>n</i> -hexane, 150 °C, 12 h, 3.16%                 | 100, 125, 150, 175 | 60 bar    |         | 2.0                               | 30                    | 157         |
| Volatile oil                         | <i>Cuminum cyminum</i> L., 16.2%                     | Hydro distillation, Soxhlet extraction, 175 °C, 3 h, 3.16%                                          | 100–175            | 20 bar    | Dynamic | 2.0, 4.0                          | Nil                   | 113         |
| Catechins, proanthocyanidins         | Grape seed, 95%                                      | Extraction with 75% methanol, 4.6%, 200 ml <i>n</i> -hexane, 12 h                                   | 50, 100, 150       | 1500 psi  | Static  | Nil                               | 30                    | 112         |
| Capsaicin dihydrocapsaicin           | Peppers                                              | Nil                                                                                                 | 50–200             | 100 atm   | Static  | Nil                               | Nil                   | 158         |
| Anthocyanins phenolics               | Dried red grape skin, 45%                            | Nil                                                                                                 | 100–160            | Nil       | Static  | Nil                               | 40 s                  | 159 and 160 |
| Rosmaric acid                        | <i>Salvia rosmarinus</i>                             | Reflux with water                                                                                   | 78                 | 1.01 bar  | Nil     | Nil                               | 30                    | 161         |
| Inositols                            | <i>Pinus pinea</i> L.                                | Pressurized hydrosolvent, 5.7 mg g <sup>-1</sup>                                                    | 50                 | 10 mpa    | Dynamic |                                   | 18                    | 148         |
|                                      |                                                      | Solid–liquid extraction, 3.7 mg g <sup>-1</sup>                                                     | 60                 |           |         |                                   | 120                   |             |
| Anthocyanin and phenolic             | <i>P. cauliflora</i> skin, 18.7%                     | Low-pressure solvent extraction (LPSE) with ethanol, 22–33 °C at 120 min 13.0%                      | 80                 | 50 bar    | Static  | —                                 | 9                     | 162         |
|                                      | <i>Rubus fruticosus</i> , 12.10% and 14.27%          | Soxhlet extraction with ethanol and mixture, at 300 min and 5.02%                                   | 80                 | —         | —       | 3.0–3.8                           | 30                    | 163         |
| Polysaccharide                       | <i>Grossularia</i> , pressurized                     | —                                                                                                   | 52                 | 16 bar    | —       | —                                 | 51                    | 163         |

Table 5 (Contd.)

| Analytes      | Matrix and yield                                                                                                                                              | Reference methods and conditions                                               | Temp. (°C) | Pressure | Mode | Flow rate (ml min <sup>-1</sup> ) | Extraction time (min) | References |
|---------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|------------|----------|------|-----------------------------------|-----------------------|------------|
| Capsaicinoids | hydro-solvent extraction with water, 11.68% <i>Capsicum annum</i> , pressurized hydro-solvent extraction with water, higher than Soxhlet extraction at 20 min | Soxhlet extraction, 80 °C with ethanol at 300 min and 5.243 mg g <sup>-1</sup> | 120–240    | 200 bar  | —    | —                                 | 20                    | 164        |
| Protein       | <i>Prunus cerasus</i>                                                                                                                                         | Soxhlet extraction with <i>n</i> -hexane, 80.48%                               | —          | —        | —    | —                                 | 60                    | 165        |

wall into the plant matrix thereby releasing the targeted bioactives.<sup>117</sup> One of the reported actions of this technology involves the hydrolysis of bio-active compounds such as tricaffeoylquinic acid due to the presence of OH radicals initiated by ultrasonic waves.<sup>121</sup> The impact of this technology generates H<sub>2</sub>O<sub>2</sub> which combines with the radical leading to hydrolysis reaction and improved selectivity of the water for extraction of phenolics in *Phyllanthus amarus* (Table 5) to a notable yield other than the conventional techniques. Also, the variation of the ultrasonic power also accounts for the variation in the yield and purity of carnosic acid and rosmarinic acid from *Salvia rosmarinus*. The proficient extraction performance of tuned water under microwave-enhanced technology is attributed to the high dielectric constant of the polar molecules. These molecules are characterized with the ability to absorb irradiated energy and to re-emit it for the heating of the extraction system as compared to the commonly used *n*-hexane with low dielectric constant.<sup>41</sup>

