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Waste-to-Chemicals: Green solutions for bioeconomy markets

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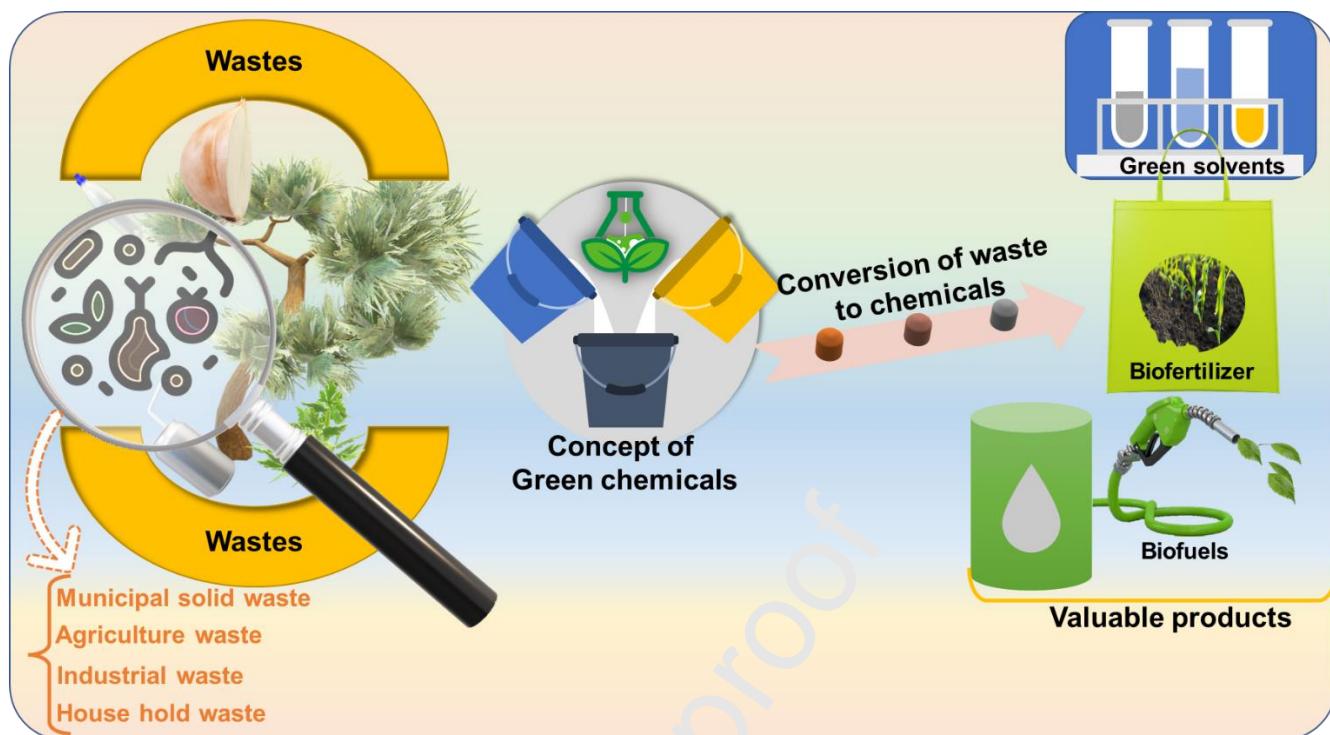
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Abstract: In the fast-developing time, the accumulation of waste materials is always in an uptrend due to population increases and industrialization. This excessive accumulation in waste materials harms the ecosystem and human beings by depleting water quality, air quality, and biodiversity. Further, by use of fossil fuel problem-related global warming, greenhouse gases are the major challenge in front of the world. Nowadays, scientists and researchers are more focused on recycling and utilizing different waste materials like a municipal solid waste (MSW), agro-industrial waste etc. The waste materials added to the

environment are converted into valuable products or green chemicals using green chemistry principles. These fields are the production of energy, synthesis of biofertilizers and use in the textile industry to fulfil the need of the present world. Here we need more focus on the circular economy considering the value of products in the bioeconomic market. For this purpose, sustainable development of the circular bio-economy is the most promising alternative, which is possible by incorporating the latest techniques like microwave-based extraction, enzyme immobilization-based removal, bioreactor-based removal etc., for the valorization of food waste materials. Further, the conversion of organic waste into valuable products like biofertilizers and vermicomposting is also realised by using earthworms. The present review article focuses on the various types of waste materials (such as MSW, agricultural, industrial, household waste, etc.), waste management with current glitches and the expected solutions that have been discussed. Furthermore, we have highlighted their safe conversion into green chemicals and contribution to the bioeconomic market. The role of the circular economy is also discussed.

Keywords: Waste to energy, bio-nase, bioeconomy, biofertilizers, green chemistry.

