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REVIEW ARTICLE

An integrated biorefinery approach for the valorization of water hyacinth towards circular bioeconomy: a review

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Abstract

Water hyacinth (WH) has become a considerable concern for people across the globe due to its environmental and socio-economic hazards. Researchers are still trying to control this aquatic weed effectively without other environmental or economic losses. Research on WH focuses on converting this omnipresent excessive biomass into value-added products. The potential use of WH for phytoremediation and utilizing waste biomass in various industries, including agriculture, pharmaceuticals, and bioenergy, has piqued interest. The use of waste WH biomass as a feedstock for producing bioenergy and value-added chemicals has emerged as an eco-friendly step towards the circular economy concept. Here, we have discussed the extraction of bio-actives and cellulose as primary bioproducts, followed by a detailed discussion on different biomass conversion routes to obtain secondary bioproducts. The suggested multi-objective approach will lead to cost-effective and efficient utilization of waste WH biomass. Additionally, the present review includes a discussion of the SWOT analysis for WH biomass and the scope for future studies. An integrated biorefinery scheme is proposed for the holistic utilization of this feedstock in a cascading manner to promote the sustainable and zero-waste circular bio-economy concept.

Keywords *Eichhornia crassipes* · Sustainable bioprocess · Biomass · Bioproducts · Value addition · Sequential extraction

Introduction

Eichhornia crassipes, commonly known as water hyacinth (WH), is an aquatic macrophyte belonging to the *Pontederiaceae* family. It originated in South America and spread worldwide in the late eighteenth century due to its highly invasive nature. WH was considered an ornamental plant due to its attractive flowers and foliage and was distributed widely. Once it escaped from cultivation, it became a severe pest, obstructing navigation and interfering with fisheries and other water activities. Because of the various social-environmental issues provoked, it became the world's most notorious aquatic weed. Since then, research has been ongoing to develop strategies for its eventual application to humanity (Malik 2007; Ren and Zhang 2007; Zhang et al. 2010; Shu et al. 2014).

The climatic conditions in tropical and subtropical regions favor the growth of WH. Once infested, it proliferates, forming a dense mat over the water surface within a few weeks. It shows high productivity in summer and maintains its population from year to year despite its decrease in winter. It floats freely and propagates fast by asexual and sexual means; however, it commonly proliferates vegetatively through root stalks (Coetzee et al. 2017; Kitunda 2017). The rapidly growing WH blocks sunlight. Excessive growth increases the transpiration pull resulting in heavy and rapid water loss. The obstructed movement in heavily choked waterbody hampers the oxygen exchange, and decaying vegetation creates a foul smell. The decaying vegetation provides a breeding ground for mosquitoes and creates other health and hygiene-related issues. As a result, there is an overall imbalance between flora and fauna. Fishing, boating, swimming, irrigation, hydropower projects, and other activities are all impeded (Thamaga and Dube 2018; Dersseh et al. 2019).

Physical, chemical, and biological treatment methods attempted to control and eradicate this weed (Williams et al.

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2005; Wilson et al. 2007; Greenfield et al. 2007; Tipping et al. 2014) are shown in Fig. 1. These methods require high costs and labor, but effective eradication is still impossible. WH repeatedly regrows, making all the efforts in vain (Williams et al. 2005; Kleinschroth et al. 2021). Moreover, excessive chemicals and biological agents adversely affect the associated biodiversity. Annual eradication of WH imposes an enormous and unnecessary burden on developing countries' economies. As WH does not produce food or revenue, it is unappealing to face the costs of eradicating this pest.

Reversing the perspective, WH is blessed with the potential for rapid growth, outranging other species. This exclusive property makes it a potential candidate to be utilized as a sustainable feedstock for various industries. This review aims to analyze the green potential of WH for its practical and sustainable utilization. The suggested multi-objective approach will be beneficial in developing cost-effective procedures compared to the single-objective methods proposed earlier. Most reports discuss WH for fuel and energy (Gunnarsson and Petersen 2007; Ganguly et al. 2012; Rezania et al. 2015; Bote et al. 2020a; Gaurav et al. 2020; Li et al. 2021), WH management and valorization (Yan et al. 2017; Sindhu et al. 2017; Guna et al. 2017), or contaminant removal from water bodies (Dhote and Dixit 2009; Mishra and Maiti 2017; Priya and Selvan 2017; Ting et al. 2018; Li et al. 2021; Madikizela 2021). Here, we have discussed the valuable bio-actives extracted from the WH biomass as primary bio-products, followed by the generation of secondary bio-products by biochemical, green synthesis, and thermochemical routes. To the best of our knowledge, a detailed discussion on WH extractives, including bio-actives, cellulose, and WH-based nano-particles, has been done for the first time. An extensive review of fuel, supercapacitor, catalyst, and other product generation from WH via thermochemical route has been done, which is lacking in the existing literature. Apart from this, here we have included the recent advancements in WH biomass applications in environmental and other sectors. Integrative and sustainable biomass utilization is the focus of the review, with the long-term goal of developing WH biorefinery. This review suggests a novel, systemic approach for utilizing WH biomass based on its compositional traits and gives an updated insight into its valorization. The sustainable utilization of WH biomass for phytoremediation, followed by its extraction and conversion to generate high-valued compounds, will enable the monetization of this weed. A systematic and integrative approach will benefit businesses, society, and the environment by promoting a circular economy for WH management (Fig. 2). We also discuss the benefits, shortcomings, and outlook of WH biorefinery via a SWOT analysis.

Primary bioproducts: phytochemicals extracted from WH

The aquatic macrophyte, WH, has existed in local environmental conditions since its introduction as an esthetic plant. The plant is highly stress-tolerant and has a high survival rate in harsh situations like water contaminated with heavy metals, dyes, and algae blooms. Its unwelcome, enormous, and recurring growth in water bodies prompted researchers to explore this weed for beneficial compounds. Several researchers have reported the composition of WH; a few of the reports are summarized in Table 1. Most reports discuss WH composition on a dry weight basis. WH is a simple biomass with a major portion of the mass composed of cellulose and hemicellulose, with a low amount of lignin. Therefore, WH can be a good source for harvesting cellulosic material. It is a good source of antioxidants, sterols, proteins, fatty acids, cellulose, vitamins, minerals, pigments, and other plant-based metabolites, as discussed in Table 2. However, the levels may vary depending on plant

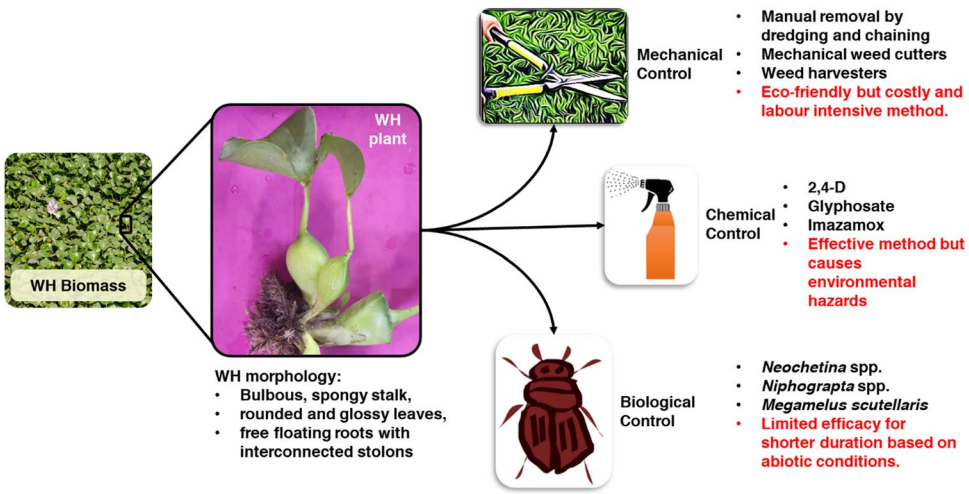

Fig. 1 Morphology and control measures for water hyacinth

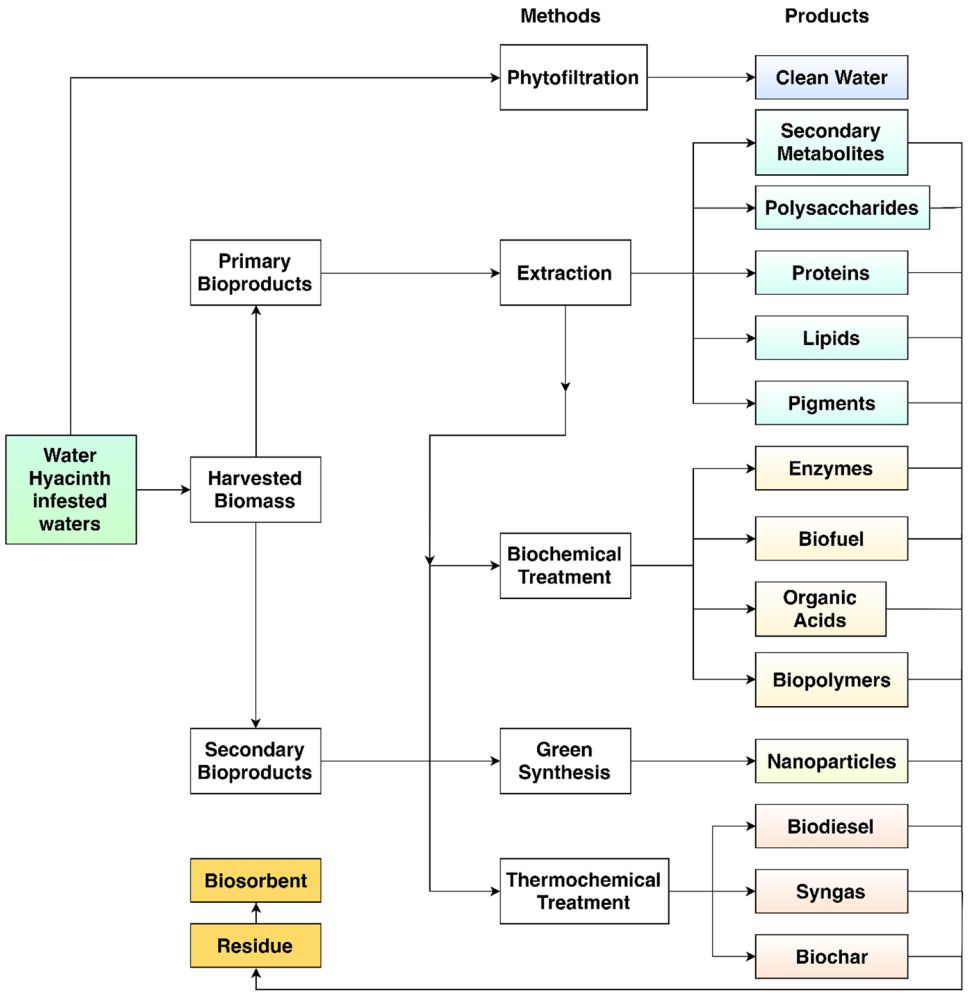

Fig. 2 Integrative approach for potential WH biorefinery

Table 1 Compositional analysis of WH biomass (% dry weight)

Cellulose	Hemicellulose	Lignin	Ash	N content	References
31	22	7	15		(Bolenz et al. 1990)
21.5	33.9	7.01	12.1	1.8–3.2	(Deshpande et al. 2008)
21.5	33.9	7.01	12.1		(Abo-Elmagd and Housseiny 2012)
18.1 ± 0.2	28.2 ± 0.11	7.03 ± 0.09			(Zhang et al. 2016)
24.8 ± 2.0	30 ± 1.75	5.6 ± 2.5	10.9 ± 0.76	2.80 ± 0.08	(Varanasi et al. 2018)
57 ± 0.7	25.6 ± 0.6	4.1 ± 0.1			(Tanpichai et al. 2019)
52.06 ± 0.38	17.6 ± 0.45	8.66 ± 0.33	16.2 ± 0.98		(Pakutsah and Aht-Ong 2020)
45.5	21.76	8.31			(Oyeoka et al. 2021)

maturity and local environmental circumstances. Antioxidant additives, therapeutic factors, and structural biopolymers could be obtained from WH for applications in food, pharma, and other industries. Furthermore, after extracting inhibitory plant phenolics, residual structural biopolymers could be an ideal substrate for bioconversions to produce other valuable commodities. As discussed in Table 2, WH extractions provide more insights into its composition. The compositional review serves as an essential step to identify the range of possible applications for each by-product for consideration of WH as a potential biorefinery raw material.

Plant sterols

Ganguly et al. (1977) isolated sterols and confirmed the presence of β-sitosterol and stigmasterol from the dried pollen and pistils of WH. The existence of glycosides and phenolic compounds were also reported. Authors suggested

Table 2 Plant metabolites extracted from WH biomass

Metabolite	Plant part	Extraction method	Solvent used	Method/assay	Key results	References
Plant Sterols						
Beta-sitosterol and stigmasterol	Dry pollen powder and pistils	Solid–liquid	n-hexane, ethanol	Liebermann-Burchard test	The role of sterols and amino acids in pollen germination gets established	(Ganguly et al. 1977)
Phytoconstituents	Leaves, stem, and roots	Soxhlet		BF3-butanol derivatization, GC–MS	Organic acids, sterols, and squalene (terpenoid) were identified	(Fileto-Pérez et al. 2015)
Sterols (stigmasterol)	Leaves and stalks	Soxhlet, SFE	Dichloromethane, CO_2	Mathematical modeling, GC–MS	Total yield (η_{total}): 0.64–0.73 wt.% Stigmasterol yield (η_{stig}) was 0.20–0.22 wt.% Yield increased by 1.88 wt.% with a cosolvent, ethanol	(Martins et al. 2016; de Melo et al. 2016)
Plant growth regulators						
Zeatin and Zeatin riboside	Roots, shoots, leaves, flowers	Solid–liquid	80% ethanol	Soybean callus bioassay Column chromatography	Cytokinin peaks were detected in all plant parts	(Nagar and Saha 1985)
Humic acid	Leaves, stems, roots	Solid–liquid	Benzene-methanol, 2:1 v/v	Removal of uronic acids using 0.1 M NaOH to obtain humic acids GC/MS, FTIR, 1H NMR	HA in WH confers metal binding capacity to the plant	(Ghabbour et al. 2004)
Aqueous extract as fertilizer	Shoot	Solid–liquid	Water	Randomized block experiment, nutritional quality, biomass yield of tomato	The net yield of tomato plants increased by 1.84 times with foliar spray	(Elgala et al. 2022)
Antioxidants and therapeutic factors						
Glutathione	Leaves	Solid–liquid	Na-phosphate–EDTA buffer	Mathematical modeling, isoelectric point, glutathione assay, DPD assay, HPLC	HPLC Highest EG, 40 nmol eg/gdp was observed for freeze-dried leave extract	(Bodo et al. 2004b, a)
Phenylphenalene-related compounds	NA	Solid–liquid	Ethyl acetate	Reversed-phase HPLC, NMR	Two new phenylphenalene derivatives were isolated and identified, along with others	(DellaGreca et al. 2008, 2009)
Antioxidants, phenolic compounds	Petiole, leaves, flowers	Solid–liquid	Water, ethanol	TPC assay, DPPH assay, iron (Fe^{2+}) chelating activity, reducing power test, inhibition of lipid peroxidation test Fish oil stability test, HPLC	Gallic, protocatechuic, gentisic, and p-hydroxybenzoic acids were identified	(Surendraraj et al. 2013)

Table 2 (continued)

