Cellulosic pine needles-based biorefinery for a circular bioeconomy

Rana, Ashvinder K.; Guleria, Sanjay; Gupta, Vijai Kumar; Thakur, Vijay Kumar

Published in:
Bioresource Technology

DOI:
10.1016/j.biortech.2022.128255

First published: 01/01/2023

Document Version
Publisher's PDF, also known as Version of record

Citation for pulished version (APA):
Rana, A. K., Guleria, S., Gupta, V. K., & Thakur, V. K. (2023). Cellulosic pine needles-based biorefinery for a circular bioeconomy. *Bioresource Technology*, *367*, [128255]. https://doi.org/10.1016/j.biortech.2022.128255

Bioresource Technology 367 (2023) 128255

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Cellulosic pine needles-based biorefinery for a circular bioeconomy

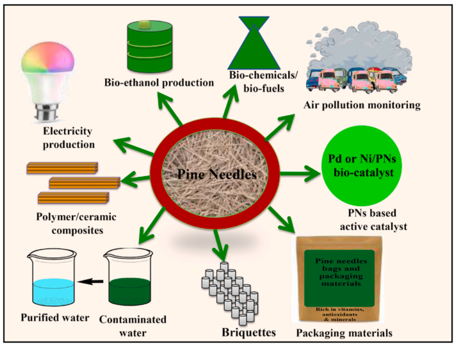
Ashvinder K. Rana [a], Sanjay Guleria [b], Vijai Kumar Gupta [c], Vijay Kumar Thakur [c,d,e,*]

[a] *Department of Chemistry, Sri Sai University, Palampur 176061 India*
[b] *Natural Product-cum-Nano Lab, Division of Biochemistry, Faculty of Basic Sciences, Sher-e- Kashmir University of Agricultural Sciences and Technology of Jammu, J&Kashmir, India*
[c] *Biorefining and Advanced Materials Research Center, Scotland's Rural College (SRUC), Kings Buildings, West Mains Road, Edinburgh, UK*
[d] *School of Engineering, University of Petroleum & Energy Studies (UPES), Dehradun 248007, Uttarakhand, India*
[e] *Centre for Research & Development, Chandigarh University, Mohali 140413, Punjab, India*

HIGHLIGHTS

- Chemical composition, physicochemical properties and extraction of nano cellulose.
- Need of pine needles valorisation and their utilisation in multidimensional fields.
- Pine needles role as antibacterial, bio-catalyst, reinforcing and adsorbing agents.
- Potential of Pine needles in comparison to other biomasses in multiple applications.
- Current challenges in utilisation and future prospectus of Pine needles wastes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Pine needles
Gasification
Bio-adsorbents
Polymer composites
Packaging materials
Electronic devices

ABSTRACT

Pine needles (PNs) are one of the largest bio-polymer produced worldwide. Its waste, i.e., fallen PNs, is mostly responsible for forest fires and is a major challenge. In present article, we have reviewed differenteffortsmadeto tackle this situation. PNs have been used in various fields such asin composite, water purification industries, electronic devices, etc. Gasification is one of the appealing processes for turning PNs into bio-energy; pyrolysis technique has been employed to create various carbon-based water purification materials; saccharification combined with fermentation produced good yields of bio-ethanol; Pd or Ni/PNs biocatalyst showed good catalytic properties in variousreactionsand pyrolysis with or without catalyst is an alluring technique to prepare bio-fuel. Nano cellulose extracted from PNs showed appealing thermal and mechanical strength. The air quality of nearbyenvironment was examinedby studying the magnetic properties of PNs. Packing materials made of PNs showed exceptional ethylene scavenging abilities.

---

[*] Corresponding author.
E-mail address: Vijay.Thakur@sruc.ac.uk (V.K. Thakur).

https://doi.org/10.1016/j.biortech.2022.128255
Received 27 September 2022; Received in revised form 27 October 2022; Accepted 28 October 2022

1. Introduction

The circular bio-economy has provided a potential solution to world challenges like environmental and food security threats (Hoang et al., 2022b; Usmani et al., 2020; Ates et al., 2020). In this context, assimilating pine needles (PNs) through biotechnologies to produce valuable products and metabolites may significantly enhance the sustainable circular bio-economy. The transformation of biomass or PNs into biomaterials and bio-energywill not only maintain the energy-environment network but will also replace petroleum products with alternate energy feedstock, leading to amuch healthier environment (Atabani et al., 2021; Bhatia et al., 2021; Moscariello et al., 2022). Every year, forest fires, due to highly flammable waste PNs, all over the world, more specifically in the northwest Himalayas region, arecausing significantharm to flora and fauna and arealso thebiggest source of climate change, as it destroys the forest land and emits the greenhouse gaseous in the atmosphere. As per the report submitted by Robert Scribbler ("Fires ravage forests in Himalayas, threatening health and biodiversity," 2017), in 2018, approximately 21,000 wildfire incidents took place in the Himalayan region in India and caused the death of seven people and threatening abouta hundred villages. To tackle the situation Government of India mobilised Mi-17 helicopter fire suspension craft and 9000 fire-fighters in fire affected 21 districts of two Indian states ("Fires ravage forests in Himalayas, threatening health and biodiversity," 2017; Indian Express, 2016). Global warming is today a global issue, and all these activities/local disastershave caused an increase in atmosphere temperature by about 0.6 °C since 1977 and ultimately declinedthe glaciers ("Fires ravage forests in Himalayas, threatening health and biodiversity," 2017). In addition to it, PNs, whenfall to the ground during the summer season, develop a thick acidic carpet on the forest floor and causea reduction in the water absorbance behaviour of soil below the carpet, thus creates an unhealthy environment for other species to grow. Besides that, the highly flammable nature of needles also causes them to catch forest fire easily and thus may lead to soil erosion.

As per the report from Uttarakhand Energy development agency (UREDA), India, 0.343 million hectares of land in Uttarakhand state is covered by pine forests and produces around 0.258 million tonnes of dry biomass every year (Uttarakhand Renewable Energy Development Agency, 2018; Bisht and Thakur, 2020; Uttarakhand Renewable Energy Development Agency, 2018). The pine straw yields reported in bales per acre per year in different parts of the USA include 650 to 725 in U.S. Southeast (Dickens et al., 2003), 300 in Texas (Taylor and Foster, 2004), 500 in Florida (Duryea, 1989), 280 in the south and north Carolina (Blevins et al., 2005) and 260 coastal South Carolina (Gresham, 1982).

Therefore, productive efforts will be needed in the near future to address pine needle trash. PNs may be a suitable solution to check the world's energy crisis because they are biocompatible (Sengar et al., 2020). However, as per the report submitted by Sengar et al. (2020) there are 5 major barriers, i.e., technological, economic, legal and regulatory barriers, human resources and market-related barriers restricting theutility of energy generationon a large scale. So, there is an urgent need to frame some policies to tackle these barriers. No doubt, the PNs are also used by local people for bedding animals, as a source of fire, as reinforcement materials in bricks, etc. (Sundseth, 2009). However, its consumption is on a small scale; thus, extra efforts are required to tackle overproduced pine wastes. Uttarakhand, a small state inIndia, produces around 2 million tons of PNs waste yearly (12); has established an electricity power generation plant of 100–150 KW utilisingPNs wastes (Khan, 2012). In addition, Uttrakhand state of India is also producing cooking charcoal from waste biomass to fulfil the needs of thousands of people (Khuller, 2019). No specific data on PNs contribution tototal bio-energy is available in the literature; it may be due to under utilization. But Globally, in year 2019, about 655 Terawatt hour (TWh) of bio-power was created from waste biomass, which includes all solid wastes, industrial and municipal wastes, bio-gas and liquid bio-fuels and shares about 68 %, 17 %, 13 % and 2 % of total bio-energy production, respectively (World BioenergyAssociation, 2020) (Fig. 1a). Further among different continents, Asia, shares about 39 % of all bio-power production from solid wastes, lies at top of the list followed by Europe, America and Africa (Fig. 1b). Electricity only (designed to produce electricity only) and combined heat and power plants (CHP) (produces both heat and electricity) were reported to generate about 428 TWh and 280 TWh bio-power in same year, respectively. Electrical power industry nowadays is facing huge challenges such as distribution of electricity, data transmission, loss of electricity during distribution, power flow management, distribution circuit analysis, etc., which are imposing direct impacts on its operation as well as control of power stations. The technology related to computers and software engineering, telecommunications and microprocessors, offers wide opportunities to tackle these challenges. Further, information technology also helps in managing and sharing information between people within the power station (Ohri and Ohri, 2007). The importance of several catalysts, including zeolite, noble and non-noble metals, electrocatalytic materials, and metal–organic frameworks in biomass conversion into biofuels was thoroughly examined by Hoang et al. (2022a). They advocated that the conversion of biomasses into fuels, specifically 2, 5-dimethyl furan, utilizing these catalysts, may solve the current environmental and energy issues. The same group in another study demonstrated that 2-methyl furan isolated from waste biomass through catalytic valorization technique could become a promising alternative to fossil fuel because of similar properties (Hoang, 2021). From the existing literature, we can conclude that PNs wastes could be a game changer in bio-energy production and needs special attention from industrialists/scientists. Recently, researchers have tried to use PNs waste as reinforcement in composites/concrete in plastic/concrete industries, or to develop packaging materials, as adsorbents for pollutants' removal from waste water, for developing electronic devices, etc. Thus in the present review article, we have highlighted the PNs wastes as a sustainable bio-based circular economy that promotesa greener environment. Several case studies on the bio-processes utilizing PNs wastesbio refineryto produce bio-polymers, bio-adsorbents for water treatment, bio-catalysts, and radical scavenging packaging materials have been reviewed. Besides that, the bioconversion of PNs into energy/bio-fuels/bio-chemicals and their role in bio-pollution monitoring and antibacterial/antimicrobial agents,has also been thoroughly examined. Chemical, physical and mechanical properties of PNs wastes and cellulose nano fibers or cellulose nano crystals extracted from PNs have also been subject of matter in the present study, as these properties may impact their reinforcing or adsorbing nature.

2. Pine tree and pine needles

Pines are evergreen trees or conifers shrubs found in almost all parts of the world, most commonly in Asia, Europe, North America, Mediterranean Africa and different island countries (see supplementary materials). Pine belongs to the Pinus genus of plants, which includes >120 species worldwide (Myers, 2022). Strobus and Pinus (both are American timbers) are the two subgenera of the Pinaceae family that make up the majority of pine species. Some of the other common species of PNs are Chir pine (Pinus roxburghii: occurs in the Himalayan Region of Asia), Turkish pine (Pinus brutia: occurs in Italy, Greece, Bulgaria, Turkey and Ukraine),Aleppo Pine (Pinus halepensis:occurs in the Mediterranean region), Austrian pine (PineusNigra: occurs in South Europe, North Africa and Turkey), etc. (Myers, 2022). Pine forests cover a larger area (0.89 million hectares land) of land in the Himalayan regions and occur at an altitude of 450 to 2300 m (Bisht and Thakur, 2020; Uttarakhand Renewable Energy Development Agency, 2018). It primarily covers the Himachal Pradesh, Jammu Kashmir, Uttarakhand, Sikkim, Arunachal Pradesh and West Bengal states of India.

A wide range of pines can endure harsh climates (deserts, rainforests), and it is unusual that you will encounter native pines south of

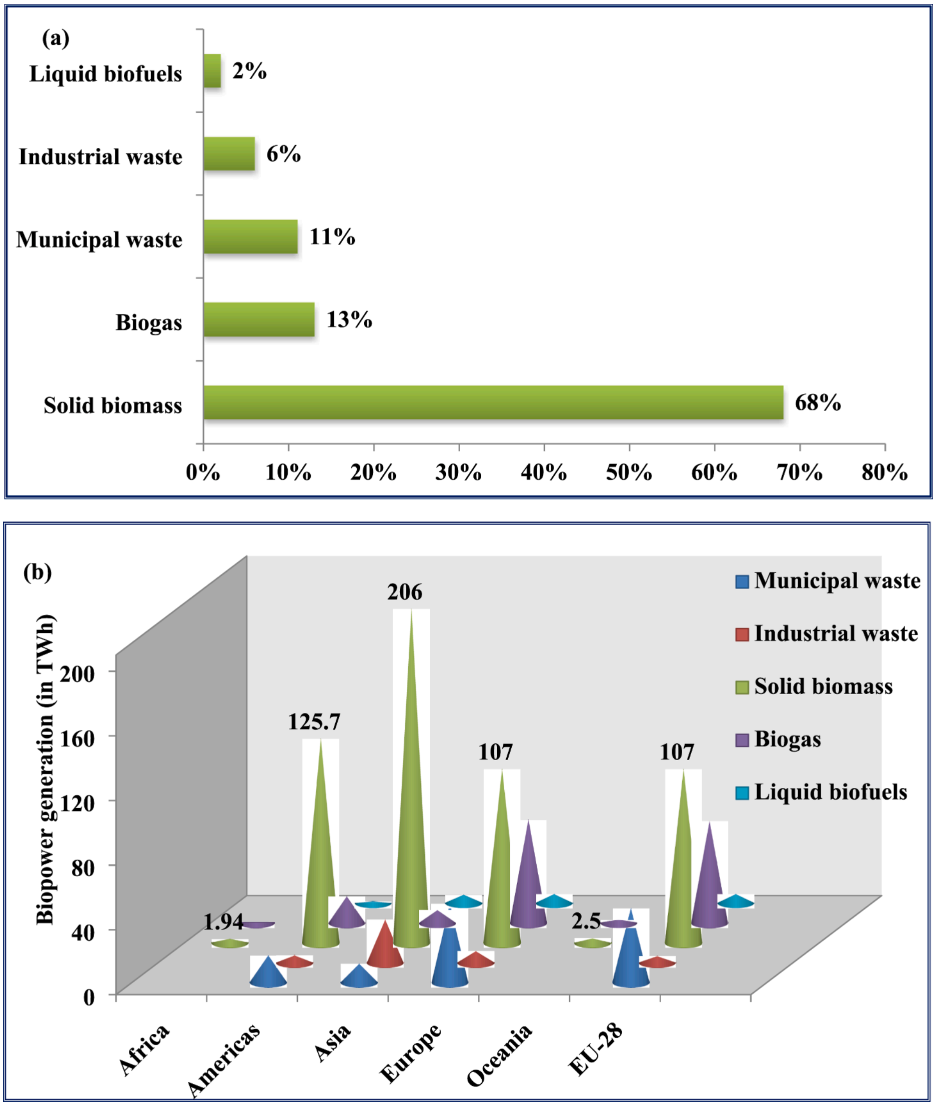


Fig. 1. Bio-power generation (a) globally and (b) in continents in year 2019. Figure copied from Ref. (World BioenergyAssociation, 2020).