Graphical abstract:



Abbreviations:

<i>MSW</i>	<i>Municipal solid waste</i>
<i>SARS</i>	<i>Severe acute respiratory syndrome</i>
<i>PET</i>	<i>Polyethylene terephthalate</i>
<i>WTE</i>	<i>Waste to energy</i>
<i>CO+H₂</i>	<i>Syngas</i>
<i>WCO</i>	<i>Waste cooking oil</i>
<i>NDG</i>	<i>Nitrogen-doped Graphene</i>
<i>CH₄</i>	<i>Methane</i>
<i>EU</i>	<i>European Union</i>
<i>SCFs</i>	<i>Supercritical fluids</i>
<i>ILs</i>	<i>Ionic Liquids</i>
<i>DESs</i>	<i>Deep eutectic solvents</i>
<i>SDGs</i>	<i>Sustainable development goals</i>
<i>GCPs</i>	<i>Green chemistry principles</i>
<i>AD</i>	<i>Anaerobic digestion</i>

1. Introduction

As we know, the world population is growing day by day tremendously. Due to many activities, this increase in population added many waste materials to the environment. Further, due to other environmental processes' waste materials are also added to the environment. These waste materials nowadays become enormous problems for the world. So, we need some suitable method for the treatment of this waste.

On the other hand, chemicals are also a significant issue because they enter the food chain and create many cases for animals and humans. Therefore, it's time to develop green chemicals which are eco-friendly. It was also known that there are various micro-organisms are also used to convert waste materials into green chemicals. One of the well-known processes for this is anaerobic digestion (AD) (Singh Siwal et al., 2020). Using AD, the organic waste materials in polluted water are converted into methane (Marshall et al., 2013). Anastas introduced the concept of green chemistry in 1999. The main focus of green chemistry is the reduction of use or complete elimination of organic solvents or toxic chemicals by green solutions or green chemicals. The mainly used green solvents are amphiphilic, deep eutectic and ionic liquid-based solvents (Mishra et al., 2022; Pacheco-Fernández and Pino, 2019).

Further, with the increase in population, the consumption of resources also increases, badly affecting the economy of developing countries. So, the problem of helping to waste the economy also arises (Kaur et al., 2022a; Sheoran et al., 2022). To overcome this circular problem economy is introduced. Circular economy worked by increasing the value of resource materials by increasing its transformation into high-value products and eliminating minimum waste with a lower value. Using the circular economy approach, the lifespan of

products also increases by changing the product's design. Further also introduced the concept of reuse after the end of product functions (Clark et al., 2016).

The role of chemistry is not only to manufacture toxic chemicals, plastics, and various additives which create environmental pollution but also to be responsible for the environment's safety by introducing green chemicals from waste materials and processing them for the circular economy. For the production of chemicals nowadays, oils are the best source of chemicals. But this source has some significant problems, so we need to find another carbon source for preparing chemicals. These problems are solved by using the following approaches:

1. Local resources by supporting the development of rural carbon sources
2. Geopolitical problem
3. By decrease in emission of greenhouse gases
4. Find out alternative carbon sources in place of fossil fuels has less cost.

The exploitation of biomass represents several potential solutions to each of these issues (Iaquaniello et al., 2018). Thus, we need various other waste materials to develop green chemicals and contribute to bioeconomy markets using the circular economy concept. The complete model of the circular economy is shown in **Fig. 1**.