Metabolite	Plant part	Extraction method	Solvent used	Method/assay	Key results	References
Anti-oxidant enzymes	Shoots, roots	Solid–liquid	Phosphate–EDTA buffer	Seedlings grown with Pb $(NO_3)_2$ tested for lead content Tolerance index, enzyme activity, SEM–EDX	Increased SOD, CAT, APX, and POX activity was observed in response to Pb toxicity	(Malar et al. 2014)
Polar and non-polar extracts	Roots, stalks, leaves, flowers	Soxhlet, solid–liquid	Dichloromethane, methanol: water: acetic acid mixture (47.5:47.5:5.0, v:v:v)	DPPH assay, TPC assay, GC–MS	Sterols, fatty acids, long-chain aliphatic alcohols, and aromatic compounds—with concentrations ranges 9.80–22.6%, 7.42–13.1%, 0.17–1.26%, and 0.15–0.40% (wt%), respectively were obtained	(Silva et al. 2015)
Two antioxidant peptides	Leaves	Solid–liquid	Acid, alkali	Estimation of superoxide anion radical scavenging activity, ABTS, reducing power, metal-chelating capacity, DPPH assay, RP-HPLC	Peptides were isolated and identified by amino-acid sequencing	(Zhang et al. 2018c)
Antiparasitic activity	Leaves	Solid–liquid	Water	Chemical analysis of extract Antimalarial activity, trypanocidal activity, and leishmanicidal activity were tested	$IC_{50,}$ 49.9 ± 1.03 g/mL against *Plasmodium falciparum* FCB1, EC_{50}, 103 ± 3.02 g/mL against *Leishmania donovani*. LC_{100}, 210 ± 2.23 g/mL for *Trypanosoma brucei* GVR 35	(Elagib 2020)
Phenylphenalenones (PhPs) compounds	Shoot, roots	Solid–liquid	Ethanol, methanol–water, hexane	Antiprotozoal activity against *Trypanosoma cruzi* (Y strain), cytotoxicity test, NMR	19 PhPs were identified, including 2 new compounds $EC_{50,}$ 37.7 ± 6.6 µM for compound 3 and 66.6 ± 14.4 µM for compound 4 was observed	(Costa et al. 2021)

Table 2 (continued)

Metabolite	Plant part	Extraction method	Solvent used	Method/assay	Key results	References
Shikimic acid (SA)	Stem, leaves, roots	Ultrasound	Methanol–water	TPC, antioxidant activity, SA recovery	The highest yield of 3.1% at 30 min was observed in the UAE for the stem Maximum TPC (11.1 mg GAE/g biomass) observed for leaves while stems show the maximum antioxidant activity of 87.7% within 10 min of sonication	(Ganorkar et al. 2022)
Allelopathic potential						
Allelopathic effects		Solid–liquid	Methanol	Antimicrobial assay, anti-algal paper disc diffusion bioassay TLC, GC–MS, FTIR, H-NMR	An alkaloid (18, 19-Seco-15 beta-yohimb) was detected in active fraction (A)	(Shanab et al. 2010)
Eutrophication control	Whole plant	NA	NA	Algal growth, antioxidant enzyme activity, nitrate reductase activity, 2-D gel electrophoresis, mass spectrometry	The purification mechanism of eutrophic water by WH was explored by a proteomics study	(Li et al. 2015)
Antialgal compounds	Roots of purple-root WH	Solid–liquid	Methanol, ethyl acetate, water	Antialgal activity, XRD, NMR	Three 7-phenyl-substituted phenalenone and four phenol derivatives were identified as the main bioactive compounds against BGA (*Microcystis aeruginosa*)	(Cheng et al. 2021)
Pigments						
β-carotene enriched extract	Shoot	Solid–liquid	Acetone	HPLC	0.0137% β-carotene was found	(Panchanadikar et al. 2005)
Cellulose						
Cellulose nanofibers (CNFs)	Stem	Soxhlet, ball milling, cryo crushing, sonication, lyophilization	Toluene-ethanol, NaOCl, NaOH solution	FE-SEM, FTIR, XRD, TGA, CA, CTE	Average diameter: 20–100 nm (SEM) and 25 nm (TEM)	(Thiripura Sundari and Ramesh 2012)
Cellulose for membrane	Dry fiber	Solid–liquid	Toluene-ethanol (2:1 v/v), NaOCl, NaOH solution	Flux and rejection test, FTIR	Prepared membrane at cellulose diacetate concentration 15% and evaporation time 10 s gives: flux: 461 L/m^2.h rejection coefficient: 64.3%	(Istirokhatun et al. 2015)

Table 2 (continued)

Metabolite	Plant part	Extraction method	Solvent used	Method/assay	Key results	References
Cellulose for slow-release fertilizer (SRF)	Plant	Refluxed	Toluene/ethanol (2:1 v/v), NaOCl, NaOH solution	Water holding capacity, biodegradation in soil, and the minerals release kinetics of cellulose-grafted-poly(acrylamide) SRF TEM, FTIR	The biodegradability of the composite, the potential to absorb and retain water in the soil, and the synchronized release of N and P prove its potential as SRF	(Rop et al. 2018, 2019)
CNFs and nano papers	Fibers	Solid–liquid	Water, $NaClO_2$, KOH solution	FE-SEM, FTIR, XRD, TGA, transparency, wettability, mechanical properties, CA, and CTE measurement	Average diameter: 10 − 30 nm and lengths of several µm	(Tanpichai et al. 2019, 2021)
CNFs	Stems	Solid–liquid, high-pressure homogenization	NaOH, $NaClO_2$, solution	FTIR, SEM, TEM, BET, Rheological properties, WRV, TGA, XRD	Average diameter: 5 to 50 nm CNFs prepared within 10 defibrillation cycles	(Pakutsah and Aht-Ong 2020)
CNFs	Stems	Solid–liquid, high-pressure homogenization	Water, NaClO, NaOH solution	FTIR, FE-SEM, WRV, XRD, and TGA	Average diameter: 16.8 nm	(Sun et al. 2020)
Nanocrystalline cellulose	Stems	Solid–liquid, sonication	NaOH, H_2O_2, HCl solution	FTIR, TGA, SEM	Particle size analysis (PSA) shows a 93-nm size for the sonicated sample	(Packiam et al. 2021)
WH fibers for biocomposites	Fibers	Solid–liquid	NaOH, silane solution	XRD, FTIR, TGA, DTG, SEM, AFM	The mechanical, thermal, and dynamic properties of composites indicate its suitability for lightweight applications	(Sumrith et al. 2020)
Cellulose fibers	Leaves	Solid–liquid	NaOH, HCl solution	Oil sorption studies of cellulose and polyurethane composite FTIR, SEM, CA measurement	Engine oil sorption in the range of 3.91–12.5 g/g	(Sittinun et al. 2020)
Cellulose	WH	Solid–liquid, microwave treatment	NaOH, H_2O_2 solution	Oil adsorption studies for hydrophobic cellulose-PVA aerogel FTIR, XRD, SEM, Thermal conductivity, TG-DSC, BET	A maximum oil adsorption capacity of 43.3 g/g was observed for diesel oil Adsorption remains stable for up to 10 cycles	(Nguyen et al. 2021)
Cellulose nanocrystals (CNCs) for packaging films	Stem	Solid–liquid	Ethanol–benzene, NaOH, $NaClO_2$, H_2SO_4 solution	XRD, TEM, FTIR, TGA, DMA, and WVP were done for the cellulose-PVA-gelatin biodegradable films	WH CNCs diameter: 20–50 nm Film tensile strength: 13.8 MPa	(Oyeoka et al. 2021)

Table 2 (continued)

Metabolite	Plant part	Extraction method	Solvent used	Method/assay	Key results	References
CNFs	Fibers	Refluxed, ball milling, sonication	Ethanol, nitric acid (4:1, v/v)	Electrochemical measurement was done for CNF/PPy/PVP conductive aerogels AFM, FE-SEM, FTIR	Electrical conductivity: 0.1 to 6.23 S/cm	(Ewulonu et al. 2020)
Cellulose	Shoots	Soxhlet	Toluene-ethanol (2:1 v/v), NaOH, H_2O_2 solution	Dye adsorption studies FTIR, TGA, DTG, XRD	Maximum dye adsorption capacity: Crystal violet = 20.5 mg/g Congo red = 39 mg/g	(Salahuddin et al. 2021b)
Miscellaneous						
Ash water extract as a medium		Solid–liquid	Water	The efficacy of WH ash water extract as a green medium for cross-coupling reaction was tested. EDX	Higher alkali metals, Ca, Cu, Mg, and K, in WH ash make the medium basic and effective	(Sarmah et al. 2017)
Carbon dots for the borax sensor	Leaves	Refluxed	Nitric acid, water	Quantum yield, Borax sensing experiment, Paper-based sensor FTIR, Zeta potential, and XPS	Detection of borax in actual food samples could be done	(Prathumsuwan et al. 2019)
WH powdered biomass	Shoot	Solid–liquid	Water, KOH solution	A release test in water and soil was done for slow-release fertilizers (SRFs)	SRFs make the nitrogen fertilization process more efficient	(Silva et al. 2021)
Plasticizer for self-compacting concrete (SCC)	Whole plant	Solid–liquid	Water, ethanol	The consistency, strength, and water absorption capacity of self-compacting concrete (SCC) were tested GC–MS	Ketones, aldehydes, alcohols, and fatty acids present in WH facilitate binding. Superplasticizer replacement with 20% WH extract was suggested	(Okwadha and Makomele 2018)
Handmade paper and bio-compost	Stems	Solid–liquid	KOH, H_2O_2 solution	The yield, brightness, and strength of the paper were studied	Bleached pulp brightness: 37.2%; Tear index: 6.79 m Nm^2/g; Tensile index: 49.2 N m/g	(Islam et al. 2021)

the presence of sterols to protect the plant from desiccation, glycosides as a source of sugars, and phenolic compounds to repel approaching insects (Ganguly et al. 1977). GC–MS analysis of the lipophilic extract of WH was found to yield sterols of up to 1.12 wt% in roots and 4.45 wt% in flowers. Stigmasterol was present in WH with a yield of 4.44 g/kg of biomass, making WH a rich source of this compound (Silva et al. 2015).

Fileto-Perez et al. (2015) isolated fatty acids in WH through sequential extraction using solvents of increasing polarity in a soxhlet apparatus followed by derivatization with BF_3. A total of 24 compounds were identified, which included 20 carboxylic acids, three steroids (including β-stigmasterol), and one terpenoid (squalene) (Fileto-Pérez et al. 2015). Supercritical CO_2 was also used for sterol extraction. A maximum yield of total sterols ($\eta_{\text{Total Sterol}}$) was 0.35 wt%, the concentration of total sterols ($C_{\text{Total Sterol}}$) 38.3 wt%, and the concentration of stigmasterol (C_{Stigm}) 26.4 wt% was obtained at pressure 300 bar and 2.5 wt% ethanol as a co-solvent (Martins et al. 2016). De Melo et al. (2016) extended the work by utilizing yield response as a selectivity element in yield optimization using mathematical modeling. Total sterol yield increased from 0.64 to 1.88 wt%. Also, selectivity for stigmasterol increased at 40 °C compared to 60 °C (de Melo et al. 2016). The structures of the main phytosterols found in WH extracts are shown in Fig. 3(a)–(c).

Plant growth regulators

The plant hormone cytokinin was observed in WH extract (Nagar and Saha 1985). Results indicated the presence of zeatin (Z) and zeatin riboside (ZR) in both leaves and root extracts. The qualitative difference among the hormone found in different parts of the plant was attributed to the metabolic conversion of the hormone. Humic acid (HA) was isolated from the dried powder from different parts of the WH plant after successive extractions for lipids and uronic acids. The freeze-dried HA samples contained amino acids, monosaccharides, macroelements, and microelements and could be used for soil improvement (Ghabbour et al. 2004). Elgala et al. (2022) performed a randomized block experiment in which an aqueous extract of WH shoot was sprayed over tomato plants as a source of nutrients. The net yield of tomato plants increased by 1.84 and 1.63 times compared with the control (without foliar spray) and commercial synthetic chemical solution treatment, respectively (Elgala et al. 2022).

Antioxidants and therapeutic factors

WH aqueous extract has shown effective anti-parasitic activity against drug-resistant parasites. The extract was rich in steroids, flavonoids, alkaloids, tannins, and proteins with high antioxidant activity making it an effective and inexpensive anti-parasitic agent (Elagib 2020). A polar extract with a yield of 10 wt% for roots and 28.8 wt% for stalks from WH was rich in antioxidants and phenolics (Silva et al. 2015). Aboul-Enein et al. (2011) separated nine active fractions from WH, including alkaloid, propanoid, phthalate, and phenyl derivatives. Antibacterial, antifungal, antioxidant, and anticancer properties were evaluated, which showed promising medicinal potential (Aboul-Enein et al. 2011). WH ethanolic extracts rich in natural antioxidants increased the shelf life of unsaturated fish oils. HPLC analysis revealed the presence of phenolic compounds such as gallic, protocatechuic acid, gentisic acid, p-hydroxybenzoic acid, and others (Surendraraj et al. 2013). The structure of p-hydroxybenzoic acid is shown in Fig. 3(d). Two antioxidant peptides with a molecular weight of 442.3 and 278.2 Da were purified from WH leaf hydrolysates using gel filtration chromatography and RP-HPLC. They were identified as Phe-Phe-Glu and Leu-Phe, using MALDI-TOF–MS. The separated peptides could be used in food and pharma industries as natural antioxidants, as evident from free-radical scavenging assays (Zhang et al. 2018c).

Optimized process for fast and efficient extraction of glutathione using factorial 3^3 design reported 40 nmol equivalent glutathione (EG) per gram of dried plant (Bodo et al. 2004b). Freeze-dried samples exhibit the highest glutathione activity, while the EG value deteriorates rapidly when samples are heated above 60 °C. Two new phenylpropanoid derivatives with a potential role as phytoanticipins and phytoalexins were isolated from the ethyl acetate extract of WH. Compounds were characterized using ^{1}H and ^{13}C NMR after HPLC-based purification (DellaGreca et al. 2009). The study was extended further by Coasta et al. (2021), who extracted 19 phenylphenalenones (PhPs) from WH. Structures of four newly discovered PhPs were elucidated using ^{1}H and ^{13}C NMR. Furthermore, the two main PhPs, 2-hydroxy-8-(4-hydroxyphenyl)-phenalen-1-one (PPO1), and 2-hydroxy-8-(3,4-dihydroxyphenyl)-phenalen-1-one (PPO2) were tested for their antiprotozoal activity against *Trypanosoma cruzi* and cytotoxic activity against mammalian cells (NCTC-L929). Both PhPs showed moderate activity with EC_{50} value 38–67 μM (EC_{50} -50% effective concentration) against *T. cruzi* in comparison to standard drug benznidazole (EC_{50} value 16 μM) and no cytotoxicity against NCTC-L929 at the highest tested concentration of 200 μM (Costa et al. 2021). A general structure of PhP derivatives is shown in Fig. 3(g).