the equator. They may grow in these conditions, but most prefer a hilly environment with good soils and regular rainfall. There are 40 common species of PNs, and the average height of these trees varies from species to species but generally lies between 20 and 120 ft. Although they lose their oldest needles in the fall, pine trees keep some of their greenery throughout the year. Some pine species need fire to keep their population growth stable. PNs have dark green-shaded leaves ranging from 3 to 5 in. Depending on their production region, the width and length of the thin and long needles may vary significantly from species to species. PNs smell strongly of pine and have a bitter taste of resin. Compared to the Picea subgenera, which includes fir and spruce trees, the needles of the Strobus or Pinus subgenera are mostly thinner, longer and more flexible (Encyclopaedia Britannica, 2022). PNs have numerous medicinal properties and have traditionally been used to treat approximately 80 % of human diseases. When no other source of Vitamin C was available, PNs tea was used to eradicate scurvy. In addition, it can also be utilised to treat respiratory and congestion problems ("Pine Needles Information, Recipes and Facts," 2022). PNs powder is a rich source of vitamin A, essential oils and alkaloids, and its ethanol extract has antimutagenic solid, antitumor, antiproliferative and antioxidant properties (Ghosh and Ghosh, 2011; Kwak et al., 2006). A vastnumber of PNs species exist throughout the world, which can return nutrients to the forest, serve as mulching materials, or act as a source of nutrients when added to the soil. However, in the present report, our primaryfocus will be to review the possible applications of different valorised PNs products (see supplementary materials) in multiple fields, including composites, bio-adsorbents in water purification, food packaging materials, etc.

3. Pine needle's chemical conversion into pure cellulose, cellulose nanocrystals and cellulose nano fibers and their relative physico-chemical properties

With the advancement in nanotechnology, nanocellulose has become a focus of research because of its nano scale dimensions, exceptionally reactive nature and alluring physic-chemical properties such as light-weight, high tensile strength, better aspect ratio, optical transmittance and minimal expansion on heating nature (Rana et al., 2022a, 2022b,2021; Trache et al., 2022). Due to these remarkable properties, nano celluloses are finding their use in multiple fields, such as developing highly efficient adsorbents, air filters, automobile parts, etc (Beluns et al., 2021; Platnieks et al., 2021; Zielińska et al., 2021). Numerous researchers have also tried to convert PNs and other lignocellulosic wastes into pure cellulose and then into nanocelluloses, such as cellulose nanofibers (CNFs) and nanocrystals (CNCs), in order to use them efficiently (Rana and Thakur, 2021) (Fig. 2).

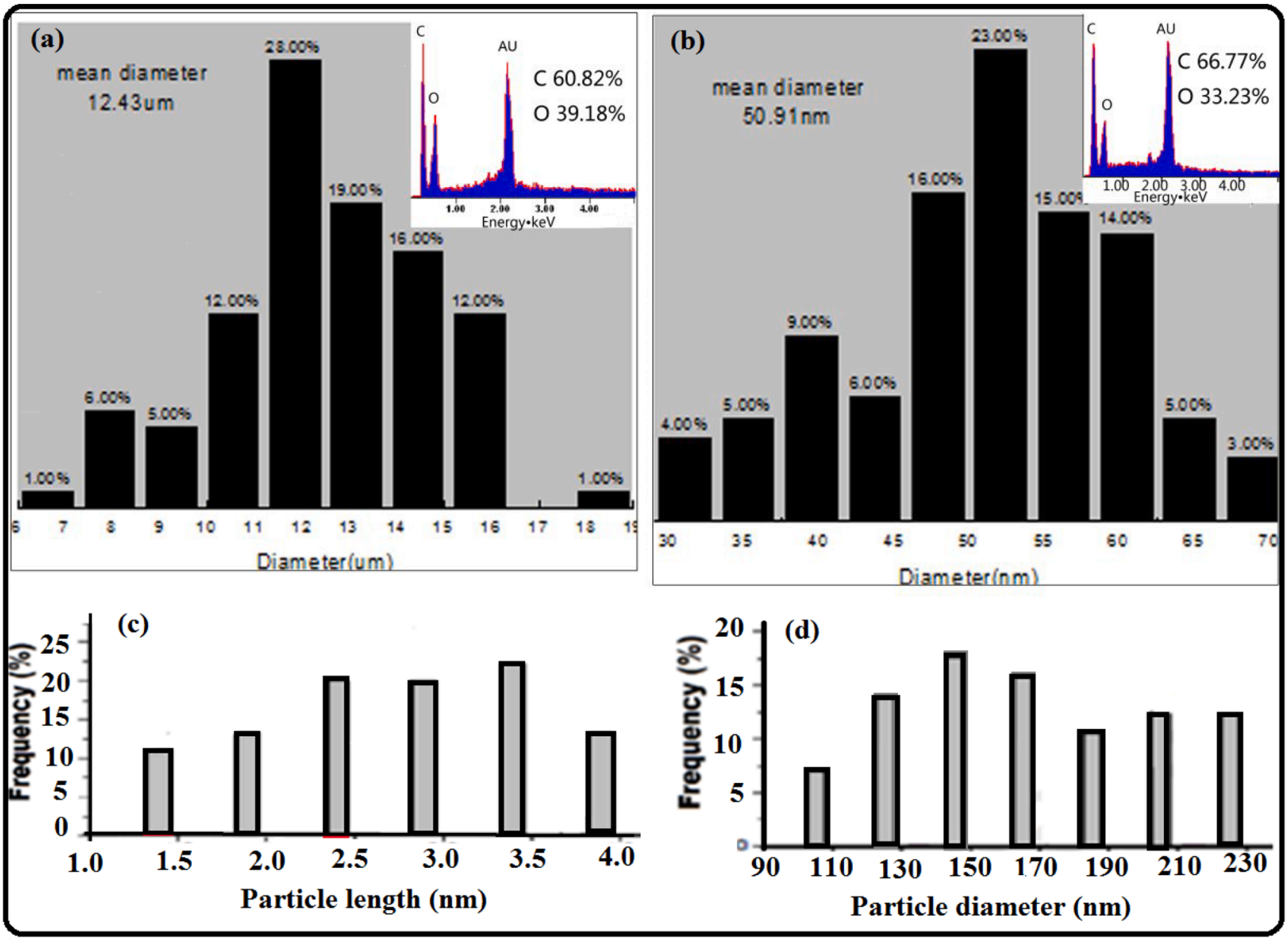


Fig. 2. (a) Diameter distributions of chemically purified cellulose (inset: elemental composition), (b) diameter distributions of CNFs (inset: elemental composition) (Xiao et al., 2015) [Images a & b Reprinted with permission from Ref. (Xiao et al., 2015) Copyright 2015, Elsevier), (c) particle diameter and (d) particle length distributions of CNCs (Moriana et al., 2016) [Images c & d Reprinted with permission from Ref. (Moriana et al., 2016) Copyright 2016, Elsevier)].

3.1. Pure cellulose

Alkaline treatment was followed by bleaching to isolate the pure cellulose (Fig. 2a) from PNs wastes. Alkaline treatment was carried out by repeatedly (three times) treating the milled samples with 4.5 wt% NaOH solution for 2 h at 80 °C under constant stirring. The resulting-samples were then bleached five times with sodium chlorite (1.7 % w/v) for 4 h at pH: 4.8 and 80 °C under mechanical stirring (Moriana et al., 2016). The yield of pure cellulose was noted to be 29.10 %.

3.2. Cellulose nanocrystals

CNCs were prepared from bleached cellulose through inorganic acid hydrolysis techniques (Moriana et al., 2016) (Fig. 2c&d). Many chemical techniques are available for the extraction of CNCs (21–24); however, inorganic acid treatment was chosen since it is a simple technique and can be completed quickly. Bleached fibers were treated with preheated 65 % sulphuric acid at 40 °C for 40 min with constant magnetic stirring for conversion purposes. Afterwards, ice cubes were added to the reaction mixture to stop the reaction and finally, the obtained suspension was washed with water by centrifugation at 25,000 g for 20 min at 10 °C. Further, the suspension was ultra-sonicated for 10 min at 7125 W/ml power density. CNC yields of CNCs were found to be 45 ± 2 % and 13 % when calculated from dried, bleached fibers and PNs, respectively.

3.3. Cellulose nanofibers

For the purpose of synthesis of CNFs (Fig. 2b) from PNs, Xiao et al. (2015) initially isolated nanocellulose microfibrils from PNsby employing a series of chemical treatment processes, i.e., dewaxing with benzene/ethanol mixture (2:1), delignification with acidified sodium chlorite solution (4–5 times until product turns white) for 1 h at 75 °C, hemicelluloses removal process which includes the treatment with 5 % KOH for 2hr at 90 °C and finally neutralization of residues with 1 % HCl solution. The obtained microfibrilswere then ultrasonicated (60 kHz) for 30 min to convert them into fibrils (100–200 nm), which were again sonicated for 1 h after dispersing 0.5 wt% of fibrils in 450 ml of distilled water to synthesize nanofibers (30–70 nm width). The fabricated nanofibers showed good crystallinity (66.19 %) as well as a good thermal properties (degradation peak of 352 °C) over raw PNs (crystallinity: 58.58 %; degradation peak: 342 °C), which demonstrated the promising application of synthesised nano cellulose in the field of thermoplastic composites. Tang et al. (2021) used a combined approach of cellulose and pectinase bioenzyme method for the synthesis of CNFs (having an average width of 31 nm) from PNs and reported 20 % cellulose content in PNs.

3.4. *Comparative view of different properties of raw pine needles, pure cellulose, cellulose nanocrystals and cellulose nano fibers extracted from pine needles*

The comparative view of % crystallinity, chemical composition and thermal stability of raw PNs, pure cellulose, CNCs and CNFs extracted fromPNs have been given in Table 1 (Moriana et al., 2016; Xiao et al., 2015). It has been observed from Table 1 that the % cellulosic contents increases after extraction of pure cellulose or CNCs from PNs wastes and was found to be maximum in the case of CNCs. However, its negative side is that we have to compromise on the thermal stability of fibers after theirconversion to CNCs or extraction of cellulose. The higher the cellulosic contents in PNs or theirextracted derivatives more will be percent crystallinity. Maximum % crystallinity was found for CNCs flowed by pure cellulose, CNFs and PNs fibers. In general, it will not be fair to compare the different properties of PNs and nano cellulose extracted from PNs, since these properties varyfrom species to species, time of collection, region of collection, techniques employed for their extraction by different researchers, etc.. However,we have still made a comparative view. Further, the proximate analysis result of PNs wastes clearly indicates the presence of 70.03 % volatile matter contents in it, which supports the highly flammable nature of PNs (Bisht et al., 2014). The mechanical strength of raw PNs has also been given in Table 1 (Dong et al., 2014; Font et al., 2009; Xiao et al., 2015), which clearly indicates thatraw PNsare mechanically tougher and can be utilised as reinforcing material or as filler to provide strength to different polymer composites.

4. Valorisation or recycling of pine needles in multidimensional fields

Pine needles, due to their biodegradable, adsorbing, antioxidant properties and remarkable mechanical and thermal strength, have been utilised in multiple fieldssuch as bio-composite manufacturing, food packaging, water purification, air pollution monitoring and furniture and garments industries (Fig. 3). For valorisation of PNs wastes, numerous strategies such as pyrolysis, anhydrous pyrolysis, hydrothermal treatment, saccharification cum fermentation and gasification have been applied to derive the various valorised products such as bio-energy, bio-fuels, electricity and bio-chemicals (Fig. 3) (Fuentes, 2017; Mandal et al., 2019). Further, the by-products leftover after PNs valorisation such as bio-charor activated bio-chars as it is or after the chemical treatments or blending with nano particles were utilised for purification of waste water or as bio-catalyst to carry out numerous organic reactions.