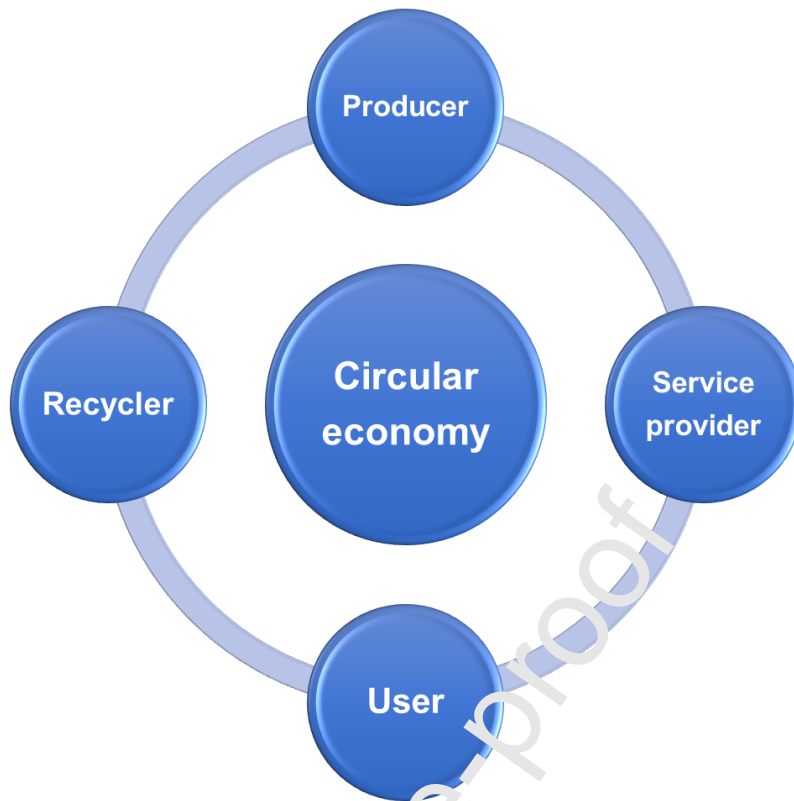


Fig. 1. A brief overview of the circular economy

Also, we know that large quantities of food waste materials obtained from agriculture, directly and indirectly, contain useful bio-based materials produced during the run of the complete food chain. Avoiding this food waste and its by-product also contributes to the bio-economy of the world and helps reduce environmental problems. This can be done by valorising food waste materials into valuable products, as shown in **Fig. 2** (Capanoglu et al., 2022).

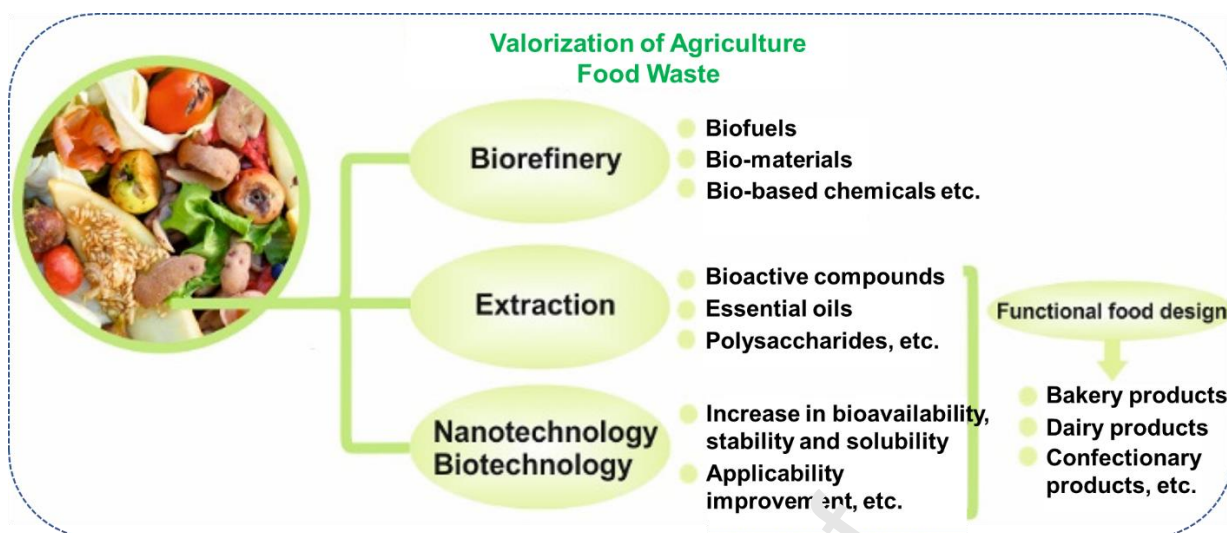


Fig. 2. Valorisation of agricultural food waste into valuable products. Reprinted with permission from Ref. (Capanoglu et al., 2022).

Using waste from fruits and vegetables is the most complex and essential task in food sustainability. These low-cost waste materials are high-value-based because they are rich in fibres, enzymes, polysaccharides, organic acid etc. From a socioeconomic point of view, these bio-waste materials are used as raw materials in chemical industries at very low-cost (Awasthi et al., 2022).

Behalf of our knowledge, this article first presents the relationship between waste materials with the bioeconomic market and sustainable development, which does not solve the problem related to waste management and deals with the formation of biodegradable bioproducts by solving major issues of environmental pollution. Herein the present review articles dealing with the types of different waste material and their conversion into green chemicals, which is not causing an environmental problem. Further, we also related it to the circular economy, and the result is observed for bioeconomy markets. In this way, the role of green chemistry is much studied.

2. Types of waste material

Different types of waste materials are produced in an amount of million tons per year on the earth and are increasing daily. Some waste materials are dumped by landfilling, and some by burning. These methods create environmental pollution. The cement industry is the most prominent cause of greenhouse gases and carbon dioxide production. This waste type is a typical concrete constituent (Rana et al., 2023; Shah et al., 2021).

Further, this municipal, household, industrial, and agricultural waste are also known, creating more significant concern to humans, plants and animals. The most effective is directly on the ecosystem (Akpan and Olukanni, 2020; Siwal et al., 2021). The classification of waste materials shown in Fig. 3.