WH ethyl acetate extract was found to be effective against lead-induced toxicity. The test was performed on the albino rat, and the extract was effective in recovering the cellular damage caused by lead acetate (Ahmed et al. 2016). The heavy metal tolerance of WH was attributed to the presence of antioxidant enzymes: ascorbate peroxidase (APX),

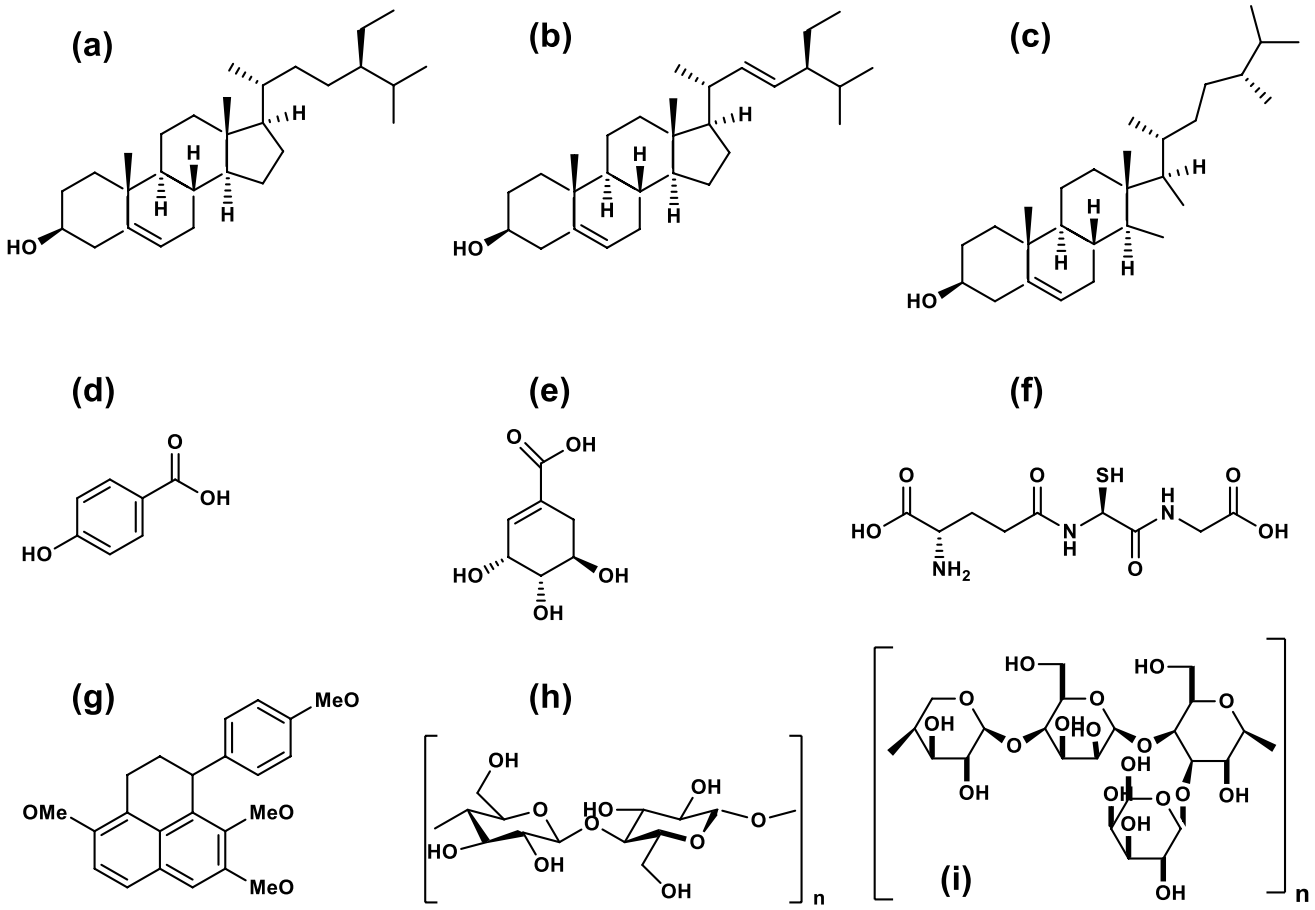

Fig. 3 Structures of some key phytoconstituents isolated from WH Biomass. Phytosterols: (**a**) β-sitosterol; (b) stigmasterol; (c) methyl cholesterol; medicinal applications (Martins et al. 2016). Phenolic compounds: (**d**) p-hydroxybenzoic acid, antioxidative and anti-inflammatory (Surendraraj et al. 2013); (**e**) shikimic acid, a precursor for antiviral oseltamivir phosphate (Ganorkar et al. 2022); Antioxidant: (**f**) glutathione (Bodo et al. 2004b); Antiprotozoal (DellaGreca et al. 2008; Costa et al. 2021): (**g**) phenylphenalene derivatives; Biopolymers: (**h**) cellulose; (**i**) hemicellulose; wide applications in food, pharma, biofuels, and environmental sectors (Istirokhatun et al. 2015; Tanpichai et al. 2021; Oyeoka et al. 2021)

peroxidase (POX), superoxide dismutase (SOD), and catalase (CAT) (Malar et al. 2014). Ultrasound-assisted (UAE) along with conventional extraction was performed for different parts of WH to extract shikimic acid (SA) [Fig. 3(e)], a precursor for synthesizing the antiviral drug oseltamivir phosphate (Tamiflu®) (Ganorkar et al. 2022).

Allelopathic potential

WH was found effective for the purification of eutrophic water. Proteomic analysis revealed the synthesis of proteins associated with oxidation–reduction processes, nitrogen-phosphorus uptake, and metabolism in response to the stimulus. Synthesized proteins enhanced the nutrient uptake rate, hindering the growth of algae (*Microcystis aeruginosa*). The secretion of allelochemicals further synergized the effect (Li et al. 2015). Shanab et al. (2010) studied the allelopathic potential of WH's methanolic extract. The crude extract was separated into five fractions. Each fraction demonstrated antibacterial, antifungal, and antialgal activity. Furthermore, the active components responsible for these activities were identified to be alkaloid and phthalate derivatives (Shanab et al. 2010). Similar phthalate-based therapeutic bio-actives have been isolated from WH, as discussed in "Antioxidants and therapeutic factors" section. (Aboul-Enein et al. 2011). However, special care should be taken while analyzing the data as xenobiotic compounds may be accumulated in the plant from the polluted water sites (Saeidnia and Abdollahi 2013; De Laet et al. 2019). The allelopathic potential of ethyl acetate fraction of purple-root WH (PRWH) was tested against blue-green algae (BGA). Eleven new phenylphenalene derivatives have been isolated and characterized. Seven have shown potential bioactivity against BGA when tested for *Microcystis aeruginosa* (Cheng et al. 2021). WH was found quite effective in controlling algal blooms (Qin et al. 2016). Fenced cultivation of WH in Dianchi lake, China

was done to study its potential to purify algal blooms. The effect of water quality, algae distribution, and accumulation of nutrients like total nitrogen and phosphorus on effectiveness of WH was studied.

Pigments and other chemicals

A convenient and straightforward method to extract β-carotene from WH was patented by Panchanadikar et al. in 2005. The powdered plant material was extracted in an organic solvent, then enriched in acetone and filtered (Panchanadikar et al. 2005). Levelunic acid was synthesized through acid-catalyzed hydrolysis of WH at 150–175 °C. The yield of levelunic acid was 53% w/w of C6 sugars (Girisuta et al. 2008). The typical scheme for extracting phytometabolites is summarized in Fig. 4.

Cellulose

Cellulose nanofibers (CNFs) were extracted from WH by different methods [Fig. 3(h)–(i)]. The diameter of extracted CNFs was in the range of 10 – 30 nm. Alkaline treatment was sufficient to remove most of the lignin, making WH a sustainable source of cellulose (Thiripura Sundari and Ramesh 2012; Tanpichai et al. 2019). The size of nanofibrillated cellulose (NFC) fibrils decreases from 23 to 17 nm on high-speed homogenization; however, it increases the time by fourfold. The tensile strength increased almost threefold from 5.87 to 15.2 MPa, while the contact angle increased from 21.2 to 36°. These changes were attributed to a decrease in the porosity of the nanocellulose (NC) paper (Tanpichai et al. 2021). CNFs (5–50 nm) were simply prepared from WH biomass by subjecting extracted cellulose

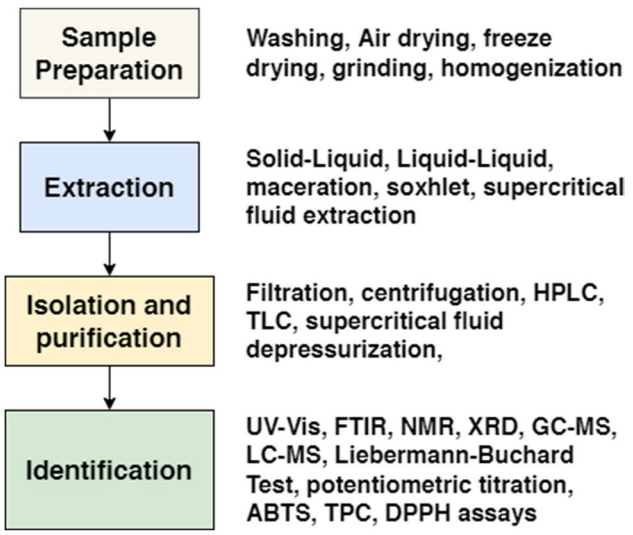

Fig. 4 Schematic diagram of the general process for extracting plant metabolites

to ten defibrillation cycles. However, prolonged mechanical treatment resulted in higher water retention capacity (WRC) and specific surface area; a gradual decrease in crystallinity index, thermal degradation temperatures, and degree of polymerization were observed. A suspension of CNFs showed a steady increase in viscosity with the formation of a gel-like structure with shear-thinning behavior that was fitted better with a Herschel-Bulkley fluid model rather than a Bingham plastic model (Pakutsah and Aht-Ong 2020). WH cellulosic fibers can be extracted under milder conditions using a high-pressure homogenizer. CNFs with the highest water retention percentage (WR%) was obtained after five passes, while a decrease in crystallinity (CrI%) was observed as the number of passes increased from 1 to 5. TGA and DTG analysis revealed that CNFs could maintain thermal stability when used as reinforcements in bioplastics (Sun et al. 2020).

Nanocrystalline cellulose of mean particle size 93.0 nm was obtained from WH with the help of sonication. A slight decrease in the degradation temperature from 253 to 227 °C was observed while processing the raw fibers indicating its potential applicability (Packiam et al. 2021). WH fibers (WHFs) were investigated as green reinforcement material. Bio-epoxy composites augmented with NaOH and silane-treated WHFs were synthesized. Composites were found suitable for lightweight applications as indicated by the tensile strength, flexural, impact, hardness, thermal, dynamic, and surface morphology tests (Sumrith et al. 2020). In a recent study, epoxy composites were fabricated by reinforcing WH fibers. Different ratios of fiber to resin content were evaluated in which 35 wt% of fiber content shows improved composite properties for various applications (Dass and Chellamuthu 2022). Cellulosic WH fibers were reinforced with polyurethane at fiber loadings of 1–7 wt%, and the resulting composites were tested for oil adsorption. The maximum oil sorption capacity of 10–15 g/g was obtained with higher fiber loadings due to increased porosity at higher fiber concentrations (Sittinun et al. 2020). Microwave-assisted cellulose aerogels derivatized with polyvinyl alcohol (PVA) with a PVA/cellulose ratio of 4:3 showed an optimum capacity of 38.5 g of diesel adsorbed per gram of sorbent and 43.3 g/g with motor oil. Reusability studies indicated adsorption remained stable for up to 10 cycles. Moreover, the low thermal conductivity of aerogel (0.030 W/mK) also opens up potential applications as a thermal insulator (Nguyen et al. 2021).

Biodegradable films for food packaging applications were reported using WH CNFs. WH CNFs were reinforced in polyvinyl alcohol (PVA) and gelatin to synthesize composites. The effect of PVA, gelatin, and cellulose nanocrystal (CNC) concentration on tensile strength and elongation was optimized. The maximum tensile strength of 13.6 MPa and 80.7% elongation at break was obtained at

the optimum value of 10 wt% for PVA, 5 wt% for gelatin, and 7 wt% for CNC. For a film with higher strength, a decrease in water absorption, water vapor permeability (WVP), and moisture uptake was observed (Oyeoka et al. 2021). WH cellulose was acetylated and used for membrane synthesis. The membranes were characterized for filtration of humic acids giving 65% rejection and a permeate flux of 460 Lm^{-2} h^{-1} at a transmembrane pressure of 0.5 atm (Istirokhatun et al. 2015).

Apart from the conventional applications, WH cellulose was also utilized to synthesize conductive aerogel for microelectronics, solar cells, and batteries. WH CNFs were blended with conducting polymers polypyrrole (PPy) and polyvinylpyrrolidone (PVP). The synthesis was optimized using Box-Behnken response surface methodology (RSM) by changing the ratios of CNF, PPy, and PVP. The electrical conductivity of the composite aerogels ranged from 0.1 to 6.23 S/cm, with an optimal value of 5.21 S/cm. (Ewulonu et al. 2020).

Slow-release fertilizers (SRF) were synthesized from WH cellulose to avoid fertilizer losses or the dose-dependent toxic effects of high concentrations of fertilizers. Polyacrylamide was grafted on the extracted cellulose, and the composite polymer was used as the carrier for the SRF. Different blends of polymer, nano-hydroxyapatite, and fertilizer were investigated along with nutrient release kinetics (Rop et al. 2018). Poly(ammonium) acrylate-co-acrylic acid-Sgrafted WH cellulose was explored further as a soil conditioner. The polymer hydrogel (PHG) was tested for its moisture-holding capacity and biodegradability (Rop et al. 2019). However, WH biomass could also act as a cross-linking agent for formulating SRFs (Silva et al. 2021).

The ability of WH cellulose as a biomedical nanocarrier for delivering the anticancer drug (methylene blue, MB) was assessed. The release of MB was found to follow first-order kinetics. A maximum release percentage value of 52% was obtained for MB at pH 7.4. Cell viability for the breast cancer cell line, MCF-7, decreased about seven times when the concentration of MB increased from 12.5 to 100 mg/mL. Simultaneously, only a moderate cytotoxic effect was observed for the normal cell line (WI-38) (Salahuddin et al. 2021b).

Miscellaneous

WH ash extract was used as a green medium for the palladium-catalyzed Suzuki reaction. EDX analysis reveals the presence of metals in WH ash, giving rise to the corresponding metal hydroxides imparting basicity to the medium (Sarmah et al. 2017). Acid-treated WH dried leaves were pyrolyzed to obtain carbon dots (CDs) which were then used to fabricate paper-based fluorescent sensors for on-site borax detection with a detection limit of 11.9 µM. The developed sensors were low-cost with high photostability (Prathumsuwan et al. 2019).

In 2018, Okwadha and Makomele reported a different but potentially significant application of utilizing WH extract as a plasticizer for producing self-compacting concrete. The presence of lignocellulose and saturated/unsaturated fatty acids in the extract was theorized to be responsible for the plasticizing effect (Okwadha and Makomele 2018). A recent study produced handmade paper by pulping and bleaching WH biomass using potassium hydroxide (KOH) and H_2O_2, respectively. The black liquor waste was used as a supplement for composting the kitchen waste. A significant and beneficial increase in bio-compost nitrogen and potassium content was observed (Islam et al. 2021). WH mulch could increase soil moisture by about 33% and control weed growth (Abdalla and Hafeez 1969). It exerts a selective allelopathic effect on weeds, decreases soil salinity, and improves soil texture (Anaya et al. 1987).

Apart from the above uses, WH biomass has been extensively explored as fish feed, ruminant fodder, and soil mulch. The possibility of incorporating WH in fish feed was studied for *Labeo rohita* fingerlings, *Ctenopharyngodon idella* fingerlings, and rainbow trout (Mahmood et al. 2018; Debnath et al. 2018; Rufchaei et al. 2020). The inclusion of some percentage of WH in the fish diet was found to improve fish immunity against pathogens, *Lactococcus garvieae* and *Streptococcus iniae* (Chang et al. 2013; Rufchaei et al. 2020). Various trials done on animals have suggested its possible application as cattle fodder (Agarwala 1988; Abdelhamid and Gabr 1991; de Vasconcelos et al. 2016). WH should not be offered as a sole feed for ruminants. A maximum of 50% replacement in the complete feed diet could be done without adverse health effects (Abdelhamid and Gabr 1991). Various pre-treatments for effective silage production from WH have been suggested to make the feed more palatable for animals (Bolenz et al. 1990).

Secondary bioproducts

Phytochemical-rich extract for green synthesis

WH is a rich source of various phytochemicals, which could be utilized for the green synthesis of nanoparticles without adding any extra reducing and capping agent. Synthesis of multiple nanoparticles based on WH metabolites has been reported, as summarized in Table 3.