4.1. *Recycling as reinforcing agents in polymer composites*

Due to their synergistic effects, the use of PNs fibres as reinforcing agents in the synthetic or biodegradable matrix could be a promising choice for recycling PNs fibres (Thakur et al., 2013; Thakur and Singha, 2010). This would not only make the resulting polymer composites biodegradable but will also boost their mechanical strength (Thakur and Singha, 2010). However,the length of fibers and their amount in polymer composites play a very significant role in imparting mechanical strength to composite materials. Singha and Thakur (2010, 2009, 2008a, b) and Thakur and Singha (2010) used PNsof different lengths, i.e., particle, short and long fibers, for reinforcing the matrix and reported that particle fibers reinforced composites are mechanically and thermally tougher than short and long fibers reinforced ones (Table 2). Use of compatibilizer (Cogurcu, 2022; Sinha et al., 2018) or surface-treated PNs (Cogurcu, 2022; Long and Wang, 2021; Ma et al., 2014; Sinha et al., 2018; Wang et al., 2022; Wang and Long, 2021) has also been preferred to enhance the interfacial adhesion between matrix and PNsand thus increase the mechanical strength of composite materials (Jové-Sandoval et al., 2018; Long and Wang, 2021; Ma et al., 2014; Singha and Thakur, 2009, 2008b; Sinha et al., 2018; Thakur and Singha, 2010; Wang and Long, 2021) (Fig. 4). It has been noticed that surface functionalization or treatment of PNswith sodium hydroxide alone (Wang et al., 2022) or in combination with hydrogen peroxide (Sinha et al., 2018) significantly enhances the strength of polymer composites. Different types of matrices such as urea–formaldehyde (Singha and Thakur, 2009, 2008b; Thakur and Singha, 2010), phenol–formaldehyde (Singha and Thakur, 2010), resorcinol formaldehyde (Singha and Thakur, 2008a), polylactic acid (PLA) (Sinha et al., 2018), soil (Jové-Sandoval et al., 2018; Kandel et al., 2020) as well as cement (Cogurcu, 2022; Khitab, 2020, 2020; Long and Wang, 2021; Wang et al., 2022; Wang and Long, 2021) were tested and explored for the fabrication of PNsreinforced composites. However, considering the easy availability and reinforcing ability of PNs, researchers in the future should focus their attention on exploring some new surface treatment techniques, such as benzoylation, acetylation, binary mixture graft copolymerization, esterification, etherification, etc., to increase the compatibility between fiber and matrices. In addition, the potential of other thermoplastic (polypropylene, polystyrene, etc.)/thermosetting (epoxy, polyester, etc.)/biodegradable matrices (starch, polyurethane, etc.) or different compatibilizers or/and conversion of PNsinto nano forms and their further utilization as reinforcing agents could also be a subject matter in the future.

4.2. *Valorisation into bio-adsorbents for water purification*

Numerous methods have been developed for the sustainable valorization of PNs and other biomass wastes into effectivebio-adsorbents/absorbent (bio-char/activated carbons/hydrogels) that can effectively remove water contaminants. PNs, magnetically modified PNsand/or their native biochars, either as is, or after activation with a strong acid (Pandey et al., 2022), weak acid (Pandey et al., 2022), oxidization (Anastopoulos et al., 2020; Philippou et al., 2020) and loading with magnetic (Avcı et al., 2022; Khan et al., 2015; Nicolaou et al., 2019; Philippou et al., 2019; Yaqub et al., 2022), cuprous oxide nanoparticles (Khan et al., 2015) and Au/Fe-metal organic framework (Liu et al., 2021) have been successfully employed for the removal of various contaminants, including methylene blue dye (Pandey et al., 2022; Yaqub et al., 2022), reactive black-7 dye (Khan et al., 2015), malachite green dye (Hammud et al., 2015), Cr (VI) (Liu et al., 2020), Cu (II) (Nicolaou et al., 2019), Al(II) (Wu et al., 2019), Pb(II) and La (III) (Wu et al., 2019) heavy metals, thorium and uranium radioactive metals (Choudhary et al., 2020; Philippou et al., 2020, 2019), caffeine (Anastopoulos et al., 2020), trichloroethylene (Ahmad et al., 2013), sulfadiazine (Avcı et al., 2022) and tetracycline (Liu et al., 2021) from wastewater (see supplementary data). It can be noted from the supplementary data that magnetic particles loaded PNs have remarkable potential for removal of pollutants from contaminated water, and their ability to adsorb the pollutants further increases after conversion into biochars and/or subsequent activation or loading with nano particles. MoldedmassonPNs, activated carbons and magnetic particles loaded PNs followed the multilayer adsorption Freundlich model (Ahmad et al., 2013; Liu et al., 2020; Yaqub et al., 2022), while PNsderived biochars, their activated forms and magnetically modified biochars samples followed the monolayer Langmuir adsorption model. Further, moldedmasson PNs and oxidized biochar utilized for adsorption Cr(VI) and thorium metals followed pseudo first kinetics while all other samples showed pseudo second order adsorption kinetics (Liu et al., 2020; Philippou et al., 2020). Parameters such as temperature, pH, time, adsorbate and adsorbent concentration impact significantly the adsorption rate and their adsorption efficiency. Two types of techniques, namely hydrothermal and pyrolysingtechniques have been used for the conversion of PNsinto biochars. The hydrothermal technique, which forms solid biochar called “hydrochar”, is the most advanced and suitable technique for conversion since, through this methodology, wet samples can be converted into biochar at a comparatively lower temperature using water as a medium in a closed system. However, the pyrolysis technique needs

Table 1
Chemical composition and different properties of raw PNs and pure cellulose, CNCs and CNFs extracted from PNs.

Name of fibers	Chemical Composition					Ultimate analysis/proximate analysis results	Thermal stability	% Crystallinity	Tensile Strength (MPa)	References
	Cellulose (%)	Lignin (%)	Hemicelluloses/ pectin (%)	Ash contents (%)	Moisture (%)					
Raw PNs	23.5 ± 0.5	–	23.5 ± 0.7	–	–	Ultimate analysis: Ash: 1.31 %; carbon:52.60 %; hydrogen: 07 %; oxygen: 40.10 %.Proximate analysis: Moisture content: 9.76 %; ash: 4.37 %; volatile matter: 70.03 % and carbon: 15.83 %	Onset: 217.7 ± 0.6 °C; T_{max} (DTG maximum peak temperature): 358.0 ± 0.1 °C; % Residue: 30.5 ± 0.3 %	32 ± 4 %	–	(Bisht et al., 2014; Moriana et al., 2016)
Raw PNs (Pinus pinaster)	38.7	20.1	17.7	4.5	12		Decomposition takes place in between 223 °C (IDT) and 350 °C (FDT)	58.58 %	33.40 ± 1.20 (50 mm gauge length) 33.24 ± 1.54 (75 mm) 31.41 ± 1.08 (100 mm gauge length)	(Dong et al., 2014; Font et al., 2009; Xiao et al., 2015)
Pure cellulose	75.7 ± 0.1	–	18.5 ± 0.1	–	–		Onset: 227.2 ± 0.5 °C; T_{max}: 335.9 ± 0.3 °C; Residue: 26.4 ± 0.2 %	80 ± 2 %	–	(Moriana et al., 2016)
CNCs	90.0 ± 0.5	0.8 ± 0.3	8.1 ± 0.9	–	–		Onset:211.0 ± 0.5 °C; T_{max}: 277.0 ± 1.0 °C; Residue: 28.9 ± 0.1 %	93 ± 2 %	–	(Moriana et al., 2016)
CNFs	–	–	–	–	–		T_{max}: 352 °C	66.19 %	–	(Xiao et al., 2015)

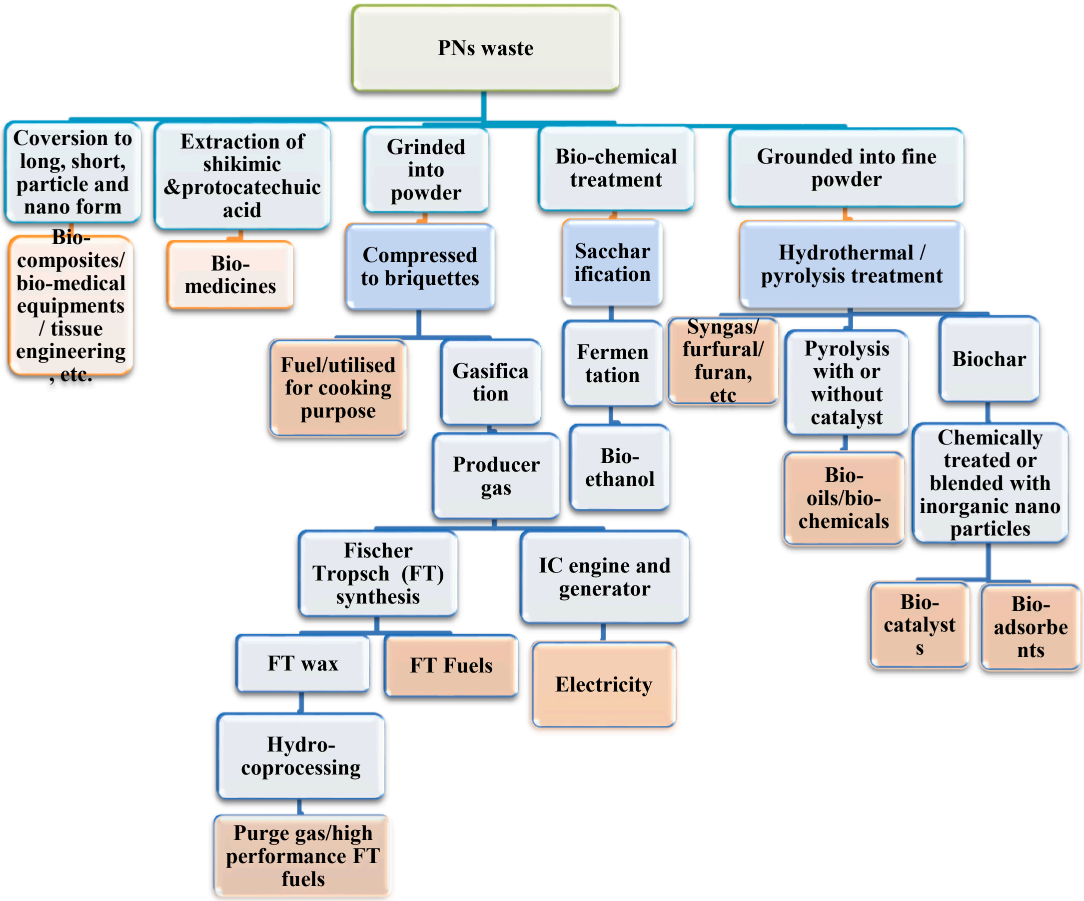


Fig. 3. Scheme for valorization and recycling of PNs wastes (Fuentes, 2017; Mandal et al., 2019).

temperature higher than 450 °C and the product produced is called pyrochar. Further, in the hydrothermal technique, carbohydrates are decomposed mainly, whereas, in the case ofpyrolysis, all the constituents, such as lignin, pectin, celluloses and hemicelluloses get decomposed (Correa et al., 2019).

4.3. *Antioxidant potential of pine needles extract and its role in food packaging*

PNs extract (PNE) is widely known for its antioxidant properties. Thus it has been successfully used in various proportions (5–20 % v/w) to enrich and increase the antioxidant activities of chitosan (CH) film, attributed to the prevalence of antioxidant curcuminoid phenolic compounds in PNE, and to develop active polymeric packaging materials for food applications (Kadam et al., 2021). The CH/PNE films showed a decrease in water vapour permeability from 2.18 ± 0.02 to 1.67 ± 0.11 g mm/m^2 h kPa and oxygen permeability from 0.259 ± 0.01 to 0.08 ± 0.01 cm^3 mm/m^2 day Pa, upon an increase in PNE amount from 5 to 20 %. However, increasing the extract from 5 to 20 wt% also resulted in a modest increase in film thickness from 0.032 ± 0.003 to 0.041 ± 0.009 mm. Further, to analyze the antioxidant properties, total phenolic compounds, 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2′-azino-bis (3-ethylbenzthiazoline-6-sulphonic acid (ABTS) scavenging activities of fabricated CH/PNE integrated film were analyzed and were noticed to be enhanced with an increase in the amount of PNE. A maximum of 40 and 44 % ion scavenging activity was noted against DPPH and ABTS at 20 wt% PNE, respectively. Kumar et al. (2021) developed PNs-based active paper and subsequently loaded it with different amounts of nano zeolite (5, 10, 20 and 30 v/w %) for ethylene scavenging and possible application in packaging. When the zeolite concentration was enhanced from 5 to 30 %, water permeability and ethylene scavenging characteristics were seen to be improved from 5.18 ± 0.34–3.88 ± 0.33 g/cm^2/day and 13 to 62 %, respectively, and thusopened up a new approach to using pine needle waste for food packaging. In another study, Kumar et al. (2022) incorporated microfibrilled cellulose and halloysite nanotube into PNs waste for developing ethylene scavenging nano composite paper. The synthesized PNs/microfibrilled cellulose/ halloysite nanotube 30 % nano-composite system displayed excellent ethylene scavenging tendency (>200 μL/L) on the 10th day of banana storage. In addition, the packaging system also slows down the senescence and ripening processes. A chemical-free mechanical pulping process was developed and used by Gupta et al. to make sheets from PNs for internal use and to prevent the articles from damaging during transportation. Cotton linter pulp along with sizing agents such as starch, alum and bentonite in different proportions, were mixed with PNs pulp to enhance the quality of packaging materials (Gupta et al., 2020). Maximum tensile strength of 107.4 N was noted when packaging material made up by mixing 80 % pine pulp with 20 % cotton, 3 % alum, 1 % rosin and 1 % bentonite. People in distant areas may find it advantageous to develop a small enterprise for packaging materials from waste pine to completely utilise the dried PNs andcreate job opportunities in the community.