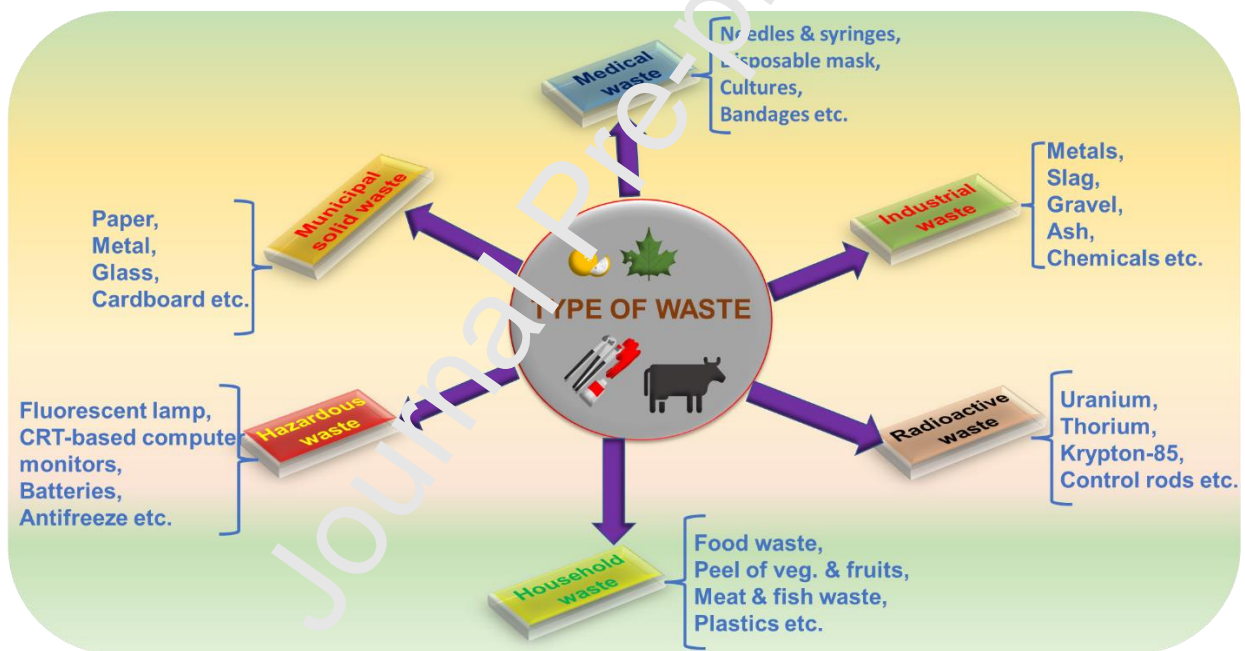


Fig. 3. Classification of different types of waste materials.

2.1. Municipal waste

Municipal waste is commonly known as municipal solid waste (MSW), garbage and trash. The major constituents of municipal waste are plastic, paper, food, cardboard, glass etc. Further, the waste thrown by the public everywhere is known as MSW. Commonly the MSW

is produced in houses, hospitals and schools. This massive increase in MSW required more attention toward reducing, using, and decreasing terrible environmental effects by adopting a waste management process (Siwal et al., 2022). The measurement of municipal waste management with their method and decisions over the ecological life cycle assessment process is used (Zhang et al., 2021). For environmental and socio-economic benefits, researchers worldwide are dedicated to new technologies that help reduce waste and manage produced waste. Using unique techniques, we can convert SMW into valuable products. These techniques may include anaerobic digestion, pyrolysis of waste, incineration or burning, gasification, production of biofuels etc., that convert MSW into value-added products and alternative energy sources (Rajendran et al., 2021). In MSW and municipal wastewater, harmful viruses like SARS-CoV-2 were also found. So, there is the threat of transmission of SARS-CoV-2 by pollution to humans (Anand et al., 2022; Siwal et al., 2020). MSW can produce energy by breaking C-H-O bonds due to the presence of organic materials in MSW (Noor et al., 2020). Various types of MSW in an urban area are shown in **Fig. 4**.



Fig. 4. Various types of municipal solid waste.