Mochochoko et al. (2013) demonstrated the synthesis of silver nanoparticles (Ag-NPs) using WH cellulose as a reducing and capping agent. Effects of reaction time and solution pH on NPs synthesis were studied. Highly monodispersed, stable, and spherical particles with an average diameter of 2.68 ± 0.69 nm were produced under alkaline conditions (pH: 11) (Mochochoko et al. 2013). AgNPs are found effective against *Staphylococcus aureus*

Table 3 Green synthesis of nanoparticles using WH extract

Nanoparticles	Sample	Precursor solution	Application	Shape	Average diameter (nm)	Key results	References
Cellulose-silver	WH plant shoot	$AgNO_3$, cellulose	NA	Spherical	2.68 ± 0.69 (pH 11)	Small, stable, and highly monodispersed particles were obtained	(Mochochoko et al. 2013)
Platinum	WH fresh leaves	Hexachloroplatinic acid	NA	Spherical	3.7 (TEM), 73.3 (DLS)	Zeta potential: − 0.0536 mV	(John Leo and Oluwafemi 2017)
Iron oxide	WH fresh leaves	$FeSO_4$	Antibacterial activity	Rod shaped	NA	A maximum zone of inhibition was obtained with nanoparticles (100 µg/mL)	(Jagathesan and Rajiv 2018)
Silver	WH fresh leaves	$AgNO_3$	Colorimetric sensing of heavy metal ions	Spherical	10.5	Good selectivity towards Hg^{2+}	(Oluwafemi et al. 2019)
Copper	Flower	$CuSO_4$	H_2O_2 detection	Spherical	12–13	The minimum level for H_2O_2 detection was 0.1%	(Roy et al. 2019)
Magnetic iron (Fe_3O_4)	Leaves	Fe^{3+} and Fe^{2+} solution (Fe^{3+}: Fe^{2+} = 2:1)	Role as a regulator in fermentative hydrogen production	Spherical	13.5 ± 3.7	Hydrogen yield, $Y(H_2/S)$ of 83.2 ± 2.19 mL/g $_{substrate}$ was obtained with WH-magnetite-NP at 20 mg/L	(Zhang et al. 2021)
Silver	Leaves	$AgNO_3$	Antibacterial and anti-corrosion activity	Spherical	16–65	At higher AgNP (0.4 mg/L), a low aluminum corrosion current density of 1030 µA/cm^2 was observed Activity against *E. coli* was observed	(Hublikar et al. 2021)
Cr_2O_3/ZnO composite	WH aqueous extract	$Zn(NO3)_2.H_2O$, $Cr(NO_3)_2.H_2O$	Photodegradation of MB dye	Aggregates	NA	Maximum MB degradation efficiency of 85% was observed for 0.08CrZn catalyst within 90 min	(Zelekew et al. 2021)
Activated carbon-copper oxide (CuO/AC) catalyst	Roots	$CuSO_4$	Reactive red 2 (RR2) dye decolorization by WAO	NA	NA	100% dye decolorization was observed for 6 g/L of catalyst dose	(Ayalkie Gizaw and Gabbiye Habtu 2022)

and *Escherichia coli*. The anticorrosion activity of AgNPs was tested by adding them to 1 M HCl solution in which pre-weighed aluminum coupons were submerged. A low corrosion current density was observed as the charge transfer resistance values increased with increasing AgNP concentration (Hublikar et al. 2021). Colorimetric studies indicated the excellent sensitivity of Ag-NPs prepared using WH extract for heavy metal ion detection, especially Hg^{2+} ions (Oluwafemi et al. 2019).

Rod-shaped iron oxide nanoparticles (FeNPs) were generated using WH leaf extract, and their antibacterial activity was analyzed against *Staphylococcus aureus* and *Pseudomonas fluorescens*. One hundred micrograms per milliliter FeNPs gives the highest zone of inhibition against studied microbes, while the lowest was observed at 25 µg/mL (Jagathesan and Rajiv 2018). Magnetic iron nanoparticles (FeNPs) of spherical shape with an average particle size of 13.5 ± 3.7 nm were synthesized from WH extract. The authors studied their role as a regulator in the fermentative hydrogen production from the lignocellulosic hydrolysate. Hydrogen production was increased by 23.5% with an optimum yield ($Y_{H2/S}$) of 83.2 ± 2.19 mL/g substrate on the addition of WH-magnetite-NP (20 mg/L) in the fermentation medium. This was due to increased hydrogenase activity, the critical enzyme for biochemical hydrogen production in the presence of WH-magnetite-NP (Zhang et al. 2021).

Roy et al. (2019) synthesized spherical copper nanoparticles (Cu-NPs) with 12–15-nm diameter using WH flower extract. These biogenic Cu-NPs instantly detected the presence of hazardous hydrogen peroxide (Roy et al. 2019). WH aqueous extract was used to produce spherical platinum nanoparticles (Pt-NPs) with an average diameter of 3.74 nm, while the hydrodynamic aggregate size was 73.3 nm (John Leo and Oluwafemi 2017). Synthesis of Cr_2O_3/ZnO photocatalysts was performed using WH aqueous extract. The maximum degradation efficiency of 85% was achieved for MB dye within 90 min in the presence of 0.08-CrZn catalyst, which was attributed to efficient electron/hole separation and high porosity of the synthesized heterocatalyst (Zelekew et al. 2021).

Biochemical conversion

Lignocellulosic materials, including plant dry matter or agro-wastes, are rich sources of biopolymers like cellulose, hemicellulose, and lignin, which could be converted into bioethanol and other valuable products by biochemical routes. In this context, a considerable amount of WH biomass with high cellulosic contents makes a sustainable raw substrate for fermentative productions. Table 4 summarizes the fermentative production of different valuable compounds using WH biomass as substrate.

Cellulolytic enzymes and bioethanol

Bioconversion of WH biomass into ethanol to be used as a motor fuel was carried out using yeast *Pichia stipitis* NRRL Y-7124. Dilute acid hydrolysis was performed with 1% (v/v) sulfuric acid, followed by heat treatment. Optimum fermentation conditions identified were an aeration rate of 0.02 vvm, a temperature of 30 °C, and pH 6.0, giving the highest ethanol yield ($Y_{p/s}$) of 0.35 g_p/g_s with 76% of total sugar utilized (Nigam 2002). The potential of WH as promising biomass for ethanol production was compared using simultaneous saccharification and fermentation mode (SSF) and separated hydrolysis and fermentation mode (SHF). The higher ethanol concentration of 16.9 g/L and 0.17 g/g-dried biomass yield was produced with WH substrate using recombinant *Escherichia coli* (KO11) under SSF compared to water lettuce (Mishima et al. 2008).

Cellulase and xylanase were produced in SSF using WH substrate with a mixed culture of *Trichoderma reesei* and *Aspergillus niger*. A yield of 46.3 FPU/gds (gram dried substrate) for cellulase and 57.2 IU/gds for xylanase was observed when the mixed culture was used (Deshpande et al. 2008). Cellulase was produced using WH substrate by *Aspergillus terreus*. Afterward, the crude enzyme was used to hydrolyze alkali-treated WH biomass. The hydrolysate was then fermented by *Kluveromyces marxianus*, giving a maximum ethanol concentration of 8.4 g/L, which was further increased by 10% with the addition of commercial pectinase (Narra et al. 2017).

Carboxymethyl cellulase (CMCase) and protease were produced in WH using solid-state fermentation (SSF) by 12 different fungal strains. *Ulocladium botrytis* gave the best yield, with yeast extract as the best nitrogen source for CMCase and malt extract for protease production. Enzyme recovery of 40.3 and 56.3%; purification fold of 47.3 and 51.8; and specific activity of 852 and 1470 U/mg (unit per milligram) was reported for CMCase and protease, respectively (Abo-Elmagd and Housseiny 2012). Endoglucanase enzyme was produced by the bacterial strain *Bacillus subtilis* PF1 in SSF using WH. The enzymatic yield of 17 IU/gds for endoglucanase activity and 12 IU/gds for filter paper activity was observed within 30 h of fermentation. The addition of TiO_2 nanoparticles (NPs) increased the thermal stability of enzymes (Khan et al. 2022). The ability of 100 fungal strains to produce hydrolytic enzymes using WH biomass was assessed. About five strains generated hydrolytic enzymes, among them, the strain *Trichoderma harzianum*, made the maximum yield. The highest enzyme yield of 149 ± 14.3 IU/gds for xylanase, 16.4 ± 0.6 IU/gds for cellulase, and 128 ± 14.8 IU/gds for β-d-xylopyranosidase was observed (Arana-Cuenca et al. 2019).

Pre-treatment of WH biomass with the dilute acid treatment (DAT) method and the novel method of using crude

Table 4 Fermentative products using WH as a raw substrate

Product	Microbe	Microbial strain	Fermentable sugars/ method	Product yield	Key results	References
Bioethanol						
Bioethanol	Fungi	*Pichia stipitis* NRRL Y-7124	Total sugar utilized 76.0 ± 0.32% (treated), 20.1 ± 0.17% (untreated)	0.35 gp/gs (gram product per gram substrate)	Ethanol yield: 0.35 g_p/g_s (treated)	(Nigam 2002)
Bioethanol	Yeast	*Saccharomyces cerevisiae* NBRC 2346	Total sugar utilized (treated): 35.2% (untreated): 25.1%	0.14 g/g dry biomass	Ethanol concentration (*S. cerevisiae)*: 14.4 g/L	(Mishima et al. 2008)
	Recombinant bacteria	*Escherichia coli* KO11		0.17 g/g dry biomass	Maximum ethanol concentration (*E.coli* KO11): 16.9 g/L	(Mishima et al. 2008)
Bioethanol	Yeast	*Saccharomyces cerevisiae*	Pre-treatment with pure glycerol gives reducing sugar yield (mg/g dry biomass): 719; dilute acid: 714; crude glycerol: 705; BMIMA: 584; EMIMDP: 422	0.4–0.5 mg/mg of glucose	For WH, crude glycerol pre-treatment was comparable to the conventional method and more effective than ionic liquid pre-treatment	(Guragain et al. 2011)
Bioethanol	Yeast	*Kluveromyces marxianus* (42 °C)	Pre-treatment with 0.5% (w/v) NaOH at two different conditions, i.e., RT for 24 h and 121 °C for 30 min	NA	Ethanol concentration: 8.4 g/L at 42 °C Pectinase supplementation gives 1.04–1.11-fold higher ethanol	(Narra et al. 2017)
Bioethanol	Yeast	*Saccharomyces cerevisiae*, *Scheffersomyces stipitis* co-culture	Max concentration of reducing sugars: 35 g/L	0.33 g_p/g_s	Maximum ethanol concentrations of 9.8 g/L with *Saccharomyces cerevisiae* and *Scheffersomyces stipites* (co-culture)	(Singh and Bishnoi 2013)
Bioethanol	Yeast	*Kluyveromyces marxianus* K213	Reducing sugar (treated biomass): 223.5 mg/g dry biomass	0.43 g/g glucose	Maximum ethanol concentration: 7.34 g/L	(Yan et al. 2015)
Bioethanol	Yeast	*Saccharomyces cerevisiae* MTCC 173, *Zymomonas mobilis* MTCC 2428 (mixed culture)	Maximum sugar yield by enzymatic saccharification: 425.6 mg/g	NA	Ethanol concentration: 13.6 mg/mL	(Das et al. 2016)
Bioethanol	Yeast	*Saccharomyces cerevisiae*	Reducing sugar 403 mg/g	NA	Ethanol concentration: 1.29 g/L	(Zhang et al. 2016)
Bioethanol (different pre-treatments)	Yeast	*Phanerochaete chrysosporium* for microbial pre-treatment, *Saccharomyces cerevisiae* for ethanol	Reducing sugar 431 mg/g (microbial and dilute acid combined pretreatment)	NA	Bioethanol concentration: 1.40 g/L	(Zhang et al. 2018b)

Table 4 (continued)

Product	Microbe	Microbial strain	Fermentable sugars/ method	Product yield	Key results	References
Bioethanol	Yeast	*Saccharomyces cerevisiae*	Steam explosion with enzymatic hydrolysis gives reducing sugars: 0.51 g/g of WH	0.23 g/g of dry matter	Ethanol concentration: 7.13 g/L	(Figueroa-Torres et al. 2020)
Enzymes						
Hydrolytic enzymes	Fungi	*Trichoderma harzianum* strain PBCA selected, among others	Solid-state fermentation	NA	Enzyme activity (IU/g dry matter): Xylanase: 149; CMCase:16.4; β-d-xylopyranosidase: 128	(Arana-Cuenca et al. 2019)
Cellulase	Fungi	*Aspergillus terreus* D34	Pretreatment with 0.5% (w/v) NaOH at two different conditions i.e., RT for 24 h and 121 °C for 30 min	NA	NA	(Narra et al. 2017)
Carboxymethyl cellulase (CMCase) and protease	Fungi	*Ulocladium botrytis* and others	Solid-state fermentation, enrichment with natural additives	NA	Maximum enzyme activity (U/g): CMCase: 30.0; Protease: 26.1	(Abo-Elmagd and Housseiny 2012)
Cellulase and xylanase	Fungi	*Trichoderma reesei*, *Aspergillus niger*, and mixed culture	Solid state fermentation	NA	Maximum enzyme activity (IU/mL) for CMCase: 6.95; β-glucosidase: 0.995; Xylanase; 5.1; FPA: 2.49 FPU/mL; Protein: 12 mg/mL with WH medium supplemented with Toyoma Ogowa, whey and peptone, and WH	(Deshpande et al. 2008)
Cellulase	Bacteria	*Bacillus subtilis* PF1	Solid state fermentation The thermal stability of the enzyme in the influence of TiO_2 NPs was assessed	NA	EG (endoglucanase): 17 IU/gds; FPU (filter paper unit): 12 IU/gds Optimum enzyme activity (EG) was observed at 60 °C and pH 5.0 in the presence of TiO_2 NPs	(Khan et al. 2022)
Biogas and biodiesel						
Biogas	Sewage sludge (SS)	NA	Anaerobic co-digestion	Biogas yield of 812 mL/L with WH, cow manure, and SS	Biogas composition: CH_4: 65%, CO: 14%, other gases: 21% other gases after 800 h	(Tasnim et al. 2017)

Table 4 (continued)

Product	Microbe	Microbial strain	Fermentable sugars/ method	Product yield	Key results	References
Energy recovery (hydrogen, methane, and MFCells)	Acidogenic culture	NA	Anaerobic digestion	Hydrogen: 41.4 L/kg COD; methane: 35.7 L/kg COD	Maximum energy recovery: 60% COD removal: 94%	(Varanasi et al. 2018)
Biogas and biomethane	Anaerobic inoculum	NA	Lab-scale batch digesters	Biogas: 474.9 mL/g VS, methane: 213.9 mL/g VS	Biogas composition: 63.2% CH_4 and 36.7% CO_2	(Keche et al. 2022)
Methane enrichment	Methanogenic sludge	NA	Sonic wave and biosurfactant (Iturin A) assisted pre-treatment	Biomethane: 69 L/kg COD	Maximum production obtained for sonic wave combined Iturin A with alkaline pH pre-treatment on the 23rd day	(Sethupathy et al. 2022)
Biogas and biomass pellet	Microbial culture	NA	Batch anaerobic digestion was done to produce biogas with WH juice. Biomass pellets with leftover WH fibers	Specific methane yield: 237.37 L CH_4/kg VS added	Biogas consists of 68.67% CH_4, 18.23% CO_2, and 13.10% other gases	(Hudakorn and Sritrakul 2020)
Biomethanation	Anaerobic sludge	NA	Anaerobic digestion	Biogas yield: 274.4 N. mL /batch for AWAO	AWAO increased the methane potential of WH by 24% and was better than WAO and unpretreated biomass	(Castro and Agblevor 2020)
Biogas and briquette	Cow dung	NA	Anaerobic digestion	0.26 m^3 biogas formed on 32nd day	Biogas consists of CH_4: 45.2%, CO_2: 26.3%, moisture: 4.51%, H_2S: 0.50%, other gases 23.5%	(Bote et al. 2020b)
Biogas	Waste-activated sludge	NA	Anaerobic co-digestion The effect of dilute acid-thermal pre-treatment and the addition of cattle dung biochar (BC) was tested	Maximum biogas yield: 235 mL CH_4/g VS with 1% BC	Biogas composition: CH_4: 68.2, CO_2: 22.5, H_2: 6.65, N_2: 2.69	(Suthar et al. 2022)
Biodiesel and bioethanol	Yeast	*Saccharomyces cerevisiae*	Lipid extraction, alkaline transesterification, fermentation for bioethanol	Biodiesel:3.32–6.36% Pigments: 1.6–3.97 mg/g, Glycerol: 22.6–92.7 mg/dL Bioethanol: 0.43 g/g of glucose	Biodiesel properties were within the recommended fuel standards The iodoform test confirms the bioethanol production	(Shanab et al. 2018)

Table 4 (continued)