4.4. *Antibacterial/medicinal importance*

The food industry has recently come under a lot of stress owing to the microbial contamination of foods. Such contamination might cause foods to degrade, which in turn may exacerbate human diseases and financial losses (Dorotíková et al., 2022; Su et al., 2022). The microbial contamination of food and drinking water may be responsible for a

Table 2
Mechanical strength and thermal stability of different, i.e., PNs reinforced soil, cement and plastic polymer composites.

Type/Length of PNs reinforcement and its amount	Matrix Type	Binder or fiber surface modification technique employed	Composites with optimum amount	Optimized mechanical strength	Thermal stability of optimized samples	Ref.
Length: 1–2 cm; Amount: 0–1 wt% of matrix	Dry soil	0–7.5 % of the dry weight of soil	0.5 wt% of PNs and 2.5 wt% of lime	Compressive Strength: Increased about 2.13 times or approx 113 %, when compared to pure soil	——	(Kandel et al., 2020)
Length: 13, 25 and 50 mm; Amount: 1–5 wt% of cement	Cement	–	1 wt% of 13 mm of PNs reinforce cement	Compressive Strength: 60 MPa (approx.); Flexural Strength: 12.75 MPa	–	(Khitab, 2020)
Type: Red PNs; Length: 30, 40, 50 mm; Amount: 0.25–1 % by volume of mixture	Cement (kg/m^3): 890; Water (kg/m^3): 160; Sand (kg/m^3): 1050Silica Fume (kg/m3): 230	Fibers Alkali treated with 5 % NaOH solutions prior to reinforcement and polycarboxylic ether (1.60–2.50 %) was utilized as plasticizer during composite fabrication	0.50 % of 30 mm reinforce cement mixture	Compressive Strength: 132 MPa (approx.) Flexural Strength: 22.46 MPa	–	(Cogurcu, 2022)
Length: 30 mm; Amount: 0.5–2.0 % by volume of block	1.0: 0.49: 2.636: 1.615 (cement: water: stone: sand)	1. Soaked in tab water 2. Soaked in boiling water 3. Treated with alkali water	0.1 % by volume fortified cement mixture composites	Composites fabricated with boiling water treated fibers showed maximum strength and resulted were computed through digital image correlation technique	–	(Wang et al., 2022)
Type: Masson pine needle fibre (MPNF); Length: 30 mm; Amount: 0.5–2.0 % by volume	0.49:1:1.615:2.636 (water:cement: sand:stone)	1. Masson Raw PNs 2. Dilute alkali treated 3. Treatment with boiling water4. Water soakedfibers (Fig. 4)	1 % fibers contents reinforce cement mixture composites	Mechanical strength order: Alkali treated fibers based composite (Compressive strength 41.92 ± 0.09 MPa; Tensile strength: 2.85 ± 0.08 MPa) > Boiling water treated (37.47 ± 0.09 MPa; 2.71 ± 0.06) > soaking fibers (35.16 ± 0.12 MPa; 2.46 ± 0.09 MPa)		(Long and Wang, 2021)
Type: Masson pine needle fibre; Length: 30 mm; Amount: 0.5–2.0 % by concrete volume	Portland Cement	1. 2 % alkali treatment 2. Boiling water treatment 3. Tab water treatment	0.5 % loaded cement mixture composites	Mechanical strength order: Alkali treated fibers reinforced (peak stress: 27.84 ± 0.04 MPa; elastic modulus: 22618 ± 109 MPa) > boiling water treated (25.99 ± 0.07 MPa; 23046 ± 101 MPa) > tab water treated (23.36 ± 0.07 MPa; 21719 ± 189 MPa)		(Wang and Long, 2021)
Types: Pinus halepensis (99 mm), Pinus pinea (118 mm) and Pinus pinaster (127 mm); Amount: 25 % loading by volume with soil	Soil (Adobe bricks) composing of 9.28 % silt, 65.48 % sand and 26.24 % clay	–	–	Mechanical strength order:Pinus halepensis fortified soil bricks (Flexural strength: 0.22 MPa; Compressive strength 3.1 MPa > Pinus pinea (0.16 MPa; 3.3 MPa) > Pinus pinaster (0.10 MPa; 2.5 MPa)	–	(Jové-Sandoval et al., 2018)
Length: 200 μm; Amount: 10–40 wt %	Resorcinol-formaldehyde resin	–	30 wt% fibers stacked RF composites	Ultimate Tensile Strength: 16.50 N/mm^2; Ultimate Compressive strength: 2370 N/mm^2; Ultimate	IDT: 252 °C; FDT: 948 °C and Final Residue: 42.0 %	(Singha and Thakur, 2008a)

(continued on next page)

Table 2 (*continued*)

Type/Length of PNs reinforcement and its amount	Matrix Type	Binder or fiber surface modification technique employed	Composites with optimum amount	Optimized mechanical strength	Thermal stability of optimized samples	Ref.
				Flexural strength: 307.84 N/mm^2		
Length: 74 μm; Amount: varied from 4.59 to 22.39 wt% with respect to matrix	Different proportion of PLA/ ethylene vinyl acetate (EVA) (77.98–63.43:13.76–11.19 wt%)	Compatibilizer Used: PLA-g-maleic anhydride (amount was varied from 3.67 to 2.99 wt%); Treatment: Fibers treated with 15 % alkaline solution (4 h at 75 °C) followed by 2 % hydrogen peroxide (at 45 °C for 8 h)	Optimized strength was noted, when 74.56 wt% of PLA was loaded with 13.16 % EVA, 8.77 % treated PNs, and 3.51 % of Ma-g-PLA.	Tensile strength: 37.14 MPa; Flexural strength: 79.83 MPa and Impact strength: 36.88 KJ/m^2	Major weight loss takes place in between 200 and 394 °C, specimen with optimum strength showed only 8 % wt. loss in defined range	(Sinha et al., 2018)
Raw PNs of different length i.e. 200 μm, 3 mm length and 6 mm length were used as reinforcement; Amount: varied from 10 to 40 wt%	Urea formaldehyde matrix	—	30 wt% fibers stacked urea formaldehyde composites	Tensile strength: 244.5, 200.5 N and 191.5 N; compressive strength: 1895, 1775 and 1685 N; and flexural strength: 107, 80 and 60 N; when loaded with 30 % of particle, 3 mm and 6 mm of pine needle, respectively.	200 micronfiber reinforced matrix: IDT- 235 & FDT-805 °C; 3 mm fiber loaded matrix: IDT-226; FDT-805 °C	(Singha and Thakur, 2009, 2008b; Thakur and Singha, 2010)
Length: 10 mm; Amount: 0–9 wt% of matrix	Phenolic resin (Different ingredients such as compound mineral fiber, barium sulphate, petroleum coke, artificial graphite, alumina, antimony sulfide, carbon black, friction powder, vermiculite and porous iron powder were usedin different proportions)	Initially dipped into a mixture of benzene and formaldehyde (1: 1) for 24 h then steeped in 2 % NaOH for 2hr, washed with water and finally rinsed with 1 wt% sulphuric acid solution	5 wt% of fibers stacked composites	Impact strength: 0.496 MPa; hardness: 106.8 ± 3.2	–	(Ma et al., 2014)
Length: 200 μm; Amount: 10–40 wt %	Phenol-formaldehyde matrix	–	30 wt% fibers stacked PF composites	Ultimate Tensile Strength: 32.38 N/ mm^2; Ultimate Compressive strength: 101.74 N/mm^2; Ultimate Flexural strength: 386.10 N/ mm^2	IDT: 332 °C; FDT: 983 °C and Final Residue: 43.74 %	(Singha and Thakur, 2010)

significant percentage of diarrhea-related deaths worldwide. Chemical preservatives may undoubtedly efficiently inhibit the growth of microorganisms in food, but concerns about their safety and potential negative effects on health are mounting. Thus,researchers made efforts to utilise PNsextracts in the fields of pharmacology, microbiology, food preservation and medicine because of their alluring insecticidal, antibacterial, and antifungal activities (Feng et al., 2010; Ka et al., 2005; Kwak et al., 2006). Zeng et al. (2012) evaluated the antibacterial activities of water-soluble PNs-based plant extract on five food-borne bacteria, namely Staphylococcus aureus, Bacillus cereus, Proteus vulgaris, Escherichia coli and Bacillus subtilis. In vitro antibacterial assay displayed that PNs-based extract possesses considerable antibacterial activity against five bacteria, with the minimum bactericidal and minimum inhibitory concentration values in the ranges of 1.56–25 mg/ml and 0.78–12.5 mg/ml, respectively. Additionally, pine needle extract showed an impressive capability to reduce the overall counts of live bacteria in freshly squeezed tomato juice. Shikimic acid, one of the main constituents of plant needle extracts was isolated and identified as the main antibacterial compound. It possesses a variety of therapeutic qualities, most of which are important pharmacologically (Xie et al., 2012). In addition, it serves as an intermediary in synthesising numerous medications, with the antiviral agent oseltamivir being the most pertinent (Estevez and Estevez, 2012). Bai et al. (2015) also confirmed the antibacterial activities of shikimic acid extracted from PNsagainst Staphylococcus aureus. They reported that shikimic acid works by interactingwith lipids and protein constituents of the *S. aureus* bacterium membrane, leading to cell membrane impairment and microbial damage or even death. Two types of acid, i.e., shikimic and protocatechuic acid, isolated from fermented PNs, showed remarkable antithrombotic properties in vivo and in vitro (Park et al., 2016). These acids demonstrated the ability to promote fibrinolysis and to suppress fibrin production, much like aspirin. All the above discussion showed that PNsof C. deodara might be a good option as natural antibacterial/antithrombotic agents in pharmaceutical and food industries.

4.5. *Electricity generation*

Gasification is another pathway for the valorisation of PNs and waste biomass into electricity (Fig. 3). Avani Bio-energy Company developed a first pilot 9 KWH pine needle power station in the NGO's campus at Pithoragarh, Uttarakhand in 2009 (Chakrabarty, 2016). The dried PNs are initially chopped/densified into small pieces/briquettes (Mandal et al., 2019) or pellets to increase their density (>400 kg/m^3) and then fed into a gasifier plant, where these needles/pellets are burnt under a controlled supply of oxygen at a higher temperature to generate charred biomass (Clarke and Preto, 2011; Kala and Subbarao, 2017). The

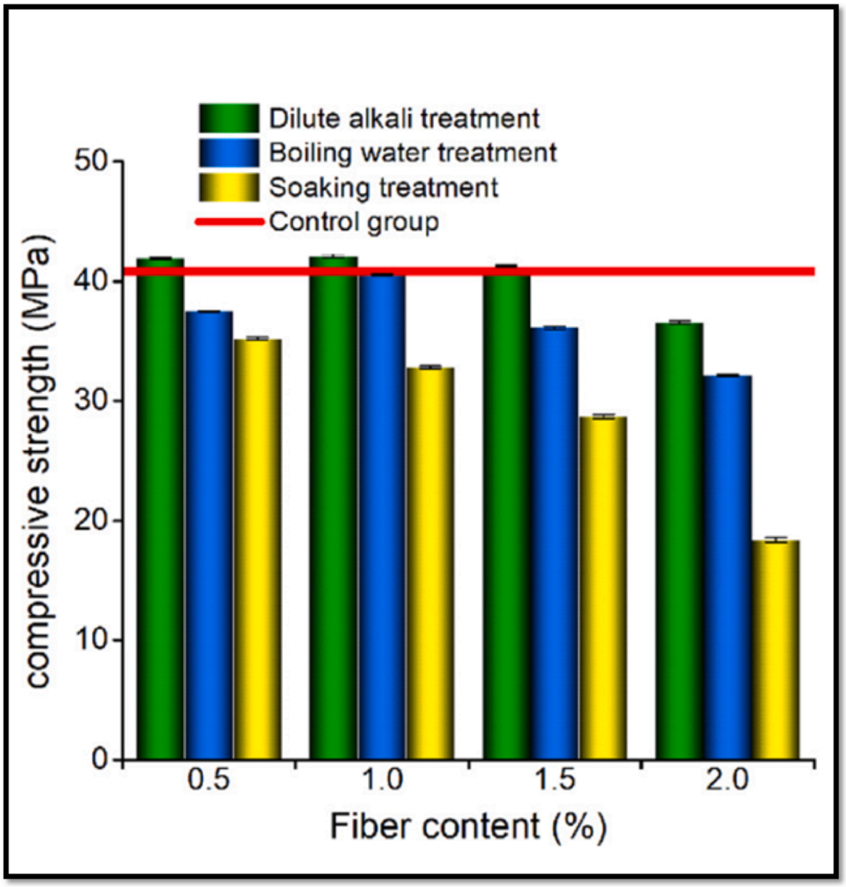


Fig. 4. Compressive strength of different PNs treated fibers fortified concrete matrix based composites (Long and Wang, 2021). (Reprinted with permission from Ref. (Long and Wang, 2021) Copyright 2021, Elsevier).

obtained charred biomass is further segregated into producer gas, which after purification, is cooled and utilised to operate a generator to produce electricity. The residual charcoal left after the separation of the producer gas is used for other household needs. About 1.5 kg of PNsproduces around one kWH of electricity and 150 gm of charcoal. On the success of the first plant, Avani energy company in 2014 set up another plant of 120 kW and the electricity produced through this PNsgasification plant was sold to the Uttarakhand-State Power Corporation Limited (UPCL) for 20 years under a Power Purchase Agreement between UPCL and Avani (Vikaspedia, 2022). Further, the state government has targeted increasingelectricity productivity by about 150 megawatts through PNsby 2030 (Hindustantimes, 2020).