## 5.2 Effect of extraction conditions on yields of biometabolites

The data in Table 6 reveals conditions of two intensified methods namely aqueous ultrasonic hydro-extraction and microwave-enhanced hydro-extraction for their potencies. From the Table 6, extraction of polyphenolic from pomegranate peel using the pulse flow aqueous ultrasonic extraction gives a yield of 41.6% at a lesser extraction time of 10 min when compared to the continuous flow techniques in ultrasonic enhanced hydro-extraction with 30 min extraction time. Also, the mild extraction conditions of phenolics in grape and *Withania somifera* which are 60 °C, 24 Hz and 65 °C, 45 Hz respectively, helped to conserve the pharmacological activities. During the extraction, the penetration of the tuned solvent led to the disruption of cell walls by acoustical cavitation.<sup>74,104</sup> Research reveals that at high temperatures and frequencies, the phenolics extracted from

plants undergo degradation during extraction which makes the extracted metabolites commercially and industrially unacceptable.<sup>104</sup>

Furthermore, the extraction of essential oil at 75 °C and 100 W gives an excellent yield of 85% in 20 min using microwave-enhanced hydro-extraction when compared to 7% yield of essential oil from cabernet franc grapes in 15 h using ultrasonic enhanced hydro-extraction.

This is because tuned hydro-solvent under the influence of microwaves has a higher penetrating ability making the solvent to easily interact with the biomaterials for extraction purposes.<sup>4,77</sup> The extraction of essential oils from plant samples mostly uses microwave-enhanced hydro-solvent than ultrasonic hydro-solvent based on its faster extraction rate.<sup>146</sup>

## 6. Current challenges and future prospects

The appreciable environmental advantage of using tunable hydro-solvent for extraction includes improved mass transfer, selectivity, extraction efficiency, higher yield and shortened extraction time. Future progressive research has been channeled on tackling challenges of large-scale operation and the design of industrial equipment that can use the hydro-solvent and extraction processes.<sup>80,157,158</sup> The possibility of recovering and reusing spent hydro-solvents to facilitate cost-effectiveness, especially the water–oil-based solvent remains a great challenge. Furthermore, bio-surfactant may bind to proteins and other bio-active molecules to affect the stability or activity of the extracted products.<sup>159</sup> In addition to these, the occasional but deleterious effect of ultrasound energy (more than 20 kHz) on the active constituents of medicinal plants exists. This is through the formation of free radicals and consequently undesirable changes in the active molecules.<sup>160</sup>