Product	Microbe	Microbial strain	Fermentable sugars/ method	Product yield	Key results	References
Biopolymers and organic acids						
Poly (3-hydroxybutyrate) (PHB)	Bacteria	*Cupriavidus necator*	Reducing sugars: 35 g/L	Dry cell weight: 12 g/L, PHB concentration: 7 g/L	WH enzymatic hydrolysate gave a higher PHB than the acid hydrolysate	(Radhika and Murugesan 2012)
Polyhydroxybutyrate (PHB)	Bacteria	*Ralstonia eutropha* MTCC 8320	Reducing sugar: 379 mg/g (for enzyme or hexose hydrolysate), 239 mg/g (for acid or pentose hydrolysate)	PHB yield (mg PHB/g raw biomass) hexose-rich hydrolysate: 36.5, Pentose-rich hydrolysate: 7.16	PHB from pentose-rich hydrolyzate shows higher glass transition temperature, while PHB from hexose-rich hydrolyzate shows higher thermal degradation temperature	(Pradhan et al. 2017)
Polyhydroxybutyrate (PHB)	Bacteria	*Ralstonia eutropha* ATCC 17699	Enzyme hydrolysis (40 FPU/g of dry WH) gives a total reducing sugar of 523 mg/g of WH	PHB yield: 0.429 g/g of reducing sugar	PHB synthesis:73%, PHB concentration: 7.3 g/L	(Saratale et al. 2020)
L-lactate	Bacteria	*Bacillus coagulans* JCM 2258	Alkaline/peroxide pretreatment gives a glucose yield of 0.14 g/g dry biomass	SSF, L-lactate yield of 0.09 g/g for WH	The ratio of SSF to separate saccharification and fermentation was 0.63 for WH, which was inferior to values obtained for corn	(Akao et al. 2012)
Substrate for microbe and mushroom cultivation						
Rhizobacteria (biofertilizer)	Bacteria	*Bacillus*, *Azotobacter* and *Rhizobium* sp.	Shake flasks culture using WH extract as culture medium	High Bacterial growth: $> 10^8$ cfu/g (crude juice)	Results were comparable to those obtained with recommended culture media, indicating WH can provide the necessary nutritional requirements for rhizobacteria growth	(Ahmed et al. 2018)
Substitute for yeast extract mannitol (YEM) medium	Bacteria	*Rhizobium. trifolii* and *Rhizobium. japonicum*	Medium formulation, optical density measurement for bacterial growth	Molasses: WH: pea husk (1:2:2) could replace mannitol	Biomass hydrolysates could replace costlier mannitol for the production of Rhizobia culture	(Gulati 1987)

Table 4 (continued)

Product	Microbe	Microbial strain	Fermentable sugars/ method	Product yield	Key results	References
Texturizer for biopesticide, *Isaria fumosorosea*	Fungi	Infectivity against *Galleria mellonella* larvae was tested	Solid-state culture (SSC)	With PR: WH (80:20), conidial yields became 1.55 times compared to parboiled rice (PR) alone	WH increases the porosity fraction (ε) of the bed and promotes oxygen transfer	(Angel-Cuapio et al. 2015)
Solid bed for mushroom cultivation	Fungi	*Pleurotus ostreatus*	Solid-state fermentation	Biological efficiency (BE) of 310% ± 85.3. with humid and sterilized WH	WH was better than straw, the commercial substrate Lead and cadmium were not detected in fruiting bodies indicating its possible utilization	(Hermoso-López Araiza et al. 2016)

glycerol (CG) and ionic liquids (ILs) were compared. Authors found IL (1-butyl-3-methylimidazolium acetate) and CG treatments resulted in 3.3 and 1.9 times higher recovery of total reducing sugars, respectively, compared to DAT. However, CG pre-treatment gives a better ethanol yield than IL. Similar results were also observed for wheat straw (Guragain et al. 2011). Alkali-treated WH was used to produce crude enzymes, by which biomass was saccharified to produce ethanol. The ethanol concentrations of 4.3 g/L, 6.2 g/L, and 9.8 g/L were recorded by *Saccharomyces cerevisiae*, *Scheffersomyces stipitis*, and both cultures, respectively (Singh and Bishnoi 2013). A 1.78-fold higher bioethanol production was achieved when simultaneous saccharification and fermentation were performed on pre-treated WH biomass using thermotolerant *Kluyveromyces marxianu*. After pre-treatment, the level of reducing sugars was recorded as 224 mg/g dried biomass, giving an ethanol concentration of 7.34 g/L (Yan et al. 2015). Steam explosion pre-treatment and enzymatic saccharification of WH biomass were reported to produce bioethanol. SSF was performed on steam explosion pre-treated WH biomass to produce xylanase and cellulase with the activity of 42 U/g and 2 U/g of dry matter, respectively. The highest ethanol concentration of 7.13 g/L and yield of 0.23 g/gds was obtained when hydrolysate was fermented with *Saccharomyces cerevisiae* (Figueroa-Torres et al. 2020).

Dilute acid pre-treatment was found best, followed by enzymatic saccharification, which was then used to produce bioethanol. Using a co-culture of *Saccharomyces cerevisiae* and *Zymomonas mobilis,* a maximum concentration of 13.6 mg/mL of ethanol was attained (Das et al. 2016). Dilute acid followed by enzymatic hydrolysis was the most effective process of saccharifying WH biomass, resulting in 402.9 mg/g of reducing sugar at optimal conditions. The solid-state fermentation produced 1.29 g/L ethanol under optimum conditions of 38.9 °C for 82 h with 6 ml of yeast inoculum (Zhang et al. 2016). A high amount of reducing sugars, 431 mg/g, was obtained when combined dilute acid hydrolysis and microbial treatment were given to WH biomass. A maximum yield of 1.40 g/L bioethanol was obtained, making it a promising way of utilizing WH (Zhang et al. 2018b).

Biofuels

Several researchers have reported biogas generation by anaerobic fermentation of WH biomass. Typically, 60–70% methane was found in the generated biogas, with 15–25% CO_2 and other gases. The considerable detail about the biogas is the absence of sulfur, which is advantageous for use as a motor fuel. A maximum value of 475 mL/g VS (volatile solids) for biogas and 214 mL/g VS for methane was recorded with a hydraulic retention time (HRT) of

45 days at 37 °C. Biogas thus produced contained 63.2% CH_4 and 36.7% CO_2, and the residual digest serves as an effective organic fertilizer for tomato cultivation (Keche et al. 2022). WH biomass was used holistically by utilizing WH shoot juice to produce biogas and the remaining fibers to produce biomass pellets. Biogas produced in this way consists of 68.7% CH_4, 18.2% CO_2, and 13.1% other gases with a specific methane yield of 237 L CH_4/kg VS (Hudakorn and Sritrakul 2020).

A significant improvement in bio-methanation was observed by subjecting the WH biomass to weak acid hydrolysis and amending the process by adding 1% cattle dung biochar (BC) (Suthar et al. 2022). WH, cow manure, and sewage sludge were co-digested anaerobically at 37 °C to produce biogas. In 1 L batch, 812 mL of biogas was produced in 800 h with 65% methane, 14% carbon monoxide, and 21% other gases (Tasnim et al. 2017). A relatively higher yield of 505 L/kg of biomethane was obtained by anaerobic co-digestion of WH and dairy wastewater proportionally than the mono-digestion of WH or dairy wastewater alone. Also, a superior quality of bio-oil and biochar was obtained by utilizing the leftover residue (Arutselvy et al. 2021).

A holistic and efficient approach for energy production using WH biomass was tested in single, two, and three-stage operations of dark fermentation, bio-methanation, and microbial fuel cells. Energy in the form of hydrogen, methane, and electricity was produced. About 60% energy recovery was obtained in an integrated three-stage process with an overall COD removal of 94% (Varanasi et al. 2018). Methane enrichment efficacy was assessed for biosurfactant (Iturin A), and sonic waves combined pre-treatment of WH biomass giving biomethane production of 69 L/kg COD at alkaline pH due to the higher cell lysis (Sethupathy et al. 2022). Biogas was produced by WH biomass and assessed for running an internal-combustion engine to generate electricity. Also, the residual waste was utilized for briquette formation (Bote et al. 2020b). The effect of wet air oxidation (WAO) and alkaline wet air oxidation (AWAO) pre-treatments on the structure of WH and its bio-methanation was studied. The highest bio-methanation of 310 ± 4.1 mg COD/g feed was obtained in the case of AWAO pre-treatment followed by WAO treatment and no-treatment. Alkaline conditions promote better cell disintegration and methanation (Castro and Agblevor 2020). The seasonal WH biomass was collected and tested for biofuel production. A variable lipid content of 6.79–10.5% was observed in WH, which produces biodiesel in the range of 3.22–6.36% via transesterification. The produced diesel had shown good stability and usability. Pigments and glycerol were obtained from the sediment of the transesterification process. Additionally, the extracted residue was subjected to mild acid hydrolysis followed by ethanol production (Shanab et al. 2018).

Biopolymers and organic acids

Cupriavidus necator bacteria was used to produce poly(3-hydroxybutyrate) (PHB) from WH hydrolysate. A maximum of 7 g/L of PHB and 12 g/L of dry cell weight was obtained in an optimized medium supplemented with $(NH_4)_2SO_4$ (Radhika and Murugesan 2012). Production of biopolymer PHB using WH and *Parthenium hysterophorus* was compared. A relatively higher yield of 36.4 mg PHB/g raw biomass was obtained using WH hydrolysate compared to 17.6 mg PHB/g raw biomass for *P. hysterophorus* hydrolysate (Pradhan et al. 2017). In another approach, hydrolysis was initially performed by adding cellulase (40 FPU/g of dry WH) after the alkaline and mild acidic pre-treatment. The hydrolysate, with 523 mg/g reducing sugars, was fermented with *Ralstonia eutropha* (ATCC 17,699) to produce PHB. A maximum PHB of 73% with a titer of 7.3 g/L and yield of 0.429 g/g of reducing sugars was obtained when the medium was supplemented with corn steep liquor as a cheap nitrogen source (Saratale et al. 2020). Thermophilic *Bacillus coagulans* was used for lactate production at 55 °C and pH 5.5. The separate saccharification and fermentation method was more effective than the simultaneous saccharification and fermentation method, as indicated by the relatively higher L-lactate yield of 0.19 g/g of dried WH biomass with the former. This was theorized to be due to the denaturation of cellulases at higher temperature conditions (Akao et al. 2012).

Nutrient medium for microbes and mushroom cultivation

WH juices and dehydrated powder were found to be an efficient medium for culturing microbes such as *Azotobacter chroococcum*, *Rhizobium leguminosarum, Bacillus megaterium,* and *Bacillus subtilis* which are helpful in agriculture (Ahmed et al. 2018). Gulati (1987) investigated the replacement of mannitol with fungal (*Trichoderma reesei*) hydrolysates of various cellulosic biomasses for preparing the YEM medium. WH, pea husk, and molasses at proportions of 2:2:1 could be used as a substitute for mannitol. Interestingly, it gave higher rhizobacterial growth than the traditional yeast extract mannitol medium (Gulati 1987). Effective utilization of WH biomass as a texturizer for bio-mycopesticide (*Isaria fumosorosea*) production was studied. WH biomass increases the porosity of the medium during solid-state fermentation, thereby improving gaseous exchange and yields. Using 20% WH in a medium of parboiled rice gave 1.55 times higher biopesticidal conidia production than using rice alone as substrate without compromising its infectivity against *Galleria mellonella* larvae (Angel-Cuapio et al. 2015). WH has also been investigated for edible oyster mushrooms (*Pleurotus ostreatus*) production as a low-cost biomass (Murugesan

et al. 1995; Nageswaran et al. 2003; Ejigu et al. 2022). The total yield was almost 20–45% higher than using paddy straw substrate. Mixing WH biomass with sawdust gave a 71% higher yield for the growth of *P ostreatus* than sawdust alone (Martínez-Nieto et al. 2014). Chen et al. (2010) reported a comparatively safer and more efficient approach of using WH to remove phosphorus and ammoniacal nitrogen from the pig farm biogas fluid sedimentation tank, followed by using the spent WH biomass for *Pleurotus geesteranus* cultivation substituting sawdust as substrate (Chen et al. 2010). This could be a unique way to treat wastewater and enrich the substrate with essential nutrients such as phosphorus and nitrogen. However, the results were also favorable when WH was procured directly from the infested canals which may be contaminated with heavy metals. The negligible presence of lead and cadmium in the fruiting bodies and spent WH substrate suggests the possible usage of WH as a cheaper substrate for mushroom cultivation. Authors suggested lower metal toxicity in mushrooms was due to their phytotoxical effects. They also suggested utilizing spent substrate as bovine fodder but after evaluating the presence of anti-nutritional factors in it (Hermoso-López Araiza et al. 2016).

Thermochemical conversion of WH

Pyrolysis, gasification, hydrothermal treatment, and combustion are some thermochemical conversion procedures used to convert WH biomass into various value-added products, as summarized in Table 5.

Hydrothermal carbonization

Hydrothermal carbonization (HTC) could be used as a green method for converting WH into a lower moisture material with enhanced carbon content. The kinetic studies for HTC of WH revealed an activation energy of 90 kJ/mol at a temperature range of 423–483 K, which was lower than the activation energy in pyrolysis treatment (Luo et al. 2011). The highest heating value (HHV) for hydrochar was 21 MJ/kg, relatively higher than WH (15 MJ/kg). This was due to the higher lignin content in the hydrochar. Lignin has higher thermal stability in comparison to cellulose and hemicellulose. Consequently, hyrdochar has a greater proportion of lignin compared to untreated WH. Furthermore, lignin has greater HHV than cellulose and hemicellulose, thus increasing the HHV value for hydrochar (Gao et al. 2013; Zhang et al. 2020). Another concern is that the WH hydrochar is more challenging to combust than hydrochar obtained from other plants such as wheat. This was because the extent of carbonization was greater for WH than other biomasses based on their compositional differences (Gao et al. 2016). HTC studies using RSM revealed temperature to be the most influential factor, in addition to the time and the biomass load for optimizing solid yield, carbon, nitrogen capture, and heating value (Román et al. 2020). Pre-treatment of WH biomass before carbonization by washing with water and acid decreased heavy oil yield, but a significant reduction in sulfur, nitrogen, and ash content was also observed (Yao et al. 2020).

Pyrolysis gas

The temperature was found to be the critical factor affecting pyrolytic products, such as bio-oil, biochar, and syngas, in fixed-bed reactor pyrolysis (Rahman 2018). A 42% increase in syngas yield was observed during the pyrolysis of WH biomass in the presence of $FeCl_3$ (Trần et al. 2020). Optimization of the process revealed particle size of less than 200 µm affords the highest yield, which can further be increased by the addition of potassium chloride (KCl), calcium oxide (CaO), or magnesium oxide (MgO), with the highest yield obtained using KCl at 900 °C (Hu et al. 2015). WH pyrolysis in a fixed bed reactor with Ni catalyst resulted in higher hydrogen production (101.2 g/kg biomass) when the process was carried out in two stages with a temperature of 650–700 °C for stage 1 and about 800 °C for stage 2 (Liu et al. 2014).

Pyrolysis oil

The pyrolysis process comprises three stages: moisture removal, devolatilization, and residual breakdown; and for WH, the pyrolysis occurs between 250 and 550 °C. GC–MS analyses of pyrolytic WH bio-oil revealed the presence of 21 compounds, including phenols, alcohols, carboxylic acids, ketones, quinines, alkenes, alkanes, aldehydes, and aromatics. The pH was reported to be 2.93, lower than regular fuels. Bio-oil was considered an environmentally benign fuel because of its HHV of 28.4 MJ/kg and lack of sulfur (Wauton and Ogbeide 2018, 2019a).

The bioenergy potential of WH leaves was higher than that of roots or stems as per the pyrolysis studies performed (Huang et al. 2020). Copper catalysts produced a higher bio-oil yield (31%), while aluminum-based catalysts favored the production of gases and light hydrocarbons over bio-oil (Gulab et al. 2019). In optimizing WH pyrolysis for bio-oil synthesis, the optimum temperature, particle size, and flow rate were found to be 450 °C, 0.6 mm, and 100 cm^3/min, respectively (Wauton and Ogbeide 2019b). A comparison study of two-stage pyrolysis of fresh, putrefied, and microbe-treated biomass with 25% (w/w biomass) clinker (silicate) catalyst indicated a higher yield of microbially or putrefied biomass (Hussain et al. 2017). Microwave-assisted fast pyrolysis was also reported with excellent results using a Ce-doped γ-Al_2O_3/ZrO_2 mesoporous catalyst (Zhang et al.