4.6. *Pine needles as bio-indicators*

PNs are good bio-monitors of air pollutants because of their waxy surface, which can accumulate particulate matter and lipid-loving gaseous pollutants (Holoubek et al., 2000). Metals may enter into plants through root uptake from soil and/or precipitation, includinga dry and wet deposition. Thus, by analysing plant material, we can monitor air pollution, which largely depends upon the place and time of sample collection. Metals act as structural components of proteins and carbohydrates in plants and thus play an important role in their growth. For example, enzyme activators like phosphorous control the activity of ATP (Wang et al., 2013), potassium controls the normal metabolism and stress response of plants (Wang et al., 2013) and magnesium, a part of chlorophyll, is responsible for photosynthesis in plants (KO et al., 2010; Wang et al., 2013). In addition to it, other metals like Ca is essential for the growth of plants' cell walls and membranes (Hepler, 2005), Fe for chlorophyll synthesis and photosynthesis regulation and Cu for root metabolism (Tsui, 1955). Zn is also essential and its deficiency causes smaller leaves and tunted growth (Hafeez et al., 2013). Similarly, Ni plays a very significant role in plant physiology, and its deficiency causes urea accumulation in plants, whereas its toxicity results in disturbances in the Calvin cycle and chlorophyll biosynthesis, N concentration in roots, overproduction of reactive oxygen species, and hindrance in the uptake of other heavy metals (Amjad et al., 2019). Further, some metals, like Pb and Cd, cause harmful impacts even in very low concentrations, whilst others show neither beneficial nor negative impacts. Despite the impact of soil composition and air or soil pollution (Serbula et al., 2013), the metal concentrations in PNsalso depend on tree age and climatic conditions (Varnagirytė-Kabašinskienė et al., 2014). Numerous researchers from Europe as well as from Asia have worked on finding the concentration of heavy metals in PNs, after collection from various species from different regions of the world (Dmuchowski et al., 2018; Lehndorff and Schwark, 2008; Pietrzykowski et al., 2014; Skonieczna and Małek, 2014; Sun et al., 2010; Tausz et al., 2005). Surprised to note that their results vary over a large range, which may be due to the influence of different climatic conditions and soil compositions/backgrounds. Thus, to eradicate the influence of climatic conditions and soil history, Juranović Cindrić et al. (2019) collected the PNssamples from different pine tree species, namely *Pinus densiflora* Siebold et Zucc., *Pinus nigra* Arnold, *Pinus sylvestris* L., and *Pinus thunbergiana*, grown in same area under identical climatic conditions for assessment of 21 types of metal concentrations using inductively coupled plasma atomic emission spectrometry (ICP-AES)/mass spectrometry (ICP-MS). Their results indicated different levels of metals among different species, which are further linked to differences in metal accumulation tendencies in species of pine trees. The discussion mentioned above about the metal accumulation behaviours of PNs suggests that these materials could be utilised for treating polluted soils.

4.7. Valorization into bio-fuels/bio-ethanol

Valorisation of PNs wastes for bio-ethanol generationusing eco-friendly enzymatic technology is quite impressive and is mostly preferred over chemical methods. To turn PNs into bio-ethanol, researchers often use saccharification followed by a fermentation procedure. Suri et al. (2022) created thexylanase-producing stable mutant BU-7 of Bacillus sp. XPB-11 utilizing low-cost chemical mutagen 5-Bromo-Uracil and subsequently utilized the synthesized mutant for saccharification of the microwave + 0.5 % sodium hydroxide pre-treated pine needle waste, releasing about 26.8 ± 2.17 mg/ml of xylose (C-5) sugar. Various reaction parameters such as time, temperature, pH/enzyme and substrate concentration were optimised to achieve the maximum activity of xylanase. Further, fermentation of the C-5 sugar using Kluyveromycesmarxianus MTCC 1498 resulted in the generation of 5.34 g/l of bio-ethanol with a yield of 3.89 %. Chemical-based integrated technology has been developed by Kumar et al. (Kumar et al., 2018) for extracting various bio-products such as organic acids, essential oils, bio-matrix, residual carbon and sugars from PNs, giving a yield of 0.2 ± 0.5 ml/g, 0.03 ± 0.1 ml/g, 64.125 ± 0.2 mg/g, and 1 ± 0.3 g and 302.20 ± 04 mg/g, respectively. Their detailed process includes extracting essential oil and organic acid in the first step through steam distillation, followed by separating resin in the next step by employing a hexane extraction technique. Then, residual cellulose is hydrolysed with sulphuric acid to give sugars and residual carbon. The collected sugar is then fermented with S. cerevisiae to bio-ethanol,yielding 18.2 g/l. Slathia et al. (2020) used three different enzymes, namely *pectinase, xylanase* and *cellulase,* separately or in combination, i.e., *cellulase* + *xylanase*, *cellulase* + *pectinase* and combination of all three enzymes, for saccharification of thermo-chemical pre-treated PNs. The pre-treatment process consists of treatingPNswith dilute hydrochloric acid (varied from 0.5 to 2 wt% at a PNsloading from 5 to 15 wt%) followed by an autoclave treatment (at 125 °C for 1 h at 15 psi).

Of the different enzymes or their combination used for saccharification, *cellulase* and *pectinase* combination gives a higher yield (0.4–0.43 mg/g) of reducible sugars after 48 and 72 h. However, after 24 h, a maximum yield of 0.4 mg/g of reducible sugars was obtained with *cellulase* and *xylanase* combination. Further, *Saccharomyces cerevisiae* (MTCC-36), either alone or in combination with the *Pichia stipitis* (NCIM-3498) yeast cultures, have been used for fermentation purposes, and maximum yield (0.2 g/g) was observable with the combined approach in comparison to *Saccharomyces cerevisiae* alone (0.144 g/g). To effectively remove lignin from pine needle wastes, Dwivedi et al. (Dwivedi et al., 2022) initially pre-treated PNswastes with 1 % sodium hydroxide + microwave (removing about 72.58 ± 0.46 % of lignin) and then carried out the saccharification of the resultant lignin-free cellulosic material with *cellulase* and *xylanase* enzymes from *Bacillus subtilis* CPS-66 and *Bacillus pumilus* XRL5, respectively, which produces around 25.64 ± 2.36 mg/ml of fermentable sugars. Further, co-fermentation of sugars with *Kluyveromycesmarxianus* MTCC 1498 and *Schizosaccharomyces* sp. EF-3 produced approx. 17.65 g/l bio-ethanol with 87 % purity. It is evident from the foregoing considerations that pine needle waste might be a significant biomaterial for bio-ethanol synthesis, which would help save Chir-Pine forests from destructive forest fires as well as the ecology and biodiversity.

4.8. Valorization into bio-oils/bio-chemicals

Recently, various types of waste biomasses have been valorised into usefulbio-fuels/bio-oil (Dhyani and Bhaskar, 2018). Among different biomass wastes,PNs are harvested widely all over the world and are available in huge amounts. Two main techniques, i.e. pyrolysis and catalytic technology, have been utilised to valorise PNs or other biomassesinto bio-oils/bio-chemicals (Hoang et al., 2021). Varma and Mondal (2018) carried out pyrolysis of PNswastes in a semi-batch reactor and examined the impact of heating rate (10 and 50 °C/min), temperature (350–650 °C), nitrogen flow rate (50–200 cm^3/min) and biomass particle size (0.25–1.7 mm) on bio-oil yield. A maximum of 43.76 % bio-oil yield was found at 550 °C pyrolysis temperature, 50 °C/minheating rate, 100 cm^3/min nitrogen flow rate, and $0.6 < d_p < 1$ mm biomass particle size. The influence of various parameters such as heating rate, temperature and inert gas flow rate on the pyrolysis potential of PNs,along with their modelling and optimization, was studied by a combined approach of artificial neural network (ANN) and response surface methodology (RSM) technique (Gupta et al., 2022). This combined strategy was discovered to be more effective in modelling the pine needle pyrolysis process in comparison to the individual ones. The product yield was found to be significantly impacted by temperature, and the maximum bi-oil production was noted at a temperature of 552.06 °C, an inert flow rate of 164.40 ml/min and a heating rate of 50 °C/min, giving a maximum of 51.11 and 51.70 % bio-oil production from RSM and ANN modelling, respectively. Pyrolysis is an effective technique for converting the PNswastes into useful bio-oils/bio-fuels. However, their low pH, high oxygen contents and low heating value, compared to other biomasses, limit their actual application as a biochemical or feedstock biofuel. Therefore efforts were made to tackle this situation by using different catalysts (Kim et al., 2020; Park et al., 2016, p. 202). Kim et al. (2020) carried out the thermal and catalytic pyrolysis of PNsover HBeta catalysts, having different SiO_2/Al_2O_3 rations (300 and 25) or without catalyst, have been carried out using pyrolyzer-gas chromatography/mass spectrometry. It has been noticed that upon pyrolysing (at 500, 600 and 700 °C) the PNswithout the catalyst, the production of phenolics and other oxygenates dominates over aromatic hydrocarbons; however, with HBeta 25 and HBeta300 catalysts, the generation of aromatic hydrocarbons, namely ethylbenzene, toluene, benzene and xylenes (BTEXs), mono aromatic hydrocarbons and other polycyclic aromatic hydrocarbons was enhanced, and maximum production of aromatic hydrocarbons was achieved when the heating rate was increased from 500 to 700 °C with the HBeta25 catalyst. The higher production of aromatic hydrocarbons with HBeta z25 compared to HBeta300, has been related to the more acidic nature of the former.

Gupta and Mondal (2021), during their pyrolysis experiment, found that the addition of catalysts ($Ni/\gamma\text{-}Al_2O_3$ or $\gamma\text{-}Al_2O_3$) improves the reaction rate, quality and distribution of products. However, between $Ni/\gamma\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$, the former one showed a remarkable tendency to enhance the production of phenols and hydrocarbons as well as to reduce the oxygen content in bio-oil (see supplementary materials), which has been attributed to the secondary pyrolysis reactions initiated by the combination of Ni and alumina. Further, the catalytic pyrolysis process requires less energy and generates better-quality bio-oil.

4.9. Other applications of different valorized products

Forest Research Institute, Dehradun, Uttarakhand State, India and Indian Institute of Technology, Roorkee, India are jointly working on a project to develop portable machines for making briquettes from PNs (Sharma, 2018). Bhoomi Thakkar and Abhinav Talwar have just founded a company, “VasshinAgro Composites” to make tableware and cutlery, including trays, plates, bowls, glasses, etc., from PNswastes for a sustainable future (Mathew, 2021). Mary Ward has identified sixteen ways for effective utilisation of PNswastes in gardening (Ward, 2021), which include acidifying soil, making compost, creating paths, controlling erosion, etc. In their latest publication, Rea Downing et al. (105) just recommended that green PNs could be used as sensors to identify the pollution level in the surrounding area. They investigated the magnetic characteristics of green PNsas a particulate matter pollution indicator and found that needle magnetism rises as air pollution levels rise.

Additionally, pine needle magnetism showed a considerable degree of geographic heterogeneity during the testing of particulate matter pollution near Salt Lake City, Utah, with the biggest increases in magnetization near highways. The impact of the 2005 earthquake on the conditions of nearly 100 mud houses made up ofPNsreinforced soil composites have been studied Hayat et al. (2017). They concluded that the severity of the damage depends upon the maintenance and construction quality and reported hairline cracks in 28 % of well-reserved houses. However, for above-average, below average and poor houses, minor, diagonal, zig-zag and major cracks have been noticed by them. Thus, using PNs to reinforce the mud bricks might be a good option for the impressive use of waste PNs. Orjola (2016) designed stools and carpets from PNswool, extracted by employing a series of steps: crushing, steaming, binding and pressing. They further transformed the wool into composites, textiles and paper. Ghosh and Ghosh (2011) utilised the PNsdried powder as bed material during solid state fermentation of glucose/whey substituted glucose into lactic acid utilizing five different strains of Lactobacilli. Guo et al. (2022) reported improvement in the egg quality, serum and gut microbiome in laying henswhen supplemented with PNE. Kumari et al. (2022) synthesised sulfonated biochar catalyst from PNs wastes and subsequently utilised it to convert fructose to levulinic acid andethyl levulinate. They reported a yield of 37 % for levulinic acid and 97 % for ethyl levulinate.

Ferlin et al. (2021) created a Pd/PNs heterogeneous catalyst to carry out the Sonogashira coupling reaction under basic conditions [1,4-diazabicyclo[2.2.2]octane (DABCO)] in an industrial waste derived cyclopentyl methyl ether (CPME) water azeotropic mixture using a continuous-flow technique (Fig. 5). For effective loading of Pd metals into PNs, needles were converted into active carbons by employing sulphuric acid treatment followed by sonication. The developed catalyst was found to have better stability and recoverability when repeatedly used multiple times. In addition, the recoverability of CPME from water via continuous liquid–liquid separation was also found to be better. Further, the flow reactor was operated continuously for a fortnight, and during that time, the synthesised catalyst showed constant efficiency and a minimal metal leaching tendency. The same group used the developed catalyst to perform Heck and Hiyama reactions in γ-valerolactone (GVL) solvent derived from biomass (Fig. 5). Better efficiency of the developed catalyst was reported by them when compared with the commercially available Pd/C catalyst (Valentini et al., 2021). Further, the capability of the catalyst was also extended to afford differently substituted (E)-1,2-diarylethenes from consecutive Hiyama–Heck reactions. Thus, depending on the above discussion, we can conclude that PNswool could serve as an alternative for all kinds of fibers.