2.2. Agricultural waste

Agricultural waste mainly consists of crops, fruits, dairy materials, vegetables, fish farms, poultry farms, etc. Waste from animals like manure, dung and crop waste like sugarcane bagasse, straw of corn, and paddies with toxic chemicals like insecticide, weedicide, and pesticide, which causes environmental problems, also come in the category of agricultural waste. This agricultural waste is mainly found in the developed area (Gaur et al., 2020; Kaur et al., 2022b). The amount of agricultural product is directly proportional to agricultural waste, like the residue of crops and its by-product. On average, about 998 million tons of waste materials are produced via agriculture (Noor et al., 2020). This total solid waste contributes approximately 80% of complete organic waste materials. Manure production is 5.27 kg/day/1000 kg live weight. The fibres considered agricultural waste are beneficial as they are used as building materials, decoration materials and many more worldwide. This is

much contributed to the world economy and cultural implications. Waste fibres are used because they are more economical, eco-friendly, easily available, and have high-strength properties. The large amount of biomass produced from agricultural waste is used as raw material in many biomedical and bio composites industries (Reshmy et al., 2022). The classification of different types of agricultural waste is shown in **Fig. 5**.

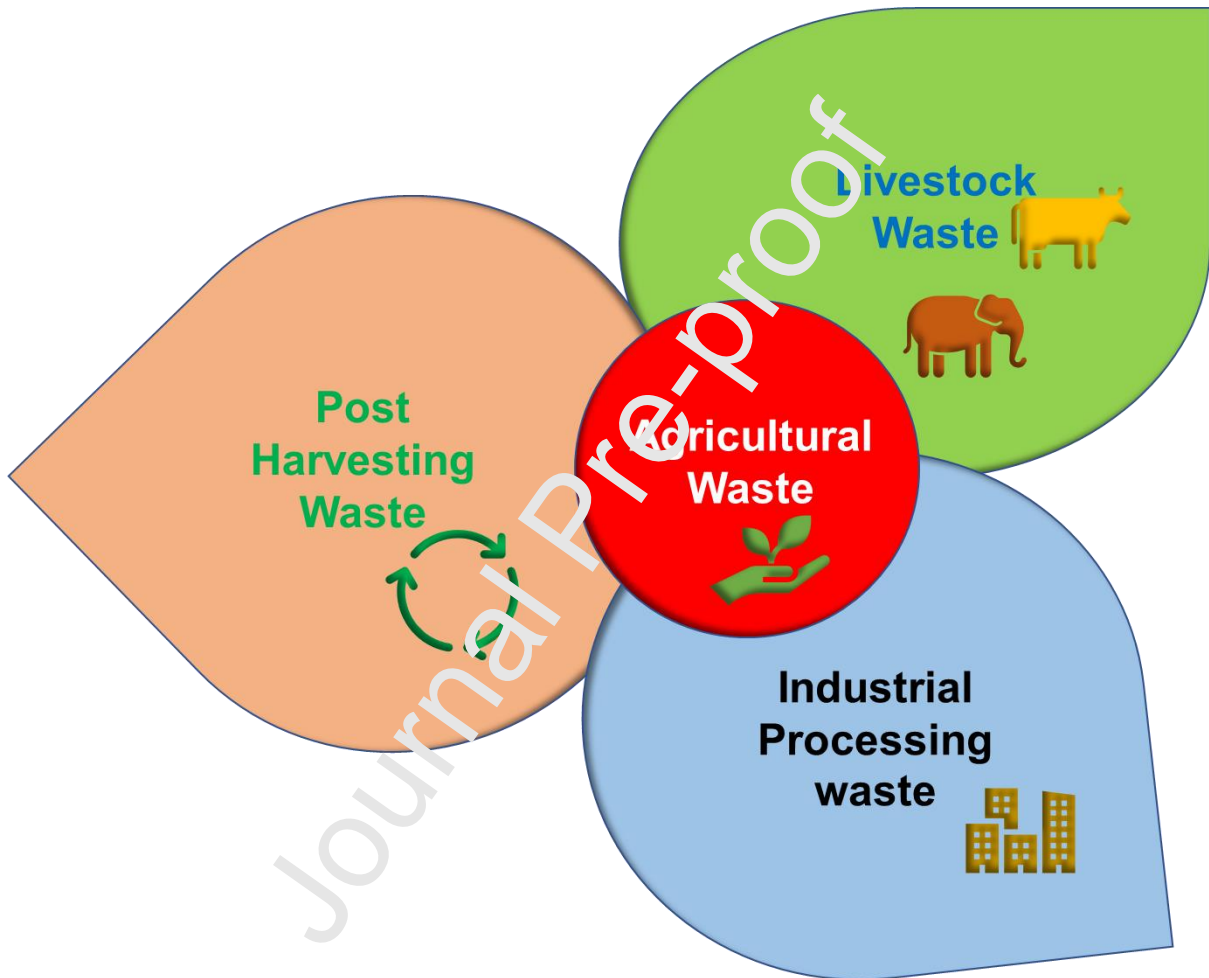


Fig. 5. Different types of agricultural waste.