Table 5 Thermochemical conversion of WH biomass

Aim/products	Method	Analysis of products	Temperature (°C)	Time (min)	Key results	References
Pyrolytic kinetics study	Pyrolysis and hydrothermal treatment	TGA	Range II: 150–210 Range II: 200–280	NA	The lower activation energy of 90 kJ/mol indicates Hydrothermal treatment was better than pyrolysis for temperatures below 280 ℃	(Luo et al. 2011)
Hydrochar	Hydrothermal carbonization	FTIR, TGA, SEM, TEM	240	240	HHV: 16.8 to 20.6 MJ/Kg	(Gao et al. 2013)
Fuel oil and fuel gas	Two-step catalytic (clinker) pyrolysis	GC–MS	400	60	Oil: 7%, fuel gases: 29%, char: 50%, and water: 14%	(Hussain et al. 2013)
Bio-oil	Hydrothermal liquefaction using an alkaline catalyst	XRD, SEM, FTIR, and NMR	280	15	Bio-oil yield-23 wt%, conversion-89% with 1 N KOH solution	(Singh et al. 2015)
Hydrochar as solid biofuel	Hydrothermal carbonization	Bomb calorimeter, BET, SEM, XPS	160–250	30–120	High heating value: 21.8 MJ/Kg	(Román et al. 2020)
Effect of various pretreatments on fuel properties	Pre-treatment: water wash, acid wash, torrefaction, and hydrothermal treatment Pyrolysis: slow/fast	TG-FTIR, Py-GC/MS, ICP-OES	Fast pyrolysis: 600 Slow pyrolysis: 50–800	NA	The highest pyrolysis effectiveness index of 0.375 was obtained for Hy-R (hydrothermal treatment of raw WH)	(Yao et al. 2020)
Bio-oil, gas, char	Two-stage catalytic pyrolysis (clinker catalyst)	GC–MS	200–600	15–75	Maximum bio-oil yield: 58.3% and conversion efficiency: 79.1% for putrefied sample	(Hussain et al. 2017)
Hydrogen production	Two-stage catalytic pyrolysis (nickel)	XRD, GC	1st stage: 650–700 2nd stage: 800	10 17	H_2, CO, CH_4, and CO_2 were obtained. H_2 production increases by increasing temperature, residence time, and catalyst	(Liu et al. 2014)
Bio-oil	Pyrolysis (catalyst-copper)	GC–MS, FTIR	150 to 450	60–100	Maximum bio-oil yield: 31.6%	(Gulab et al. 2019)
Hydrogen gas	Pyrolysis of modified WH with $FeCl_3$	SEM, EDS, XRD, FTIR, GC	540	60	Gas yield: 560 mL/kg 42% of H_2 gas with 2 M $FeCl_3$ catalyst	(Trần et al. 2020)
Syngas	Pyrolysis in the presence of catalyst KCl, CaO, MgO	SEM, XRD	900	20	Syngas yield increases with the KCl catalyst	(Hu et al. 2015)
Syngas, bio-oil, char	Pyrolysis	DTG, FTIR, NMR, GC–MS	350	0–20	Maximum bio-oil yield: 44.9 wt%	(Rahman 2018)

Table 5 (continued)

Aim/products	Method	Analysis of products	Temperature (°C)	Time (min)	Key results	References
Bio-oil	Microwave assisted fast pyrolysis (Ce-doped γ-Al_2O_3/ZrO_2 mesoporous catalyst (CAZ)	BET, XRD, NH_3-TPD	923.15	45	Maximum bio-oil yield: 20.5 wt% with CAZ catalyst	(Zhang et al. 2018a)
Pyrolytic kinetics	Microwave pre-treatment (567 W) Catalytic pyrolysis (CaO)	GC/MS, TGA, DTG	750	Pretreatment: 5 Pyrolysis: 0.33	After pre-treatment: sugar content increased from 2.73 to 9.04% Acid content decreased from 7.89 to 4.89%	(Liang et al. 2019)
Bio-oil	Pyrolysis of Pb-contaminated WH (Pb-WH)	FAAS, GC–MS, XRD	275–550	10	Bio-oil yield: 56% with Pb-WH (6 wt%)	(Jiu et al. 2015)
Char (lead leachability test)	Phosphate-assisted pyrolysis of Pb-contaminated WH	AAS, XRD, SEM–EDX	300–600	180	Stable lead salts like pyromorphite formed, and leachability was reduced to 5–7%	(Shi et al. 2017)
Bio-oil	Pyrolysis of Cr accumulated WH (Cr-WH)	FAAS, GC–MS, XRD	500	NA	Maximum bio-oil yield: 63.1 wt % for Cr-WH with Cr (0.5 wt %), HHV: 26.7 MJ/kg	(Lin et al. 2018)
Bio-oil	Pyrolysis, GC–MS, FTIR, fuel properties	TGA, GC–MS	450	NA	Maximum bio-oil yield: 44.5 wt %, HHV: 28.4 MJ/kg	(Wauton and Ogbeide 2019b)
Bio-energy and other products	Pyrolysis	TGA, DTG, TG-FTIR, Py-GC/MS	200–600	NA	HHV value of WHR: 15.7 MJ/Kg, HHV value of WHSL: 14.9 MJ/Kg, CPI for WHSL: 4.27–150, CPI for WHR: 3.18–108	(Huang et al. 2020)
Carbon fiber	Carbonization	SEM, XRD, FTIR, GC–MS	900	60	Maximum yield: 29%, Tensile strength: 600 MPa	(Soenjaya et al. 2015)
Calcined WH as phosphate-rich fertilizer	Calcination	FTIR, XRF, XRD	300–900	120	A Ca/P molar ratio of 5.07 was found in WH ashes. At 700 ℃, 34% hydroxyapatite and other C-rich phases formed, which can be utilized as a fertilizer	(Ramirez et al. 2021)

Table 5 (continued)

Aim/products	Method	Analysis of products	Temperature (°C)	Time (min)	Key results	References
Biomethane, bio-oil, and biochar	Anaerobic co-digestion followed by slow pyrolysis of residue	Biomethane potential (BMP) assay, GC–MS	Slow pyrolysis: 320 ± 15	120	The highest biomethane yield: 504 L/Kg VS fed for co-digestion mixture (dairy water: WH-1:1) Bio-oil density: 1.21 ± 0.04 g/mL, Viscosity: 1.8 ± 0.05 cSt, The calorific value of 1770 ± 11.5 kJ/kg Digestate and Biochar: good fertilizer for the tomato plant	(Arutselvy et al. 2021)
Hydrochar	Hydrothermal carbonization (HTC)	TG-FTIR, SEM, TG, DTG	180–270	10–90	Hydrochar yield: 48% at 210 K, HHV: 20.93 MJ/Kg	(Zhang et al. 2020)
Supercapacitor, oxidation–reduction, and other catalysts						
Activated carbons (ACs) as supercapacitor	$ZnCl_2$ activation	XRD, Raman, FTIR, BET, EIS	–	–	Specific capacitance: 912 F/g with KI and H_2SO_4 electrolyte, Energy density: 19.04 W h/kg, Cycle stability: 4000 cycles	(Senthilkumar et al. 2012)
Carbon microsphere for supercapacitor	Subcritical water carbonization, activation by KOH and microwave treatment	SEM, BET, electrochemical workstation	200	600	Specific capacitance: 185 F/g with KOH:C, 1:1, and 630W Cycle stability: 1000 cycles	(Kurniawan et al. 2015)
Porous WH- carbon as supercapacitor	Carbonization, KOH activation	SEM, BET, WAXD, Raman, XPS, XRD, EIS	Carbonization: 400 Activation: 400–800	Carbonization: 120 Activation: 210	Specific capacitance: 345 F/g Cycle stability: 95% capacitance retention after 10,000 cycles	(Zheng et al. 2017)
Hierarchical porous carbon (HPC) for supercapacitors and lithium-ion batteries	Carbonization, Activation with KOH	XRD, Raman, XPS, SEM, TEM, BET	Carbonization: 500 Activation: 900	Carbonization: 180 Activation: 180	Specific surface area: 2960 m^2/g Specific capacitance: 256 F/g Lithium storage capacity: 590 mAh/g	(Mo et al. 2020)

Table 5 (continued)

Aim/products	Method	Analysis of products	Temperature (°C)	Time (min)	Key results	References
Nanoporous carbon for supercapacitor	Carbonization, Activation with HNO_3 and KOH	TG-DSC, XPS, Raman, BET, SEM, TEM, EIS	Carbonization: 800, Activation: 800	Carbonization: 720, Activation: 120	Specific capacitance: 374 F/g, Cycle stability: 87.3% capacitance retention after 5000 cycles	(Lu et al. 2020)
Ni–N-doped carbon-based supercapacitor	Fast pyrolysis, activation with KOH	FAAS, FTIR, BET, RAMAN, XRD, SEM, TEM	Pyrolysis: 500 Activation: 800	Pyrolysis: 20, Activation: 60	Capacitance (Ni-absorbed WHPC): 552 F/g in 6 M KOH Stability: 97.5% capacitance retention after 10,000 cycles	(Sima et al. 2019)
Carbon from Ni-accumulated WH for supercapacitor	Carbonization of Ni-accumulated WH, activation with KOH	ICP-OES, FE-SEM, EDX, BET, ATR-FTIR, Raman, XRD, EIS	Carbonization: 500 Activation: 800	Carbonization: 60 Activation: 60	Specific capacitance: 541 F/g with 5 mg/L of Ni Cycle stability: 100% capacitance retention after 10,000 cycles Specific surface area: 3430 m^2/g	(Shell et al. 2021)
Polypyrrole on WH polyester blended textiles for supercapacitors	PPy was polymerized onto WH-polyester fabrics	FTIR, TGA, XPS, EIS	–	–	Specific capacitance: 104 mF/cm^2	(Alzate et al. 2022)
Hydrochar as adsorbent and liquid fraction for carbon-based supercapacitors	Hydrothermal carbonization (HTC), pyrolysis of crude liquid product (CLP) after KOH activation	BET, TEM, SEM, XRD, Raman, XPS, TGA, ICP-OES	HTC: 180, Pyrolysis: 800	HTC:1440, Pyrolysis: 180	Specific capacitance: 100 F/g, Cycle stability: 92% capacitance retention after 10,000 cycles Specific surface area: 2550 cm^2/g	(Saning et al. 2019)
Nitrogen self-doped porous carbon for ORR	Pyrolysis, activation with $ZnCl_2$	FE-SEM, HR-TEM, XRD, Raman spectra, BET, XPS	700	120	Specific surface area: 951 m^2/g, Onset potential at ca. +0.98 V vs. RHE	(Liu et al. 2015)

Table 5 (continued)

Aim/products	Method	Analysis of products	Temperature (°C)	Time (min)	Key results	References
Nitrogen-doped WH biochar for ORR	Carbonization of WH with $ZnCl_2$ without additional nitrogen	BET, XPS, EIS	800	60	Specific surface area: 829 m^2/g, H_2O_2 yield: 1.7 mmol/L, Current efficiency: 81.2 ± 2.5% E-Fenton kinetic constant for dimethyl phthalate (DMP) degradation: 0.318/min, 4 times higher than graphite powder	(Liang et al. 2018)
Nitrogen-doped WH graphite (NFe-WHG) with little iron for ORR	Carbonization of WH with dopamine hydrochloride and $Fe(NO_3)_3$	TEM, XRD, Raman, XPS	700	180	NFe-WHG shows an $E_{1/2}$ voltage of 0.797 V comparable to the Pt/C electrode (0.833 V) at Pt loading of 8 μg/cm^2	(Yan et al. 2019)
WH biochar as cathode catalyst (ORR) in ACSC-MFC	Pyrolysis	XRD, EDX, FE-SEM, FTIR, BET, XPS	900	120	A maximum power density of 24.7 mW/m^2 was obtained	(Allam et al. 2020)
Activated carbon from the root, shoot, and leaves for ORR	Pyrolysis with KOH activation	TGA, FTIR, Raman, XRD, SEM–EDS	730	120	Specific surface area: 1970 m^2/g, Maximum ORR onset potential: 0.9 V observed for shoots	(Morales et al. 2021)
WH-activated carbon/NiO nanocomposite (WHc/NiO) for supercapacitors	Carbonization, hydrothermal treatment	XRD, FE-SEM, TEM, three-electrode cell	Carbonization: at 700 Hydrothermal treatment: 100	Carbonization: 120 Hydrothermal treatment: 960	The specific capacitance of 250 F/g, Cycle stability: 78.4% retention after 1000 cycles	(Qiu et al. 2017)
WH hydrochar catalyst for glucose isomerization	Hydrothermal carbonization and pyrolysis of WH with endogenous calcium salts	–	400	60	Catalytic yield: 31%, selectivity: 89%, reactivity maintained for at least three runs	(Yang et al. 2022)
Esterification of oleic acid and dehydration of xylose	Hydrothermal carbonization in the presence of p-toluenesulfonic acid	XRD, TGA, NH_3-TPD, FTIR	180–240	600	Fatty acid conversions: 97%, furfural yields from xylose: 60%S	(Laohapornchaiphan et al. 2017)
WH biochar	Pyrolysis, CaO_2 activation	–	300–900	–	Degradation of 4-nonylphenol (4-NP) was 77% in 12 h	(Hung et al. 2022)

2018a). However, when supplemented with 5 wt%, CaO accorded in higher sugars and phenols, while acid formation was lower (Liang et al. 2019).

It is well-known that WH grows in water bodies that may be contaminated with heavy metals; therefore, a practical approach is to study the pyrolytic fate of such contaminated biomass. Few schemes with heavy metal biosorption followed by pyrolysis were proposed. Lead (Pb) was first adsorbed on WH biomass, which was then pyrolyzed. Pb-contaminated biomass produced higher hydrogen concentration in pyrolysis gas with 56% higher bio-oil yield. The result was attributed to the stabilization of carbonyl and carboxyl groups by Pb^{2+} ions (Jiu et al. 2015). The leachability of Pb in Pb-contaminated WH biomass was lowered by pyrolysis in the presence of phosphates (Shi et al. 2017). Similarly, pyrolysis of chromium (Cr)-polluted WH resulted in an increased bio-oil production of up to 63.1% with an HHV of 26.7 MJ/kg. Furthermore, Cr was converted into a non-toxic amorphous state in the biochar, reducing its environmental harm (Lin et al. 2018).

Calcined WH biomass was assessed for its application as phosphate-rich fertilizer. At low calcination temperatures, the principal crystalline phase was $CaCO_3$, while $Ca(OH)_2$ and Ca-phosphates such as hydroxyapatite were formed at higher temperatures (650–900 °C). Also, no hazardous elements were detected in the ashes. Authors suggested its potential application as fertilizer (Ramirez et al. 2021). Carbonization of WH was done at 900 °C to obtain carbon fibers. The fibers were non-graphitic with a tensile strength of 600 MPa and axial modulus of 42 GPa, comparable to commercial carbon fiber (Soenjaya et al. 2015).

Supercapacitors

The first instance of WH-derived activated carbon supercapacitor electrodes was by Senthilkumar et al. (2012). The carbon was activated by $ZnCl_2$; the activated carbon electrodes exhibited a high capacitance of 912 F/g in the presence of a KI electrolyte in a three-electrode configuration (Senthilkumar et al. 2012). Carbon microspheres created by subcritical hydrothermal carbonization of WH in the presence of dilute H_2SO_4 showed a capacitance of 185 F/g in a three-electrode configuration (Kurniawan et al. 2015). Supercapacitor electrodes synthesized from hierarchical porous activated carbon derived from WH showed a capacitance of 345 F/g in a three-electrode assembly at a current density of 0.5 A/g (Zheng et al. 2017). Hierarchical porous carbon was synthesized from WH leaves and employed as a supercapacitor electrode and lithium-ion battery electrode giving a capacitance of 256 F/g and lithium storage capacity of 590 mAh/g, which was much higher than commercial activated carbon and graphite (Mo et al. 2020). Lu et al. (2020) devised a novel technique for activating WH carbon using a combination of KOH and HNO_3. This carbon was fabricated into a capacitor electrode which showed a capacitance of 374 F/g in a three-electrode configuration (Lu et al. 2020).