The likelihood of a summer forest fire could be changed in the near future by using PNs as a source of natural fibres. Additionally, it might offer rural residents an alternative to what was previously viewed as a wasteful source of income. By using PNs wastes on a large scale, check dams can be constructed to prevent soil erosion during flooding. Additionally, after combining with bamboo sticks or stuffing coir bags, PNs wastes can be used to treat landslide areas and prevent gullies from soil erosion, respectively.

5. Future prospectus

Since due to the growing population, there is an increased demand of bio-energy worldwide, which can easily be met by gasifying or pyrolysing this unutilized bulk fibre. Nowadays, there is a shortage of fresh water sources; therefore, by using cheap and highly adorable bio-char developed from PNs for water purification could serve the growing demands of fresh water. Further, products manufactured from PN wastes could be used to replace plastic tableware and curtly, which pose major risks to both the environment and people. The rising need for natural sources-based antioxidant agents might be satisfied by PNs, which are a rich source of various antioxidants. Further, due to rich antioxidant properties the food packaging materials could be developed in large scale by utilizing PNs fibers. The PNs as it is or after extraction of fibers could be used to fabricate sustainable, recyclable and fire retardant biopolymer composites and thus may serve as a good substitute for synthetic fibers. Efforts in extraction of bio-chemicals or bio-fuels from PNs are very much limited and require action in large scale in the future to decrease the dependency on non-renewable fossil fuels chemicals.

6. Research needs, future directionsand limitations

Researchers have thoroughly studied the various techniques for the transformation of PNs into other energy sources, including electricity, bio-fuels, ethanol, and oil. Further, limited work has been done on the valorization of PNs wastes using catalytic technology. Research should be focused in the near future on the utilization of various catalysts such as noblesingle-phase metals (such as, Pt, Pd, Ir, Ru, Cu, Mo, and Ni) or bimetallic-system-based catalytic systems (for instance, Ru–Cu, Ni–Co, and Pt–Au), non-noble metals based catalyst (like Ni/C, $ZnCl_2$/Ni, nickel–tungsten carbide, etc.) metal oxygen framework (MOF) based catalyst [like Cu–BTC (1,3,5-benzenetricarboxylic acid) MOFs, Pd loaded Cu–BTC, etc.] and photocatalysts [like CoPz/g-C_3N_4, WO_3/g-C_3N_4, etc.] to valorizewastes PNs into bio-fuels (Hoang et al., 2022a). The conversion of PNs into small-sized briquettes through briquetting

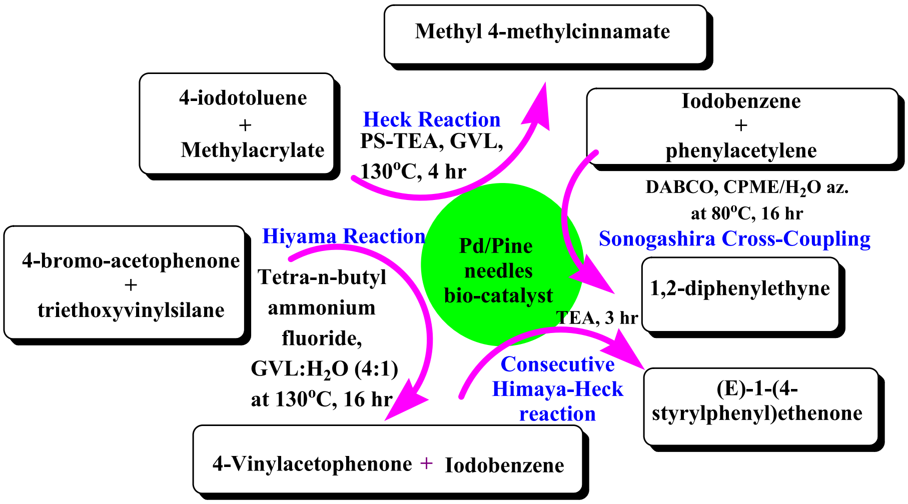


Fig. 5. Showing the role of Pd/pine needles blend as a biocatalyst in different reactions.

and further electricity production through gasification are both attractive technologies. However, ongoing actions to convert PNs into electricity are limited,so much larger-scale initiatives are needed to meet the growing world demand for electricity. The conversion of PNs into biochar, activated biochar, and modified biochar, and their utility for removing various contaminants from wastewater have all been extensively studied. However, researchers should apply some additional surface modification techniques to biochar to increase its adsorbing ability. Converting PNs waste into nano cellulose is also an appealing methodology for fully utilising PNs wastes in various applications such as nano polymer composites, nano bio-adsorbents, anti-bacterial applications, and so on. The nano/micro cellulose-derived PNs may also be used for removing contaminants from wastewater, either as-is or after surface functionalization. Therefore full consideration should be given tofuture studies. PNs have been successfully used in the concrete and plastic industries to strengthen polymer, cement, or soil in various amounts and sizes, but still, further actions are required to enhance the composite thermal/mechanical properties by either chemically modifying the PNs or extracting cellulose and their subsequent utilizationas reinforcement in polymer composites. Air pollution is a serious issue, and efforts have been made to monitor air pollution using PNs. But the endeavours are in the preliminary stage and need thorough investigationin the near future. The PNE showed good antimicrobial properties; researchers should concentrate their attention on studying the chemical composition of pine needle extract and other antimicrobial compounds in addition to the shikimic acidpresent in PNs. Further, efforts for manufacturing of tableware and cutlery from PNs are required at a large scale level, and PNs wasteutilisation for gardening purposes should be fully considered for a sustainable future.

No doubt, PNs wastes may play a crucial role incircular bioeconomy; however, there are certain limitations which may affect/limit its large/small-scale utilization (Sengar et al., 2020). These include transportation cost in rural areas, lack of expertise/small scale units in electricity/charcoal generation, lack of proper marketing, high fuel transportation cost, when fuel is generated in rural areas, storage and safety issues, seasonal availability, difficulty in serving the demand due to irregularities issues, cost in preparing the different PNs based derivatives/valorized products such as bio-chars, activated carbons, functionalized PNs and bio-fuels/bio-oils, lack of expertise in functionalization of PNs wastes/bio-chars and their utilization of as adsorbents, as reinforcement and development of bio-catalysts, etc. Also lack of funding from the government may be thebiggest challenge in the effective utilization of PNs.

7. Cost analysis

On comparing PNs cost/kg with traditional natural fibers, it has been noticed that PNs are the cheapest and most promising biomass available throughout worldwide, whose average cost per barrel lies between 0.25 and 0.30 US$ (See supplementary file) (Dittenber and GangaRao, 2012). According to Dhaundiyal and Tewari (2015), PNs are substantially better than coal in terms of the economic benefits of bio-energy generation at different CO_2 emission reduction and taxation from years 2004–2014. They reported a yield of approx. 2.335 Mg hm^{-2} yr with respect to power generation, which would make PNs competitive with coal at the carbon tax rate of about US$ 5.2/tonne of CO_2. Further, a 2.22 % increment in the yield (0.736 Mg hm^{-2} yr) of PNs has been found to reduce carbon taxation by about 0.47 % or US$ 1.865/ton of CO_2. To develop a power plant of 25 KW, approximately 3035 US$ (25 lakhs INR) are required (Hindustantimes, 2020). For collecting the PNs from local areas, companies in India generally payapprox. 0.024 US$/kg (2 INR/kg) to local peoples (Khuller, 2019). As per the data by renewable watch (Khuller, 2019),an income of 11,267 US$ (930,000 INR) can be generated annually through selling energy (140,000 units of electricity) or charcoal (21 thousand kg) produced from dried PNs by using 25 KVA power plants. Indian institute of technology, Mandi (H.P.) India has also installed a unit of 6 lakhs, with a 150 kg/h capacity for converting PNs into briquettes (6442.58 kcal/kg) (Web page, 2022). Conversion of PNs needles/biomass into biochar is cheap technology which generally costs around $350–1200 per tonne, and thus biochar has been preferred over costly activated carbon powder (cost lies in the range $1100–1700 per tonne) without compromising their adsorbing nature (Thompson et al., 2016). Conversion of PNs into nano forms i.e., cellulose nano crystals or cellulose nano fibers are generally costly compared to other biomass, because of low yield due to low cellulosic contents in dried PNs wastes. Since these PNs usually occur in hilly areas, transportation charges or cost of developing power units in that areas may be high. In addition, in hilly area it is very difficult to access the primary facilities, which in turn may hike the initial capital cost.

8. Conclusion

No doubt, PNs wastes are underutilized, but it has remarkable potential to act as feedstock for generating bio-based products and bioenergy. Due to the interdependence of the waste and production sectors within a prospective circular bio-economy, the bio refineries constitute a viable option for scaling the PNs waste management hierarchy. Numerous endeavours were made to valorise PNs wastes, which include gasification, pyrolysing, development of bio-catalyst, food packaging materials preparation, as water purification materials, as reinforcing agents in polymers, etc. The potential for gasification or pyrolysis of PNs is excellent; however, there are significant practical hurdles to overcome.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

Ahmad, M., Lee, S.S., Rajapaksha, A.U., Vithanage, M., Zhang, M., Cho, J.S., Lee, S.-E., Ok, Y.S., 2013. Trichloroethylene adsorption by pine needle biochars produced at various pyrolysis temperatures. Bioresour. Technol. 143, 615–622.

Amjad, M., Raza, H., Murtaza, B., Abbas, G., Imran, M., Shahid, M., Naeem, M.A., Zakir, A., Iqbal, M.M., 2019. Nickel toxicity induced changes in nutrient dynamics and antioxidant profiling in two maize (Zea mays L.) hybrids. Plants 9, 5.

Anastopoulos, I., Katsouromalli, A., Pashalidis, I., 2020. Oxidized biochar obtained from pine needles as a novel adsorbent to remove caffeine from aqueous solutions. J. Mol. Liq. 304, 112661.

Atabani, A.E., Tyagi, V.K., Fongaro, G., Treichel, H., Pugazhendhi, A., Hoang, A.T., 2021. Integrated biorefineries, circular bio-economy, and valorization of organic waste streams with respect to bio-products. Biomass Convers. Biorefinery.

Ates, B., Koytepe, S., Ulu, A., Gurses, C., Thakur, V.K., 2020. Chemistry, Structures, and Advanced Applications of Nanocomposites from Biorenewable Resources. Chem. Rev. 120, 9304–9362.

Avcı, R.N., Oymak, T., Bağda, E., 2022. Determination of sulfadiazine in natural waters by pine needle biochar-derivatized magnetic nanocomposite based solid-phase extraction (SPE) with High-Performance Liquid Chromatography (HPLC). Anal. Lett. 1–12.

Bai, J., Wu, Y., Liu, X., Zhong, K., Huang, Y., Gao, H., 2015. Antibacterial activity of shikimic acid from pine needles of Cedrus deodara against Staphylococcus aureus through damage to cell membrane. Int. J. Mol. Sci. 16, 27145–27155.

Beluns, S., Gaidukovs, S., Platnieks, O., Gaidukova, G., Mierina, I., Grase, L., Starkova, O., Brazdausks, P., Thakur, V.K., 2021. From wood and hemp biomass wastes to sustainable nanocellulose foams. Ind. Crops Prod. 170, 113780.

Bhatia, S.K., Palai, A.K., Kumar, A., Bhatia, R.K., Patel, A.K., Thakur, V.K., Yang, Y.-H., 2021. Trends in renewable energy production employing biomass-based biochar. Bioresour. Technol. 340, 125644.

Bisht, A.S., Singh, S., Kumar, M., 2014. Pine needles a source of energy for Himalayan region. Int. J. Sci. Technol. Res. 3, 161–164.

Bisht, A.S., Thakur, N.S., 2020. Pine needles biomass gasification based electricity generation for Indian Himalayan region: drivers and barriers. Green Build. Sustain. Eng. Springer 47–59.

Blevins, D., Allen, H.L., Colbett, S., Gardner, W., 2005. Woodland owner notes: Nutrition management for longleaf pinestraw. Coop Ext Serv NC State Univ, NC, p. 8.

Chakrabarty, A., 2016. Uttarakhand: Pine needles to power homes in Uttarakhand, Energy News, ET EnergyWorld [WWW Document]. URL https://energy.economictimes.indiatimes.com/news/power/pine-needles-to-power-homes-in-uttarakhand/54990578 (accessed 9.1.22).

Choudhary, V., Patel, M., Pittman Jr, C.U., Mohan, D., 2020. Batch and continuous fixed-bed lead removal using himalayan pine needle biochar: isotherm and kinetic studies. ACS Omega 5, 16366–16378.

Clarke, S., Preto, F., 2011. Biomass densification for energy production, Ministry of Agriculture Food and Rural Affairs. Govt. of Canada, Citeseer.

Cogurcu, M.T., 2022. Investigation of mechanical properties of red pine needle fiber reinforced self-compacting ultra high performance concrete. Case Stud. Constr. Mater. 16, e00970.

Correa, C.R., Hehr, T., Voglhuber-Slavinsky, A., Rauscher, Y., Kruse, A., 2019. Pyrolysis vs. hydrothermal carbonization: Understanding the effect of biomass structural components and inorganic compounds on the char properties. J. Anal. Appl. Pyrolysis 140, 137–147.

Dhaundiyal, A., Tewari, P.C., 2015. Comparative analysis of pine needles and coal for electricity generation using carbon taxation and emission reductions. Acta Technol. Agric. 18, 29–35.