2.3. Industrial waste

As we move toward a luxurious status, we use many things to make our life easy. Using these things is harmful and has a toxic effect that creates environmental pollution and is unsuitable for human health. The industrialisation rate increases rapidly, producing many industrial wastes like chemicals, plastics, E-waste etc. These wastes are risky for humans and create

health issues (Prabakar et al., 2018; Siwal et al., 2021a). Managing industrial solid waste is also required as it creates soil, air and water pollution. These industrial wastes are mainly waste residue, fuel residue, smelting waste, ore mining waste, fly ash, medical waste, battery waste, etc., produced during industrial production (Cai et al., 2018).

Some industrial waste may also contain heavy metals and, if not disposed of properly, may cause metal contamination and lead to severe environmental and human problems. Some metals are also cancer-causing in nature with a long degradation time. Heavy metals like Au, Mo, Ni, Ag, Cr, Cu, Zn etc., are mainly present in solid industrial waste (Canda et al., 2016). As the world population rises, food demand also increases, leading to an increase in agro-industrial waste. To solve this problem, many technologies like supercritical fluid extraction, ultrasound-assisted extraction and microwave-assisted extraction are developed, which are eco-friendly and give products with higher added value for distribution in chemical industries, food industries and pharmaceuticals (Freitas et al., 2021). Various types of industrial waste are tabulated in **Table 1**.

Table 1. Various types of industries with its waste materials.

Industries	Type of waste
Chemical Industry	Acid, base, wastewater with organic contaminants, spent solvents etc.
Construction Industry	Strong acids and bases, spent solvent, ignitable paint waste etc.
Printing Industry	Solutions contain heavy metal, ink sludge, with heavy metal, waste ink solvents etc.
Leather Industry	Benzene, toluene etc.
Metal Manufacturing Industry	Cyanide waste, paint waste, sludge etc.

Petroleum Refining Industry	Wastewater contaminated with benzene, hydrocarbon sludge etc.
Paper Industry	Waste of paint, ignitable solvents etc.

2.4. Household waste

The waste materials we generate in a locality like homes, schools and offices collected by local management called Nagarpalika/Gram Panchayat for disposal purposes are called household waste. Household waste includes that undesirable objects which arise in a home: discarded goods like furniture, clothes or toys; used packaging materials; unconsumed food; waste from the garden, peels of fruit and vegetables; bits of paper etc. Household waste needs more attention due to its high visibility and daily production by everyone. This problem can be overcome if we create some valuable products from biodegradable waste materials (Martin et al., 2006). Various types of waste materials from households are shown in **Fig. 6** (Akpan and Olukanni, 2020).