WH biomass enriched with nickel-nitrogen (Ni–N) was subjected to fast pyrolysis with KOH activation at 773 K, and Ni – N doped porous carbon material (WHPC@Ni) was prepared with a specific supercapacitance value of 552 F/g. WHPC@Ni showed a high stability of 97.5% even after 10,000 cycles. The enhanced capacitance was due to the formation of NiO.nanoparticles during the pyrolysis (Sima et al. 2019). Similarly, the capacitance of WH-carbonized biomass that was previously utilized for phytoremediation of Ni^{2+} exhibited a capacitance of 541 F/g in a three-electrode configuration (Shell et al. 2021). Polypyrrole coated on WH-polyester composite prepared by in situ polymerization showed high areal capacitance values of 104 mF/cm^2 (Alzate et al. 2022). Saning et al. (2019) fabricated a magnetic carbon adsorbent and supercapacitor electrode by activating the hydrochar obtained from WH using KOH and Fe^{3+} ions. The electrodes showed a good capacitance of 100 F/g in a symmetric two-electrode configuration (Saning et al. 2019).

Oxygen-reduction reaction

Activated carbon derived from WH was evaluated as an oxygen reduction reaction (ORR) electrode and displayed an excellent onset potential of 0.98 V against the reversible hydrogen electrode (RHE) (Liu et al. 2015). Carbonization of WH using molten salts using $ZnCl_2$ was carried out. The nitrogen-doped carbon achieved a high H_2O_2 production potential of 1.7 mmol/L at a current efficiency of 81%, which was used to degrade dimethyl phthalate through an electro-Fenton reaction (Liang et al. 2018). ORR electrode of nitrogen-doped graphite from WH containing iron (Fe) through carbonization at 700 °C in the presence of $Fe(NO_3)_3$ showed an $E_{1/2}$ voltage of 0.797 V, which is equivalent to the performance of the Pt/C electrode (0.833 V) at Pt loading of 8 μg cm^{-2} (Yan et al. 2019). The efficiency of WH biochar as an oxygen reduction reaction (ORR) catalyst was investigated. Pyrolyzed biochar obtained at 900 °C shows a power density of 24.7 mW/m^2 in an air-microbial fuel cell, which was higher than the conventional Pt/C catalyst making it an inexpensive, alluring alternative for this purpose (Allam et al. 2020). Activated carbon was prepared using WH leaves, shoot, and root samples via pyrolysis. Activated carbon derived from shoots showed the maximum ORR onset potential of 0.9 V, followed by roots and leaves (Morales et al. 2021).

Catalysis

WH-activated carbon (WHc) was prepared by pyrolyzing biomass at 700 ℃ for 2 h, followed by its utilization for synthesizing nickel oxide (NiO) doped, WHc/NiO nanocomposite for supercapacitor application. A high specific capacitance of 240 F/g was observed with 78.4% retention after 1000 cycles (Qiu et al. 2017). Apart from being a catalyst for energy applications, WH hydrochar catalyst was synthesized for catalyzing glucose to fructose isomerization reaction. Simple carbonization of biomass at 400 °C for 1 h formed the catalyst, which gives 31% fructose yield with 89% selectivity. The endogenous calcium salts eliminate the need for doping with expensive metals (Yang et al. 2022). A carbon-based catalyst was synthesized from WH leaves by giving hydrothermal treatment. The catalyst obtained at 220 ℃ contains the highest acid sites offering 97% fatty acid conversions and 60% furfural yield from xylose dehydration (Laohapornchaiphan et al. 2017). The degradation of 4-nonylphenol (4-NP) by AOP using WH biochar (WHBC) was studied. Seventy-seven percent degradation was achieved with 1.5 g/L of calcium peroxide-activated WHBC (Hung et al. 2022). More recently, degradation of reactive red 2 (RR2) dye has been reported using copper oxide-loaded activated carbon catalyst synthesized from WH roots prepared through the wet impregnation method. A 100% dye decolorization and 88.6% COD conversion were achieved at a catalyst dose of 6 g/L. However, in the presence of free radical scavengers, sodium bicarbonate and methanol, 42.9 and 59% of dye decolorization were achieved, respectively (Ayalkie Gizaw and Gabbiye Habtu 2022).

Environmental applications

WH compositional structural polymers confer the biomass surface with hydroxyl, carboxyl, and other functional groups. Hence, it acts as an efficient and economical adsorbent for multiple contaminants removal (Abdolali et al. 2014). Biosorption of pollutants such as dyes, heavy metals, and emerging pollutants using WH biomass is reported in the literature and is presented in Table 6.

Biosorption

Dyes

Removal of methylene blue dye using WH dried shoot treated with water, hydrochloric acid, nitric acid, sodium hydroxide, and sodium sulfite was studied. Water-washed WH showed an adsorption capacity of 427 mg/g due to the high specific surface area (El-Khaiary et al. 2009). Adsorption of Indosol dark-blue GL dye by WH dried roots showed a maximum adsorption capacity of 86 mg/g at pH 3. It was noted that the adsorption rate was very rapid for the initial 15 min, and equilibrium was attained after 4 h, which was independent of the initial dye concentration. Dye desorption was done by changing the pH of eluent from low to high (Khan et al. 2014). The removal of crystal violet, a mutagenic textile dye, was tested using WH dried root powder. A biosorption capacity of 323 mg/g was noted as per the Langmuir monolayer model (Kulkarni et al. 2017). WH oven-dried cellulose was investigated for crystal violet (CV) and congo red (CR) dye adsorption in an aqueous system. A maximum adsorption capacity of 182 mg/g for CV and 230 mg/g for CR was obtained. The process followed pseudo-second-order kinetics as indicated by higher R^2 values (0.99, 0.97 for CV and CR, respectively), and the theoretical and experimental q_e values were in agreement. The systems were fitted to Langmuir isotherm for CV and Freundlich isotherm for CR based on R^2 values. However, deeper mechanistic insight into the reasons leading to a difference in the isotherms followed is lacking (Salahuddin et al. 2021a).

Heavy metal ions

Purification of heavy metals-contaminated water from mining and industrial sites using WH dried powder was suggested. WH showed a maximum adsorption capacity of 47 mg/g for the lead, followed by cadmium, copper, and zinc, respectively (Schneider et al. 1995). Adsorption of lead (Pb^{2+}), cadmium (Cd^{2+}), and zinc (Zn^{2+}) ions on acid pre-treated WH dried powder was tested in binary and ternary systems. Langmuir model fitted well with the maximum adsorption capacity in the order of Pb^{2+} (26.3) > Cd^{2+} (12.6) > Zn^{2+} (12.6 mg/g). The multi-element effect on adsorption was also tested (Mahamadi and Nharingo 2010). The H_3PO_4-activated WH showed a maximum adsorption capacity of 119 mg/g for lead (Huang et al. 2014).

The effect of washing WH dried root powder with acid and alkali on the removal of chromium (VI) anions was studied. An adsorbate concentration of 5 mg/L gave an adsorption capacity of 1.28 mg/g. In comparison, at 10 mg/L, it was 0.828 mg/g, which was fitted to the Freundlich isotherm model, and the adsorption followed pseudo-second-order kinetics (Kumar and Chauhan 2019). Citric acid-treated WH was tested for heavy metal ion adsorption. Sorption capacities of 96.9 mg/g for chromium (Cr^{6+}), 78.0 mg/g for copper (Cu^{2+}), and 59.6 mg/g for nickel (Ni^{2+}) ions were obtained (Qu et al. 2019). In one recent study, the adsorption of fluoride ions was tested on hydrous aluminum- and iron oxides-doped WH-alginate beads. The effect of pH, flow rate, bed depth, and other factors was studied. Hydrous aluminum oxide-doped WH shows the highest adsorption capacity of 4.43 mg/g (Murambasvina

Table 6 WH as low-cost adsorbent for water purification

Adsorbent/plant part	Contaminant	Initial concentration range (mg/L)	Adsorbent loading (g/L)	Langmuir adsorption capacity (mg/g)	References
Dyes					
Dried WH shoot	Methylene blue	50–1000	2	427	(El-Khaiary et al. 2009)
Dried root powder	Indosol dark-blue GL	50–150	10	86	(Khan et al. 2014)
Root powder	Crystal violet	100–500	1	323	(Kulkarni et al. 2017)
WH cellulose	Crystal violet	10–15	1	182	(Salahuddin et al. 2021a)
	Congo red	10–15	1	230	(Salahuddin et al. 2021a)
Metal ions					
Whole plant (dried powder)	Heavy metal ions Pb > Cd > Cu ≈ Zn	NA	2	Pb: 47	(Schneider et al. 1995)
			2	Cd: 27	
			2	Cu: 23	
				Zn: 20	
WH dried powder (acid pre-treated)	Pb (II) > Cd (II) > Zn (II) ions	10–60	2	Pb(II): 26.3	(Mahamadi and Nharingo 2010)
		10–60	2	Cd(II): 12.6	
		10–60	2	Zn(II): 12.6	
WH activated carbons using H_3PO_4 activation	Pb (II)	1.0–200	1	118.8	(Huang et al. 2014)
Dried WH roots	Cr (VI)	2–10	14	0.63	(Kumar and Chauhan 2019)
		10–50	14	2.11	(Kumar and Chauhan 2019)
Carboxyl-functionalized WH (CWH)	Cr (VI) > Cu (II) > Ni (II)	50–300	5	Ni (II): 59.6	(Qu et al. 2019)
		50–300	5	Cu (II): 78.0	
		50–300	5	Cr (VI): 96.9	
Hydrous oxides of aluminum and iron-doped WH beads	Fluoride ions	5–50	1	4.4	(Murambasvina and Mahamadi 2020)
WH microspheres	Chromium (VI)	100–1000	1	7.7	(Carreño-Sayago 2021)
Biochar (BC450)	Cd (II)	1–1000	5	70.3	(Zhang et al. 2015)
ZnO/WH biochar	Cr (VI)	25–300	4	43.5	(Yu et al. 2018)
Biochar	Cr (III)	3190	57.1	99% removal in 15 min	(Hashem et al. 2020)
Emerging pollutants					
WH root powder	Antibiotic, sulfachloropyridazine (SCP)	0.05–1	2	227	(Liu et al. 2018)
Acid and ultrasound-treated root powder	Pesticide, (2, 4-D)	20–180	4	40	(Aswani and Pavan Kumar 2019)
WH biochar and magnetic hybrid	Ibuprofen, Cu, Zn, Ni, Co	IBP: 10 Metal ions: 50	10	Cu(II): 18.3 Zn(II): 10.1 Ni(II): 7.3 IBP: 1.0	(Lima et al. 2020)

and Mahamadi 2020). Dried and pulverized WH roots were combined with sodium tripolyphosphate and were tested for adsorption of chromium, Cr (IV) from tannery wastewater. Langmuir adsorption capacity of 7.7 mg/g was obtained (Carreño-Sayago 2021).

WH biomass biochar has also been found effective for contaminants removal by adsorption. Cadmium (Cd) adsorption capacity of 70.3 mg/g was obtained (Zhang et al. 2015). WH biochar modified with ZnO nanoparticles showed a biosorption capacity of 43.48 mg/g for Cr(Vi) (Yu et al. 2018). WH biochar was investigated for the adsorption of trivalent chromium ions from the tannery wastewater. Chromium concentration in the water reduced from 3190.1 to 27.3 mg/L. The adsorption behavior was fitted to Freundlich isotherm and pseudo-first-order kinetics. The chloride, biochemical oxygen demand (BOD), and chemical oxygen demand (COD) were also reduced by 56%, 93.4%, and 92.6%, respectively (Hashem et al. 2020).

Emerging pollutants

Adsorption of antibiotic sulfachloropyridazine (SCP) was studied using WH root powder, and a maximum adsorption capacity of 227 mg/g was obtained. Adsorption followed acid–base interactions and was favored by acidic pH conditions (Liu et al. 2018). WH root powder was used as a low-cost adsorbent to remove 2,4-dichlorophenoxy acetic acid (2, 4-D), a common pesticide from an aqueous environment. A maximum monolayer adsorption capacity (q_{max}) of 40 mg/g was obtained using acid and ultrasound-treated biosorbent (Aswani and Pavan Kumar 2019). Magnetic WH-based biosorbent was investigated for its ability to adsorb ibuprofen and remove copper, zinc, nickel, and cobalt. The value of q_{max} (mg/g) was found to be 18.3 for Cu(II), 10.1 for Zn(II), 7.33 for Ni(II), and 1.02 mg/g for IBP. The selectivity was in order, Cu > Zn > Ni (Lima et al. 2020).

Phytoremediation

WH possesses an enormous capacity for bioaccumulating pollutants and could be utilized as a pollution bioindicator (De Laet et al. 2019). WH has been found to accumulate pollutants such as heavy metals, dyes, antibiotics, and several other contaminants. Pollutants, especially organic contaminants, increase the levels of ammoniacal nitrogen in domestic and industrial wastewater, giving rise to algal blooms and further deteriorating the water quality. Details on the application of WH for phytoremediation are shown in Table 7. WH plants could be utilized for the phytoremediation of lead. An increase in antioxidant enzymes such as superoxide dismutase, catalase, ascorbate peroxidase, and peroxidase in plant tissue was observed when exposed to a high lead concentration of 800 mg/L. These enzymes play a crucial role in increasing the tolerance against oxidative stress (Malar et al. 2014). Europium metal (Eu (III)), a non-radioactive surrogate for Americium (III), a radioactive waste, was tested for phytoremediation using WH plants grown in the greenhouse. The removal efficiency of 26% was observed for Eu (III), indicating its possible utilization for phytoremediation of radioactively polluted water (Kelley et al. 1999). Phytoremediation of paper and pulp industry wastewater using WH was studied. Regression modeling was done to investigate the effect of pH and initial metal ion concentration on the plant's accumulation capacity. The studied model fits well and indicates efficient phytoremediation for heavy metals (Cd, Cu, Cr, Fe, Pb, Zn, Mn) (Kumar et al. 2020). The effectiveness of WH plants for removing heavy metals from the glass industry was tested for 40 days. Maximum removal of 91.3% for Cd, 93.6% for Cu, 92.8% for Fe, and 93.5% for Mn was observed (Singh et al. 2021).

The accumulation and biodegradation of a phosphorus insecticide, ethion, in WH plants were examined. The effect of plant-associated microbes on ethion removal was estimated by calculating the difference in the results obtained by non-sterile and sterile plants. The contribution of phytoaccumulation and phytodegradation was significantly higher (69%) than that of microbial degradation, which contributed only 12%. It suggested phytoaccumulation and phytodegradation were the primary mechanisms for ethion removal (Xia and Ma 2006). A 10-day-long randomized block experiment was performed to study the role of WH in removing chlorpyrifos, an organophosphate insecticide, from water. Removal was further increased in the presence of a root-associated bacterium identified as *Acinetobacter* sp. (Anudechakul et al. 2015). A study on the removal of antibiotic tetracyclines (TCs) and the effect of copper ions on the accumulation and translocation of TCs in WH plants concluded that combining a high concentration of copper and TCs could be more effective (Lu et al. 2014). WH was found to have excellent potential for the bioaccumulation of organophosphorus pesticides. It also effectively removed some of the organochlorine pesticides tested in an onsite study performed for irrigation canals of Mexico wetlands (Mercado-Borrayo et al. 2015). Removal of two herbicides (mesotrione and fomesafen) using WH plants was tested in the randomized block-designed experiments. About 70–92% removal was observed for mesotrione, and 22–34% for fomesafen was obtained after 14 days (Chen et al. 2019).