Dhyani, V., Bhaskar, T., 2018. A comprehensive review on the pyrolysis of lignocellulosic biomass. Renew. Energy 129, 695–716.

Dickens, E.D., Moorhead, D.J., Morris, L.A., McElvany, B.C., 2003. Straw raking in southern pine stands and fertilization recommendations.

Dittenber, D.B., GangaRao, H.V.S., 2012. Critical review of recent publications on use of natural composites in infrastructure. Compos. Part Appl. Sci. Manuf. 43, 1419–1429. https://doi.org/10.1016/j.compositesa.2011.11.019.

Dmuchowski, W., Gozdowski, D., Baczewska-Dąbrowska, A.H., Dąbrowski, P., Gworek, B., Suwara, I., 2018. Evaluation of the impact of reducing national emissions of SO2 and metals in Poland on background pollution using a bioindication method. PLoS One 13, e0192711.

Dong, C., Parsons, D., Davies, I.J., 2014. Tensile strength of pine needles and their feasibility as reinforcement in composite materials. J. Mater. Sci. 49, 8057–8062.

Dorotíková, K., Kamenik, J., Bogdanovičová, K., Křepelová, S., Strejček, J., Haruštiaková, D., 2022. Microbial contamination and occurrence of Bacillus cereus sensu lato, Staphylococcus aureus, and Escherichia coli on food handlers' hands in mass catering: Comparison of the glove juice and swab methods. Food Control 133, 108567.

Duryea, M.L., 1989. Pine-straw management in Florida's forests. Florida Cooperative Extension Service, Institute of Food and Agricultural ….

Dwivedi, D., Rathour, R.K., Sharma, V., Rana, N., Bhatt, A.K., Bhatia, R.K., 2022. Co-fermentation of forest pine needle waste biomass hydrolysate into bioethanol. Biomass Convers. Biorefinery 1–13.

Encyclopaedia Britannica, 2022. pine | Description, Conifer, Genus, Species, Uses, Characteristics, & Facts | Britannica [WWW Document]. URL https://www.britannica.com/plant/pine (accessed 9.1.22).

Estevez, M., Estevez, A.J.R., 2012. A short overview on the medicinal chemistry of (—)-shikimic acid. Mini Rev. Med. Chem. 12, 1443–1454.

Feng, S., Zeng, W., Luo, F., Zhao, J., Yang, Z., Sun, Q., 2010. Antibacterial activity of organic acids in aqueous extracts from pine needles (Pinus massoniana Lamb.). Food Sci. Biotechnol. 19, 35–41.

Ferlin, F., Valentini, F., Sciosci, D., Calamante, M., Petricci, E., Vaccaro, L., 2021. Biomass waste-derived Pd–PiNe catalyst for the continuous-flow copper-free sonogashira reaction in a CPME–water azeotropic mixture. ACS Sustain. Chem. Eng. 9, 12196–12204. https://doi.org/10.1021/acssuschemeng.1c03634.

Fires ravage forests in Himalayas, threatening health and biodiversity, 2017. Third Pole. URL https://www.thethirdpole.net/en/climate/fires-ravage-forests-himalayas-threatening-health-biodiversity/ (accessed 9.1.22).

Font, R., Conesa, J.A., Moltó, J., Muñoz, M., 2009. Kinetics of pyrolysis and combustion of pine needles and cones. J. Anal. Appl. Pyrol. 85, 276–286.

Fuentes, A., 2017. Pine Needle Pyrolysis: Bio-waste into Biofuel.

Ghosh, M.K., Ghosh, U.K., 2011. Utilization of pine needles as bed material in solid state fermentation for production of lactic acid by lactobacillus strains. BioResources 6, 1556–1575.

Gresham, C.A., 1982. Litterfall patterns in mature loblolly and longleaf pine stands in coastal South Carolina. For. Sci. 28, 223–231.

Guo, Y., Huang, S., Zhao, L., Zhang, J., Ji, C., Ma, Q., 2022. Pine (Pinus massoniana Lamb.) needle extract supplementation improves performance, egg quality, serum parameters, and the gut microbiome in laying hens. Front. Nutr. 9, 810462 https://doi.org/10.3389/fnut.2022.810462.

Gupta, P.K., Joshi, G., Rana, V., Rawat, J.S., Sharma, A., 2020. Utilization of pine needles for preparation of sheets for application as internal packaging material. Indian For. 146, 538–543.

Gupta, S., Mondal, P., 2021. Catalytic pyrolysis of pine needles with nickel doped gamma-alumina: Reaction kinetics, mechanism, thermodynamics and products analysis. J. Clean. Prod. 286, 124930.

Gupta, S., Patel, P., Mondal, P., 2022. Biofuels production from pine needles via pyrolysis: Process parameters modeling and optimization through combined RSM and ANN based approach. Fuel 310, 122230.

Hafeez, B., Khanif, Y.M., Saleem, M., 2013. Role of zinc in plant nutrition-a review. Am. J. Exp. Agric. 3, 374.

Hammud, H.H., Shmait, A., Hourani, N., 2015. Removal of Malachite Green from water using hydrothermally carbonized pine needles. Rsc Adv. 5, 7909–7920.

Hayat, A., Khan, H., Haq, R.U., Ali, M., 2017. Use of Pine-Needle Reinforced Composites in Kashmir, Pakistan–A Critical Review.

Hepler, P.K., 2005. Calcium: a central regulator of plant growth and development. Plant Cell 17, 2142–2155.

Hindustantimes, 2020. Uttarakhand gets its first pine needle power generation plant [WWW Document]. Hindustan Times. URL https://www.hindustantimes.com/india-news/uttarakhand-gets-its-first-pine-needle-power-generation-plant/story-q3x36Xl9ieJBjScnl7m3VO.html (accessed 9.1.22).

Hoang, A.T., 2021. 2-Methylfuran (MF) as a potential biofuel: A thorough review on the production pathway from biomass, combustion progress, and application in engines. Renew. Sustain. Energy Rev. 148, 111265.

Hoang, A.T., Ong, H.C., Fattah, I.R., Chong, C.T., Cheng, C.K., Sakthivel, R., Ok, Y.S., 2021. Progress on the lignocellulosic biomass pyrolysis for biofuel production toward environmental sustainability. Fuel Process. Technol. 223, 106997.

Hoang, A.T., Pandey, A., Huang, Z., Luque, R., Ng, K.H., Papadopoulos, A.M., Chen, W.-H., Rajamohan, S., Hadiyanto, H., Nguyen, X.P., 2022a. Catalyst-based synthesis of 2, 5-dimethylfuran from carbohydrates as a sustainable biofuel production route. ACS Sustain. Chem. Eng. 10, 3079–3115.

Hoang, A.T., Varbanov, P.S., Nižetić, S., Sirohi, R., Pandey, A., Luque, R., Ng, K.H., 2022b. Perspective review on Municipal Solid Waste-to-energy route: Characteristics, management strategy, and role in circular economy. J. Clean. Prod. 131897.

Holoubek, I., Kořínek, P., Šeda, Z., Schneiderová, E., Holoubková, I., Pacl, A., Tříska, J., Cudlın, P., Čáslavskỳ, J., 2000. The use of mosses and pine needles to detect persistent organic pollutants at local and regional scales. Environ. Pollut. 109, 283–292.

Indian Express, 2016. Uttarakhand forest fire: Mi-17 choppers to spray water over burning forests | India News,The Indian Express [WWW Document]. URL https://indianexpress.com/article/india/india-news-india/uttarakhand-forest-fires-mi-17-choppers-to-spray-water-over-burning-forests-2778328/(accessed 9.1.22).

Jové-Sandoval, F., Barbero-Barrera, M.M., Medina, N.F., 2018. Assessment of the mechanical performance of three varieties of pine needles as natural reinforcement of adobe. Constr. Build. Mater. 187, 205–213.

Juranović Cindrić, I., Zeiner, M., Starčević, A., Stingeder, G., 2019. Metals in pine needles: Characterisation of bio-indicators depending on species. Int. J. Environ. Sci. Technol. 16, 4339–4346.

Ka, M.-H., Choi, E.H., Chun, H.-S., Lee, K.-G., 2005. Antioxidative activity of volatile extracts isolated from Angelica tenuissimae roots, peppermint leaves, pine needles, and sweet flag leaves. J. Agric. Food Chem. 53, 4124–4129.

Kadam, A.A., Singh, S., Gaikwad, K.K., 2021. Chitosan based antioxidant films incorporated with pine needles (Cedrus deodara) extract for active food packaging applications. Food Control 124, 107877.

Kala, L.D., Subbarao, P.M.V., 2017. Pine needles as potential energy feedstock: availability in the central Himalayan state of Uttarakhand, India, in: E3S Web of Conferences. EDP Sciences, p. 04001.

Kandel, A., Timilsina, B., Bhattarai, M., Thapa, N., Koirala, P., Shrestha, S., 2020. Stabilization of soft soil with pine needles and lime. Proc. 8th IOE Grad Conf. 8, 843–848.

Khan, T., 2012. How an Uttarakhand company is producing electricity with pine needles [WWW Document]. Bus, Today https://www.businesstoday.in/magazine/features/story/uttarakhand-company-producing-power-with-pine-needles-35270-2012-12-19 (accessed 9.1.22.

Khan, A., Rashid, A., Younas, R., 2015. Adsorption of reactive black-5 by pine needles biochar produced via catalytic and non-catalytic pyrolysis. Arab. J. Sci. Eng. 40, 1269–1278.

Khitab, A., 2020. Effect of pine needle fibers on properties of cementitious mortars: pine needles-reinforced mortars. Proc. Pak. Acad. Sci. Phys. Comput. Sci. 57, 33–46.

Khuller, A., 2019. Fuel from Forests [WWW Document]. Renew. Watch. URL https://renewablewatch.in/2019/09/20/fuel-from-forests/ (accessed 9.1.22).

Kim, Y.-M., Lee, H.W., Jang, S.H., Jeong, J., Ryu, S., Jung, S.-C., Park, Y.-K., 2020. Production of biofuels from pine needle via catalytic fast pyrolysis over HBeta. Korean J. Chem. Eng. 37, 493–496.

Ko, S., Co, O., 2010. The importance of mineral elements for humans, domestic animals and plants-A review. Afr. J. Food Sci. 4, 200–222.

Kumar, A., Gupta, V., Singh, S., Saini, S., Gaikwad, K.K., 2021. Pine needles lignocellulosic ethylene scavenging paper impregnated with nanozeolite for active packaging applications. Ind. Crops Prod. 170, 113752.

Kumar, A., Deshmukh, R.K., Gaikwad, K.K., 2022. Quality preservation in banana fruits packed in pine needle and halloysite nanotube-based ethylene gas scavenging paper during storage. Biomass Convers. Biorefinery 1–10.

Kumar, V., Nanda, M., Verma, M., Singh, A., 2018. An integrated approach for extracting fuel, chemicals, and residual carbon using pine needles. Biomass Convers. Biorefinery 8, 447–454.

Kumari, N., Chhabra, T., Kumar, S., Krishnan, V., 2022. Nanoarchitectonics of sulfonated biochar from pine needles as catalyst for conversion of biomass derived chemicals to value added products. Catal. Commun. 106467.

Kwak, C.S., Moon, S.C., Lee, M.S., 2006. Antioxidant, antimutagenic, and antitumor effects of pine needles (Pinus densiflora). Nutr. Cancer 56, 162–171.

Lehndorff, E., Schwark, L., 2008. Accumulation histories of major and trace elements on pine needles in the Cologne Conurbation as function of air quality. Atmos. Environ. 42, 833–845.

Liu, D., Li, X., Ma, J., Li, M., Ren, F., Zhou, L., 2021. Metal-organic framework modified pine needle-derived N, O-doped magnetic porous carbon embedded with Au nanoparticles for adsorption and catalytic degradation of tetracycline. J. Clean. Prod. 278, 123575.

Liu, K., Tang, R., Zhu, Y., Zhang-Fa, T., Han-Bing, Z., Yan-Kui, T., 2020. Cr (VI) removal from wastewater using molded masson pine needles. J. Agric. Resour. Environ. 37, 74.

Long, W., Wang, Y., 2021. Effect of pine needle fibre reinforcement on the mechanical properties of concrete. Constr. Build. Mater. 278, 122333.

Ma, Y., Liu, Y., Shang, W., Gao, Z., Wang, H., Guo, L., Tong, J., 2014. Tribological and mechanical properties of pine needle fiber reinforced friction composites under dry sliding conditions. RSC Adv. 4, 36777–36783.

Mandal, S., Prasanna Kumar, G.V., Bhattacharya, T.K., Tanna, H.R., Jena, P.C., 2019. Briquetting of pine needles (Pinus roxburgii) and their physical, handling and combustion properties. Waste Biomass Valorization 10, 2415–2424. https://doi.org/10.1007/s12649-018-0239-4.

Mathew, A.A., 2021. Sustainability Agenda: Why this startup chose pine needles to make tablewares [WWW Document]. YourStory.com. URL https://yourstory.com/socialstory/2021/08/sustainability-agenda-vasshin-composites-tableware/amp (accessed 9.1.22).

Moriana, R., Vilaplana, F., Ek, M., 2016. Cellulose nanocrystals from forest residues as reinforcing agents for composites: A study from macro-to nano-dimensions. Carbohydr. Polym. 139, 139–149.

Moscariello, C., Matassa, S., Pirozzi, F., Esposito, G., Papirio, S., 2022. Valorisation of industrial hemp (Cannabis sativa L.) biomass residues through acidogenic fermentation and co-fermentation for volatile fatty acids production. Bioresour. Technol. 355, 127289 https://doi.org/10.1016/j.biortech.2022.127289.