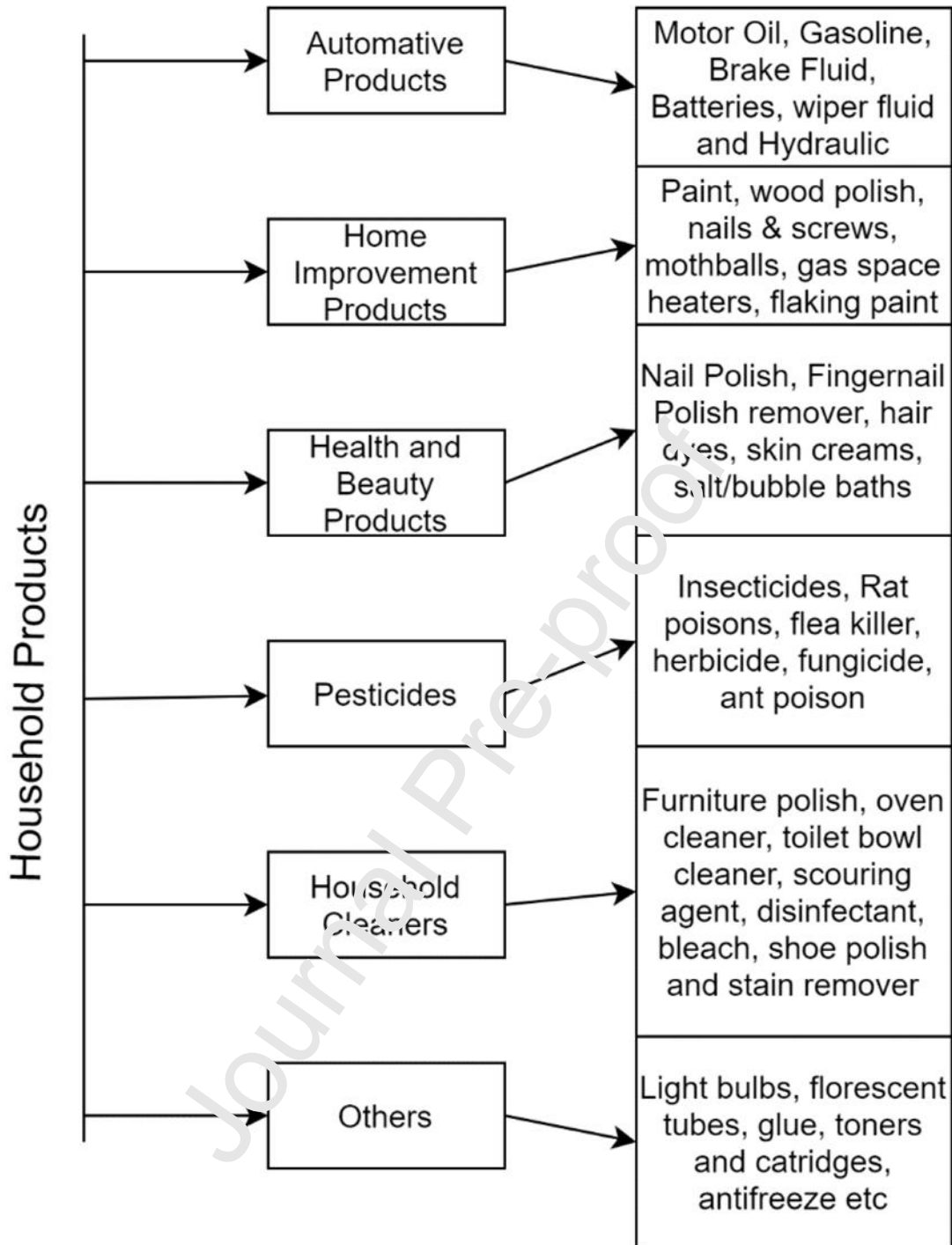


Fig. 6. Classification of household waste materials. Reprinted with permission from Ref. (Akpan and Olukanni, 2020).

3. Waste management, current glitches and their expected solutions

The above-discussed wastes harm the ecosystem and create air, water and soil pollution. The removal of this waste is helpful in the improvement of qualities of air, water and soil. For this

purpose, we need some eco-friendly, cost-effective methods to remove these pollutants from the ecosystem. Nowadays USA, China and India are the top three producing countries of MSWs. These MSWs are managed by recycling, composting, anaerobic digestion, landfill method etc. Out of these approaches, landfill is the most relevant process for managing MSWs in which waste materials are buried inside the soil at its site, which was formerly diagnosed by municipal authorities. This is further utilised in waste-to-energy processes (Nanda and Berruti, 2021). In addition, biotreatment of biodegradable solid waste was done by anaerobic respiration to give biogas and compost. Another method is incineration, which is used for combustible solid waste, which produces some carcinogenic and toxic materials. Reducing, reusing, and recycling (3R) is another suitable solid waste management method (Hamer, 2003).

Agro-industrial waste is another material that includes manures, hulls, bedding, vegetable matter, plant stalk, wheat and rice straw etc. These waste materials are generally biodegradable in nature; hence, some are converted into biofertilizers, biogas, organic manures, etc. Using different processes, i.e., dark-fermentation, photo-fermentation, direct and indirect bio-photolysis, thermal cracking, enzymatic hydrolysis, transesterification, micro-emulsion, anaerobic digestion etc., agro-industrial waste are converted into bioenergy (bio-hydrogen, biogas, bio-methane, biodiesel, bioethanol etc.) (Nair et al., 2022). Further, Chin *et al.* (Chin et al., 2022) fabricated green cement bricks by using agro-industrial waste.

Managing household waste involves many steps, like Waste collection, Garbage collection, Waste removal, Garbage transportation, and Waste processing (Ghose et al., 2006). The best suitable option for managing household waste is their segregation into degradable and non-biodegradable waste. On the other hand, the industrial waste contains many harmful chemicals, heavy metals and toxic substances and therefore, a proper disposal is required. For this purpose, some novel initiatives were taken by some countries, like Valmet's indirect

gasification plant, established by the Austrian organisation Repotec, which produces bio-fuel (Shahabuddin et al., 2020). Further, we need some cost-effective and eco-friendly methods for household waste disposal. In this manner, researchers investigate some reliable approaches for waste circulation. These methods are hydrothermal carbonization, anaerobic digestion, dendro liquid energy and ultrafast hydrolysis, which produce biofuels, fertilizers, energy and other materials (Bhatia et al., 2023). **Fig. 7** shows various novel, cost-effective, environmentally friendly waste disposal techniques.