WH was found to remove 75.1% and 54.7% nitrates from underlay and sewage water, respectively, while for phosphates, a removal capacity of 78.9% in underlay water and 86.1% in sewage water was observed. GC–MS analysis of the hexane extract of WH revealed the presence of oleic acid (35.5%), an important compound. In addition, the mechanical properties of WH fibers were also studied. WH fiber's tensile strength increases to 315 MPa when

Table 7 Studies on phytoremediation of polluted waters using water hyacinth through bioaccumulation, phytodegradation, and microbial degradation by associated bacteria

Mode	Contaminant	Contaminant category	Remark	References
Absorption, accumulation	Tetracyclines (TCs)	Antibiotics	Removal increases at high Cu concentration	(Lu et al. 2014)
Accumulation	Europium, Eu (III)	Simulated radioactive waste (substitute of Americium (III), a radioactive waste)	Eu (III) gets accumulated mainly in WH roots	(Kelley et al. 1999)
Absorption, cementing of secondary biomass waste	Radionucleotides	Radioactive waste	Cemented biomass was as per the recommended values of international nuclear commissions	(Saleh 2014)
Phytodegradation, microbial degradation	Ethion	Organophosphorus pesticide	The contribution of phytodegradation is 69%, and microbial degradation is 12% for Ethion removal	(Xia and Ma 2006)
Phytodegradation, microbial degradation	Chlorpyrifos	Organophosphorus pesticide	Removal of chlorpyrifos by WH is facilitated by a root-associated bacterium, *Acinetobacter* sp.	(Anudechakul et al. 2015)
Phytodegradation, microbial degradation	Organochlorine (OC) and organophosphate (OP) pesticides	Organophosphorus pesticides	Data suggest good removal of the OC pesticides than that of OP pesticides in a wetland with WH	(Mercado-Borrayo et al. 2015)
Phytoremediation	Oil spills	Hydrocarbon	The urea amendment shows no significant role in oil removal	(Ndimele and Ndimele 2013)
Bioaccumulation	Pb	Heavy metal	Accumulation of Pb up to 800 mg/L WH has an efficient mechanism to tolerate Pb toxicity	(Malar et al. 2014)
Bioaccumulation	Mesotrione	Herbicide	70–92% removal	(Chen et al. 2019)
Bioaccumulation	Fomesafen	Herbicide	22–34% removal	
Phytoremediation and microbial degradation	Formaldehyde	Volatile organic compounds	Removal up to 100–300 mg/L; Formaldehyde gets converted to acidoid in plant in the presence of *Eupatorium Odoratum L*	(Gong et al. 2018)
Phytoremediation and microbial degradation	Anionic surfactant, SDS	Surfactant	SDS removal efficiency strengthened in the presence of *Chromolaena odorata* L. extract	(Gong et al. 2019)
Bioaccumulation	di-n-hexylphthalate, pentabromodiphenyl ether, nitenpyram, acetamiprid	Low molecular weight organic intermediates	WH could act as a natural remediation tool and bio-indicator of emerging pollutants	(De Laet et al. 2019)
Bioaccumulation and degradation of organic dyes	Cationic dyes: rose bengal (RB), methylene blue (MB), crystal violet (CV), auramine O(AO), rhodamine B (RhB) Anionic dyes: xylenol orange (XO), phenol red (PR), cresol red (CR), methyl orange (MO)	Cationic or anionic dyes	Dye absorption trend: MO > RB > CV > RhB > MO > AO > XO > PR > CR The degradation efficiency of anionic dyes was relatively less compared with the cationic ones	(Sharma et al. 2021)

Table 7 (continued)

Mode	Contaminant	Contaminant category	Remark	References
Phytoremediation	Ammonium–nitrogen, Phosphate–phosphorous, and chemical oxygen demand	Greywater constituents	A significant removal efficiency of 52–63% was observed, making greywater reusable	(Prasad et al. 2021)
Bioaccumulation	Cd, Cu, Fe, Cr, Pb, Zn, Mn	Heavy metals	Maximum accumulation of heavy metal ions in its vegetative parts was observed at 50% effluent concentration	(Kumar et al. 2020)
Bioaccumulation	Excess nutrients (NO^{3-} and PO_4^{3-})	Ions	From underlay and sewage wastewater	(Adelodun et al. 2020)
Bioaccumulation	Cd, Cu, Fe, Mn, Pb, and Zn	Heavy metals	The most efficient reduction was observed at 25% effluent concentration	(Singh et al. 2021)
Bioaccumulation	Pb, Cu, Cd, and As	Heavy metals	WH roots were found to be better accumulators than leaves	(Peng et al. 2020)
Bioaccumulation	Cr, Pb, BOD, COD, TDS, pH	Heavy metals and others	Phytoremediation was found effective for 20% wastewater concentration	(Panneerselvam and Priya 2021)

four strands are knitted together compared to the low tensile value of 14 MPa for a single WH fiber (Adelodun et al. 2020). Domestic wastewater was treated with WH plants for 30 days in continuous mode. A moderate removal capacity of 63.26 ± 10.47%, 61.96 ± 12.11%, and 51.91 ± 5.32% was observed for ammonium–nitrogen, phosphate–phosphorous, and chemical oxygen demand, respectively. Harvesting WH plants at a regular interval of 15–20 days was suggested for efficient performance. However, the authors emphasize the need to develop a more efficient harvesting method to remove selectively matured plants and leave baby plants in the system (Prasad et al. 2021).

Phytoremediation of dye-loaded wastewater was also studied using WH plants. Absorption and degradation of both cationic [rose bengal (RB), methylene blue (MB), crystal violet (CV), auramine O (AO), rhodamine B (RhB)], and anionic [xylenol orange (XO), phenol red (PR), cresol red (CR), ans methyl orange (MO)] dyes were studied by growing WH plants. WH plants can be a potential decolorizer with a color removal efficiency of 79 to 90.8% for cationic dyes and 33.3 to 62.8% for anionic dyes (Sharma et al. 2021). The river water near a dye industry was treated with WH, and the best results were observed within 7 days with an optimized WH biomass (20%). A removal efficiency of 46% for chromium and 43% for lead was observed. A significant decrease in pH, BOD, COD, and TDS values was also observed (Panneerselvam and Priya 2021).

Phytoremediation of oil spills using WH was studied in an experiment performed in Nigeria using 45 experimental units. An increase in total petroleum carbon in WH was detected, indicating its effectiveness for oil uptake. However, no significant increase in oil absorption was observed on stimulating plants with urea (Ndimele and Ndimele 2013). Phytoremediation of formaldehyde using WH was also tested. High removal efficiency for an initial formaldehyde concentration of 100–300 ppm was observed, which was further increased on stimulating plants with 0.5 ppm *Eupatorium odoratum L.* extract (Gong et al. 2018). The efficacy of WH for removing and degrading anionic surfactant, SDS, was studied. A significant increase in ascorbate peroxidase (APX) activity was observed in response to the stress generated by pollutants. The growth of WH was regulated by using *Chromolaena odorata L.* extract as a biostimulator (Gong et al. 2019).

Biorefinery integration for circular economy

Research significance

The incredible potential of biomass as a resource-generating sustainable material has recently come to light, and there is a good chance that it will grow its market share soon

(Martínez-Ruano et al. 2018; Solarte-Toro et al. 2022). WH biomass is a fantastic feedstock for recovering nutrients and energy, in contrast to being a possible hazard to the ecosystem and environment. The current work investigates three alternative conversion methodologies, including biochemical conversion, thermochemical conversion, and green synthesis methodology, after directly extracting phytometabolites to manufacture valuable primary and secondary products from WH. The WH biomass can either be harvested directly from the infested waterbodies or after it has been used as a phytofilter to purify nutrient-laden wastewater (Fig. 2).

It is beneficial to remove all the solvent-soluble extractives, mainly different phytometabolites, including phenolic compounds, flavonoids, alkaloids, and others, to minimize contaminants during cellulose extraction. Eliminating these low molecular weight compounds is also advantageous while converting the biomass to valuable products by biochemical route, as these compounds tend to inhibit microbial growth during fermentation (Parawira and Tekere 2011; Jönsson et al. 2013). Indeed, these phytometabolite-rich extracts could be utilized for the green synthesis of nanoparticles, catalysts, or other similar commodities owing to their antioxidant potential and antimicrobial properties. Recently, the thermochemical conversion of biomass has been a hot topic among researchers as the increase in the demand for green energy has been observed. So forth, various types of thermochemical conversions have been studied for WH. However, hydrothermal conversion is suggested as a feasible process considering the high initial moisture content of the plant. It is a comparatively convenient energy efficient method and yields bio-oil, hydrochar, and other valuable products. More studies in this regard are needed.

Low-volume high-value bioproducts like phenolic compounds, flavonoids, alkaloids, and enzymes may increase the economic revenues of biomass many folds in comparison to the production of low-value bulk products such as biofuel and bioenergy alone. This is primarily due to the more significant financial and energy expenses associated with biofuel production brought on by high cultivation costs of biomass and poor value for biofuels (Escamilla-Alvarado et al. 2017). However, if procured directly from natural resources, the cultivation expense for WH might be avoided, which is an additional benefit. Hence, an inclusive approach of producing low-volume high-value and high-volume low-value products simultaneously via a suggested cascading framework could make biorefinery economically viable (Joglekar et al. 2019). Here we have provided new insights and an integrated strategy incorporating diverse sectors, which will undoubtedly increase the biorefinery's economic feasibility.

Environmental implications

Based on WH's potential for phytoremediation (Li et al. 2015; Qin et al. 2016; Ting et al. 2018; Singh et al. 2022), it is recommended to utilize or cultivate it as a phytofilter and use the harvested biomass as a biorefinery feedstock. Even though WH is widely distributed in nature (Kriticos and Brunel 2016; Thamaga and Dube 2018), this strategy can resolve the bottleneck of the steady supply of biomass in an economically sound approach. A comprehensive model for treating eutrophicated water and continual harvest of WH biomass for dry and rainy seasons has been proposed (Mahujchariyawong and Ikeda 2001). It is crucial to remember that a compositional variation is very likely based on the WH's growing environment. The targeted final products and their uses should be the basis for deciding on the overall integration to harness the economic benefits.

Rapid industrialization in recent years has resulted in global warming due to the significant release of greenhouse gases (GHGs). One of the practical options for CO_2 capture is the fixation of CO_2 in biomass. Nowadays, microalgae are employed for this purpose by applying the carbon capture and utilization (CCU) approach (Cuéllar-Franca and Azapagic 2015). Being a photosynthetic plant, it can be argued that WH would capture carbon and be considered for the CCU model, which could lower the overall carbon emissions. In the end, the residual solid waste could be used as a biosorbent to treat wastewater, whether it was produced through direct extraction, conversion, or a mix of valorization techniques. This route provides a logical and efficient way to utilize the by-products generated during the processing steps. Many research studies support the concept of using spent biomass/biochar as a low-cost adsorbent to remove a wide variety of contaminants from wastewater (Mahamadi and Nharingo 2010; Mishra and Maiti 2017; Hung et al. 2022). The proposed holistic approach addresses all three dimensions, including social, economic, and environmental, to achieve sustainability goals (Moldavska and Welo 2019).

Circular bioeconomy

Developing nations harvest tonnes of WH annually (Sethupathy et al. 2022). The damaging ecological and socio-economic effects of WH biowaste could be minimized by implementing eco-friendly circular approaches, which effectively manage biomass waste through its beneficial processing (Tanveer et al. 2022). The idea of the biorefinery is concerned with the efficient and sustainable conversion of biomass into many industrial goods, such as chemicals, materials, and energy. It may be a promising solution for turning waste into value that eventually fits into a circular economy by promoting the concept of reducing, reusing,

and recycling to ensure environmental viability. With an emphasis on reducing waste at every production stage, the integrated strategic framework suggested here would enable the well-organized exploitation of waste biomass and the generated by-products for creating value-added commodities. It offers innovative solutions to the current WH conundrum by aiming to engage with renewable resources while decreasing the reliance on fossil fuels, monetizing the waste biomass, and reducing GHG emissions (Kumar Sarangi et al. 2022; Moustakas and Loizidou 2022).

Table 8 discusses the proposed WH biorefinery's SWOT (strength, weakness, opportunity, and threat) analysis, outlining its benefits and drawbacks in the current market scenario (Usmani et al. 2021). WH biomass is a good source of phytometabolites. Harnessing WH favors green engineering approaches of reduction, reuse, and recycling while promoting bioeconomy. Significant social and environmental benefits accrue due to the holistic utilization of WH biomass in biorefinery. Concerns against these approaches include seasonal variations in biomass growth and compositional variations, geographical limitations, high initial costs, absence of infrastructure, and mature technologies. Another threat to a potential WH biorefinery is the year-round availability of biomass and the logistics for collection from distributed sites. However, opportunities exist to bolster such efforts through policies that can assist in achieving UN Sustainable Development Goals.

Future perspectives

Utilizing lignocellulosic biomass as a sustainable feedstock to manufacture valuable products has gained attention over time. Several policies, environmental regulations, and protocols have been devised in many nations to reduce the ecological danger associated with waste biomass (Khoshnevisan et al. 2021). Although the public and private sectors have implemented many waste biomass valorization schemes, appropriate commercial success is yet to be gained. This might result from the absence of integrated management regulations, which must consider the advantages and limitations of the proposed biorefinery scheme. To develop a spatially explicit biorefinery model, it should incorporate features of economic viability along with ecological, social, and environmental impacts.

Future study is still needed based on the local requirements accounting for the detailed economic, social, and environmental assessment through various simulation models (Aristizábal-Marulanda et al. 2021; Solarte-Toro et al. 2022). A regional financial analysis, considering the entire costs determined by raw material, utilities, labor, general maintenance, and administrative expenses, must be carried out before implementation (Giwa et al. 2018; Martínez-Ruano et al. 2018; Serna-Loaiza et al. 2018). There is still room for a life cycle assessment (LCA) for the WH biorefinery plan. LCA is a tool that helps in the process of identifying the steps that have a substantial environmental impact. These environmental hotspots could be addressed by process intensification (Joglekar et al. 2019). Process intensification methods may be used to extract phytometabolites or for biomass conversion procedures. Ultrasound, microwaves, supercritical or subcritical fluids, steam explosion, and other innovative technologies might be applied at the industrial scale. These novel technologies typically appear energy efficient achieving maximum yields in a shorter time (Nagula and Pandit 2016; Perino and Chemat 2019). Unfortunately, most of the current biomass conversion methods produce CO_2 and methane, the greenhouse gases (GHG) that contribute to

Table 8 SWOT analysis for potential WH biorefinery

Strengths	Weaknesses
• Sustainable use of natural resources for valued product generation	• Efficacy changes with seasonal and compositional variations
• Good asset for plant-based phytometabolites	• Geographic limitations
• Favors reduce, reuse, and recycle concepts	• Insufficient infrastructure to support smooth execution
• Waste management and promoting bioeconomy	• The high initial cost of technologies and processing setup
• Social and environmental benefits	• Supply-demand synergy is currently lacking
• Feasible processing due to the less complex constitution of WH	• Absence of fully mature technologies with minimal existence at lab/pilot scale
• The low initial cost for locally available WH	• Mass cultivation could be difficult
Opportunities	Threats
• New policies encouraging investment in the bioeconomy sector	• Year-round biomass availability threat the continuous supply of feedstock
• CO_2 fixation and reduce net GHG emissions	• Logistical issues regarding the collection
• Integrating various sectors to reduce the overall cost	• Social acceptance
• UN sustainability goals can be achieved	• The initial investment may be challenging
• Phytoremediation of eutrophic water	The high cost of bio-based products makes them less competitive in the market

global warming (Hariz and Takriff 2017). Commercialization of the green potential of WH would directly cut down on GHG emissions through CO_2 fixation, which is another crucial research topic. A sustainability index (SI) based on real-time data will help to support a strong, flourishing biomass processing sector (Joglekar et al. 2020). LCA, SI, and other models are not included in this study due to the lack of real-time data variables. The proposed integrated biorefinery model must yet undergo a region-specific techno-economic assessment for industrial scale-up to be implemented successfully.

Conclusion

WH eradication is a difficult task today, especially in poorer nations, due to the high expenses. The unique properties of this highly invasive plant make it a better alternative for developing sustainable bio-based products. WH acts as a good phytofilter, so its controlled growth will benefit the phytoremediation of water bodies, and the resulting biomass could be utilized for producing various primary and secondary bio-products. WH could become a viable resource for generating green plant-based products to fulfill the increasing demand for safe and eco-friendly products. Comprehensively, we have explored the potential for WH waste biomass valorization through direct extraction, its conversion into valued bioproducts, and its environmental implications to promote sustainability and a circular economy. WH has a high nutrient value. WH biomass is advantageous over other lignocellulosic waste due to its less complex nature, resulting in milder pre-treatment requirements. WH compositional analysis reveals the presence of fibrous polysaccharides and the absence of sticky substances, which ensures its rapid drying despite high initial moisture content. Phytoconstituents of WH could be investigated further in a specific- and application-based manner. Most of the research done to date involves using conventional solvents and methods. Process intensification is needed to make the processing more economical and efficient. The overall multi-objectives framework should be followed by emphasizing the concept of reduction, reuse, and recycling to attain the goals of sustainability and circular economy. A careful techno-economic analysis based on the local parameters is desirable to harness the maximum benefits. We have explored the cutting-edge future WH biorefinery opportunities extending the conventional methods as a commercially sustainable response to several issues confronting us today to manage WH growth and promote a circular economy efficiently.

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