Myers, V.R., 2022. 40 Species of Pine Trees and Shrubs [WWW Document]. The Spruce. URL https://www.thespruce.com/pine-trees-from-around-the-world-3269718 (accessed 9.1.22).

Nicolaou, E., Philippou, K., Anastopoulos, I., Pashalidis, I., 2019. Copper adsorption by magnetized pine-needle biochar. Processes 7, 903.

Ohri, A., Ohri, J., 2007. Role of Information Technology in Energy Management, in: Proceedings of the World Congress on Engineering and Computer Science. Citeseer, pp. 24–26.

Orjola, T., 2016. Tamara Orjola makes furniture and textiles using pine needles [WWW Document]. URL https://www.dezeen.com/2016/11/07/tamara-orjola-forest-wool-pine-needle-furniture-textiles-sustainable-dutch-design-week-2016/ (accessed 9.1.22).

Pandey, D., Daverey, A., Dutta, K., Yata, V.K., Arunachalam, K., 2022. Valorization of waste pine needle biomass into biosorbents for the removal of methylene blue dye from water: Kinetics, equilibrium and thermodynamics study. Environ. Technol. Innov. 25, 102200.

Park, J., Lee, B., Choi, H., Kim, W., Kim, H.-J., Cheong, H., 2016. Antithrombosis activity of protocatechuic and shikimic acids from functional plant Pinus densiflora Sieb. et Zucc needles. J. Nat. Med. 70, 492–501.

Philippou, K., Anastopoulos, I., Dosche, C., Pashalidis, I., 2019. Synthesis and characterization of a novel Fe3O4-loaded oxidized biochar from pine needles and its application for uranium removal. Kinetic, thermodynamic, and mechanistic analysis. J. Environ. Manage. 252, 109677.

Philippou, K., Konstantinou, A., Pashalidis, I., 2020. Thorium adsorption by oxidized biochar pine needles-the effect of particle size. Desalination Water Treat. 194, 411–416.

Pietrzykowski, M., Socha, J., van Doorn, N.S., 2014. Linking heavy metal bioavailability (Cd, Cu, Zn and Pb) in Scots pine needles to soil properties in reclaimed mine areas. Sci. Total Environ. 470, 501–510.

Pine Needles Information, Recipes and Facts [WWW Document], 2022. URL https://specialtyproduce.com/produce/Pine_Needles_10289.php (accessed 9.1.22).

Platnieks, O., Sereda, A., Gaidukovs, S., Thakur, V.K., Barkane, A., Gaidukova, G., Filipova, I., Ogurcovs, A., Fridrihsone, V., 2021. Adding value to poly (butylene succinate) and nanofibrillated cellulose-based sustainable nanocomposites by applying masterbatch process. Ind. Crops Prod. 169, 113669.

Rana, A.K., Frollini, E., Thakur, V.K., 2021. Cellulose nanocrystals: Pretreatments, preparation strategies, and surface functionalization. Int. J. Biol. Macromol. 182, 1554–1581. https://doi.org/10.1016/j.ijbiomac.2021.05.119.

Rana, A.K., Thakur, V.K., 2021. The bright side of cellulosic hibiscus sabdariffa fibres: towards sustainable materials from the macro-to nano-scale. Mater. Adv. 2, 4945–4965.

Rana, A.K., Gupta, V.K., Newbold, J., Roberts, D., Rees, R.M., Krishnamurthy, S., Thakur, V.K., 2022a. Sugar beet pulp: Resurgence and trailblazing journey towards a circular bioeconomy. Fuel 312, 122953.

Rana, A.K., Scarpa, F., Thakur, V.K., 2022b. Cellulose/polyaniline hybrid nanocomposites: Design, fabrication, and emerging multidimensional applications. Ind. Crops Prod. 187, 115356 https://doi.org/10.1016/j.indcrop.2022.115356.

Sengar, A., Sharma, V., Agrawal, R., Dwivedi, A., Dwivedi, P., Joshi, K., Dixit, G., Sharma, P.K., Barthwal, M., 2020. Prioritization of barriers to energy generation using pine needles to mitigate climate change: Evidence from India. J. Clean. Prod. 275, 123840.

Serbula, S.M., Kalinovic, T.S., Ilic, A.A., Kalinovic, J.V., Steharnik, M.M., 2013. Assessment of airborne heavy metal pollution using Pinus spp. and Tilia spp. Aerosol Air Qual. Res. 13, 563–573.

Sharma, N., 2018. IIT Roorkee to design portable briquette machines to utilise pine needles [WWW Document]. Hindustan Times. URL https://www.hindustantimes.com/dehradun/iit-roorkee-to-design-portable-briquette-machines-to-utilise-pine-needles/story-K2gxa48Tw5wEp2zISyWfQM.html (accessed 9.1.22).

Singha, A.S., Thakur, V.K., 2008a. Synthesis and characterization of pine needles reinforced RF matrix based biocomposites. E-J. Chem. 5, 1055–1062.

Singha, A.S., Thakur, V.K., 2008b. Mechanical, morphological and thermal properties of pine needle-reinforced polymer composites. Int. J. Polym. Mater. 58, 21–31.

Singha, A.S., Thakur, V.K., 2009. Study of mechanical properties of urea-formaldehyde thermosets reinforced by pine needle powder. BioResources 4, 292–308.

Singha, A.S., Thakur, V.K., 2010. Synthesis, characterization and study of pine needles reinforced polymer matrix based composites. J. Reinf. Plast. Compos. 29, 700–709.

Sinha, P., Mathur, S., Sharma, P., Kumar, V., 2018. Potential of pine needles for PLA-based composites. Polym. Compos. 39, 1339–1349.

Skonieczna, J., Małek, S., 2014. Element content of Scots pine (Pinus sylvestris L.) stands of different densities. Drew. Pr. Nauk. Doniesienia Komun. 77–87.

Slathia, P.S., Raina, N., Kiran, A., Kour, R., Bhagat, D., Sharma, P., 2020. Dilute acid pretreatment of pine needles of Pinus roxburghii by response surface methodology for bioethanol production by separate hydrolysis and fermentation. Biomass Convers. Biorefinery 10, 95–106.

Su, Z., Du, T., Liang, X., Wang, X., Zhao, L., Wang, J., Sun, J., Zhang, W., 2022. Nanozymes for foodborne microbial contaminants detection: Mechanisms, recent advances, and challenges. Food Control 109165.

Sun, F., Wen, D., Kuang, Y., Li, J., Li, J., Zuo, W., 2010. Concentrations of heavy metals and polycyclic aromatic hydrocarbons in needles of Masson pine (Pinus massoniana L.) growing nearby different industrial sources. J. Environ. Sci. 22, 1006–1013. https://doi.org/10.1016/S1001-0742(09)60211-4.

Sundseth, K., 2009. Natura 2000 in the Mediterranean region. http://ec.europa.eu/environment/nature/info/pubs/docs/biogas/Mediterranean.pdf.

Suri, P., Dwivedi, D., Rathour, R.K., Rana, N., Sharma, V., Bhatia, R.K., Bhatt, A.K., 2022. Enhanced C-5 sugar production from pine needle waste biomass using Bacillus sp. XPB-11 mutant and its biotransformation to bioethanol. Biomass Convers. Biorefinery 12, 3663–3672.

Tang, Z., Yang, M., Qiang, M., Li, X., Morrell, J.J., Yao, Y., Su, Y., 2021. Preparation of cellulose nanoparticles from foliage by bio-enzyme methods. Materials 14, 4557.

Tausz, M., Trummer, W., Goessler, W., Wonisch, A., Grill, D., Naumann, S., Jiménez, M.S., Morales, D., 2005. Accumulating pollutants in conifer needles on an Atlantic island–A case study with Pinus canariensis on Tenerife, Canary Islands. Environ. Pollut. 136, 397–407.

Taylor, E., Foster, C.D., 2004. Producing pine straw in East Texas forests. Tex. FARMER Collect.

Thakur, V.K., Singha, A.S., 2010. Natural fibres-based polymers: Part I—Mechanical analysis of Pine needles reinforced biocomposites. Bull. Mater. Sci. 33, 257–264.

Thakur, V.K., Singha, A.S., 2010. Mechanical and Water Absorption Properties of Natural Fibers/Polymer Biocomposites. Polym.-Plast. Technol. Eng. 49, 694–700.

Thakur, V.K., Singha, A.S., 2010. Physico-Chemical And Mechanical Characterization Of Natural Fibre Reinforced Polymer Composites. Iran. Polym. J. 19, 3–16.

Thakur, V.K., Singha, A.S., Thakur, M.K., 2013. Fabrication and Physico-Chemical Properties of High-Performance Pine Needles/Green Polymer Composites. Int. J. Polym. Mater. Polym. Biomater. 62, 226–230.

Thompson, K.A., Shimabuku, K.K., Kearns, J.P., Knappe, D.R., Summers, R.S., Cook, S.M., 2016. Environmental comparison of biochar and activated carbon for tertiary wastewater treatment. Environ. Sci. Technol. 50, 11253–11262.

Trache, D., Tarchoun, A.F., Abdelaziz, A., Bessa, W., Hussin, M.H., Brosse, N., Thakur, V.K., 2022. Cellulose nanofibrils–graphene hybrids: recent advances in fabrication, properties, and applications. Nanoscale 14, 12515–12546.

Tsui, C., 1955. Effect of seed treatment with micro-elements on the germination and early growth of wheat. Sci. Sin. 4, 129–135.

Usmani, Z., Sharma, M., Awasthi, A.K., Sivakumar, N., Lukk, T., Pecoraro, L., Thakur, V.K., Roberts, D., Newbold, J., Gupta, V.K., 2020. Bioprocessing of waste biomass for sustainable product development and minimizing environmental impact. Bioresour. Technol. 124548.

Uttarakhand Renewable Energy Development Agency, 2018. Uttarakhand Renewable Energy Development Agency 2018.

Valentini, F., Ferlin, F., Lilli, S., Marrocchi, A., Ping, L., Gu, Y., Vaccaro, L., 2021. Valorisation of urban waste to access low-cost heterogeneous palladium catalysts for cross-coupling reactions in biomass-derived γ-valerolactone. Green Chem. 23, 5887–5895.

Varma, A.K., Mondal, P., 2018. Pyrolysis of pine needles: effects of process parameters on products yield and analysis of products. J. Therm. Anal. Calorim. 131, 2057–2072.

Varnagirytė-Kabašinskienė, I., Armolaitis, K., Stupak, I., Kukkola, M., Wójcik, J., Mikšys, V., 2014. Some metals in aboveground biomass of Scots pine in Lithuania. Biomass Bioenergy 66, 434–441.

Vikaspedia, 2022. vikaspedia Domains [WWW Document]. URL https://vikaspedia.in/energy/best-practices/electricity-generation-using-pine-needles-in-uttarakhand (accessed 9.1.22).

Wang, Y., Long, W., 2021. Complete stress–strain curves for pine needle fibre reinforced concrete under compression. Constr. Build. Mater. 302, 124134.

Wang, Y., Gao, S., Li, W., 2022. Study on compression deformation and damage characteristics of pine needle fiber-reinforced concrete using DIC. Materials 15, 1654.

Wang, M., Zheng, Q., Shen, Q., Guo, S., 2013. The critical role of potassium in plant stress response. Int. J. Mol. Sci. 14, 7370–7390.

Ward, M., 2021. 16 Innovative Ways to Use Pine Needles in the Garden - Gardening [WWW Document]. URL https://gardening.org/16-innovative-ways-to-use-pine-needles-in-the-garden/ (accessed 9.1.22).

Web page, 2022. Cithr, Briquettes and pellets produced at center [WWW Document]. URL http://uhl.iitmandi.ac.in/research.html (accessed 10.22.22).

World Bioenergy Association, 2020. Global bioenergy statistics 2019. World Bioenergy Association.

Wu, R., Wang, Y., Xue, X., Hu, T., Gao, J., An, F., 2019. Selective adsorption and removal ability of pine needle-based activated carbon towards Al (III) from La (III). J. Dispers. Sci. Technol. 40, 186–191.

Xiao, S., Gao, R., Lu, Y., Li, J., Sun, Q., 2015. Fabrication and characterization of nanofibrillated cellulose and its aerogels from natural pine needles. Carbohydr. Polym. 119, 202–209.

Xie, J.Y., Lan, J.F., Yu, L., Wu, C.M., 2012. Study on extraction of Shikimic acid from pine needles of Pinus Elliottii Engelm by means of microwave pretreatment. Adv. Mater. Res. Trans. Tech. Publ. 752–759.

Yaqub, A., Ajab, H., Almas, A., Syed, S.M., Azam, A., Khan, M.I., Awais, M., Muhammad, I., Galal, A.M., Alshahrani, M.Y., 2022. Utilization of nano-biosorbents based on pine needles and banana peel for methylene blue removal: equilibrium, kinetics, thermodynamic study, and application. Biomass Convers. Biorefinery 12, 1787–1802.

Zeng, W.-C., He, Q., Sun, Q., Zhong, K., Gao, H., 2012. Antibacterial activity of water-soluble extract from pine needles of Cedrus deodara. Int. J. Food Microbiol. 153, 78–84.

Zielińska, D., Rydzkowski, T., Thakur, V.K., Borysiak, S., 2021. Enzymatic engineering of nanometric cellulose for sustainable polypropylene nanocomposites. Ind. Crops Prod. 161, 113188.