Table 6 Extraction using some selected hydro-solvents

| Samples                                    | Desired products                  | Experimental conditions                                                         | Extraction time (min) | Yield                        | Hydro-solvent used               | Sources     |
|--------------------------------------------|-----------------------------------|---------------------------------------------------------------------------------|-----------------------|------------------------------|----------------------------------|-------------|
| <i>Centella asiatica</i>                   | Triterpene                        | 45 °C; 600 W                                                                    | 1.83                  | 27.10%                       | Microwave enhanced hydro-solvent | 171 and 172 |
| <i>Dioscorea hispida</i>                   | Essential oil                     | 75 °C; 100 W                                                                    | 20                    | 85%                          | Microwave enhanced hydro-solvent | 173         |
| <i>Chaerophyllum macropodium</i>           | Essential oil                     | —                                                                               | 45                    | 8.10%                        | Microwave enhanced hydro-solvent | 174         |
| <i>Oliveira procumbens</i>                 | Essential oil                     | —                                                                               | 45                    | 7.91%                        | Microwave enhanced hydro-solvent | 174         |
| <i>Vitis vinifera</i>                      | Phenolics                         | 60 °C; 24 kHz                                                                   | 30                    | 24–28%                       | Aqueous ultrasonic solvent       | 175         |
| Cabernet franc grapes                      | Essential oil                     | 60 °C; 24 kHz                                                                   | 15                    | 7%                           | Aqueous ultrasonic solvent       | 176         |
| <i>Punica granatum</i> peel                | Polypenols                        | 105 W cm <sup>-2</sup> (pulse mode)<br>105 W cm <sup>-2</sup> (continuous mode) | 10<br>30              | 41.6%<br>45.4%               | Aqueous ultrasonic solvent       | 177         |
| <i>Withania somnifera</i>                  | Phenolics                         | 65 °C; 45 kHz                                                                   | 15                    | 11.85%                       | Aqueous ultrasonic solvent       | 178         |
| Fresh leaves of <i>Vernonia amygdalina</i> | Flavonoids                        | 100 °C                                                                          | 7                     | 87.05 mg                     | Microwave enhanced hydrosolvent  | 130         |
| <i>Uncaria sinensis</i>                    | Flavonoids                        | 100 °C                                                                          | 20                    | 44 mg/100 g                  | Microwave enhanced hydrosolvent  | 179         |
| Tea residues (oolong)                      | Flavonoids                        | 230 °C                                                                          | 2                     | 144.0 mg GAE g <sup>-1</sup> | Microwave enhanced hydrosolvent  | 180         |
| <i>Genita scabra</i> Bunge stem            | Polysaccharides                   | —                                                                               | 5.8                   | 15.97%                       | Microwave enhanced hydrosolvent  | 120         |
| <i>Ipomoea batatas</i>                     | Chlorogenic acid                  | 500 W, 25 KHz                                                                   | 20                    | —                            | Aqueous ultrasonic solvent       | 121         |
| <i>Phyllanthus amarus</i>                  | Phenolic compounds                | 30 W, 19 KHz                                                                    | 7                     | 27.23 mg g <sup>-1</sup>     | Aqueous ultrasonic solvent       | 155         |
| <i>Camellia sinensis</i>                   | Polysaccharide                    | 127.5–750 W                                                                     | 5                     | 37.0%                        | Aqueous ultrasonic solvent       | 181         |
| <i>Salvia rosmarinus</i>                   | Carnosic acid and rosmarinic acid | 25 °C, 100–300 W                                                                | 5                     | 21.4–29.5%                   | Microwave enhanced hydrosolvent  | 161         |
|                                            |                                   | 40 °C 150 W                                                                     | 30                    | 18.1%                        | Aqueous ultrasonic solvent       |             |
|                                            |                                   | 70 °C, 1.2 kW                                                                   | 20                    | 25.2%                        | Aqueous ultrasonic solvent       |             |
| <i>A. melanocarpa</i>                      | Polyphenolics                     | 70 °C, 144 W                                                                    | 60                    | 7.428 g/100 g                | Aqueous ultrasonic solvent       | 182         |
| <i>Malus domestica</i>                     | Gallic                            | 100 °C, 1500 W                                                                  | 20                    | 4.77 mg g <sup>-1</sup>      | Microwave enhanced hydrosolvent  | 183         |
|                                            | Flavonoids                        | 100 °C, 1500 W                                                                  | 20                    | 17.1 mg g <sup>-1</sup>      | Microwave enhanced hydrosolvent  |             |
|                                            | Ascorbic acid                     | 100 °C, 1500 W                                                                  | 20                    | 36.1 mg g <sup>-1</sup>      | Microwave enhanced hydrosolvent  |             |
| <i>Pinus radiata</i> bark                  | Phenolic compounds                | 900 W, 2450 MHz                                                                 |                       | 479 mg CE/g bark             | Microwave enhanced hydrosolvent  | 153         |
|                                            |                                   | 35 kHz, 85 W                                                                    |                       | 388 mg CE/g bark             | Aqueous ultrasonic solvent       |             |
| Moroccan <i>Acacia mollissima</i> bark     | Phenolic compounds                | 150 W                                                                           |                       | 279.7 mg GAE/g bark          | Microwave enhanced hydrosolvent  | 129         |

## 7. Conclusion, key report findings and suggestions

The toxicological impact of various organic solvents and the contamination of the bioactive extract necessitate the study and the use of hydro-solvent (water) for extraction. From this review,

it is possible to tune the properties of water to enhance its feature similar to organic solvents, increase extraction efficiency and create the possibility of the use of water in the extraction of a broad range of solutes which has been the limitation of hydro extraction. The intensified hydro-solvent system is faster and more selective for metabolite recovery than the traditional approach method. In the light this, the use of tuned solvents

with intensified techniques should be employed to forestall the contamination of bio-actives extracted from plants and to enhance the rapid extraction process.

## Author contributions

AOA, JAO, ROA conceptualized and wrote the original draft of the study; MAA, RM, SA worked on the methodology, formal analysis and data curation; AOA, JAO, ROA, MAA, RM, SA reviewed and edited the final draft. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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