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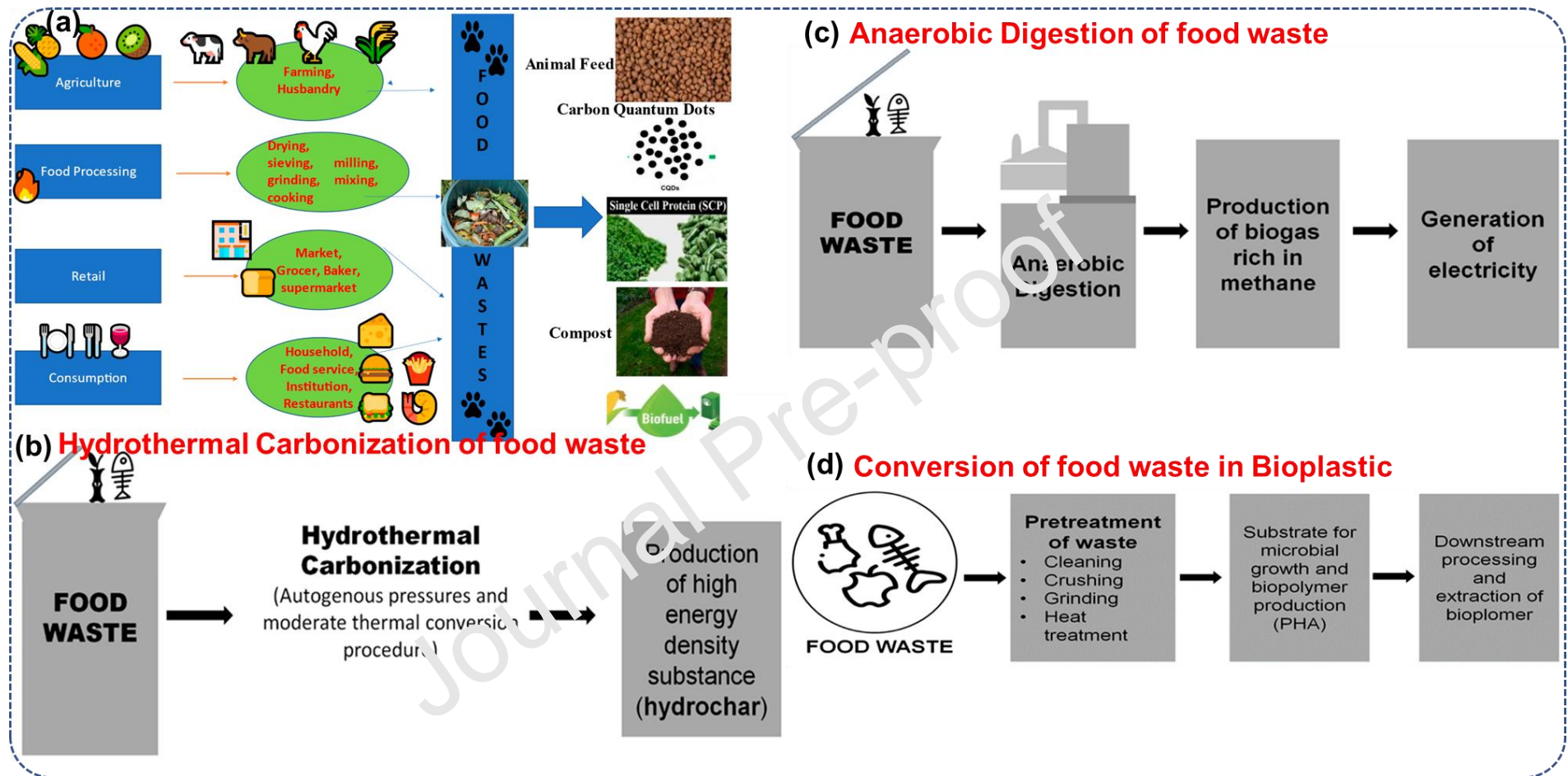


Fig.7. (a) Commercial use of food waste obtained from different sources, (b) Hydrothermal carbonization process, (c) Anaerobic digestion process of food waste, (d) Conversion of food waste into bioplastic. Reprinted with permission from Ref. (Bhatia et al., 2023).

Efficient utilization of bio-waste is necessary to complete the circular economy circle within the chemical enterprise. New technological advancements in waste processing remove the potential of bio-waste as a chemical raw material. Considerable improvement has been made in bio-waste processing and within the valorization of bio-waste to various mixtures. Bio-waste cannot be appropriate for producing commodity chemicals owing to sparse dispersal, geographical variety and complicated arrangement, whereas it is a proper raw material for hub and fine chemicals. To combine bio-waste within the existing reserve chain bio-waste processing facilities should be completed close to bio-waste resources and manufacturing zones of the fine chemicals (Guo et al., 2019).

However, a few factors of procedure intensification and removal of process efforts would obtain further uses and should develop catalysts adapted towards the specific issues and syngas design; the basic understanding and technologies to use this solution present. Short-term exploitation is thus feasible, and this idea report will facilitate this opportunity, essential for promoting a circular economy (Iaquaniello et al., 2018).

Waste-to-chemical (WtC) processes have gained significant attention as a sustainable waste management and resource recovery solution. However, like any emerging technology, WtC processes have challenges or glitches. This article will explore some of the current glitches associated with WtC processes and their potential solutions.

1. Variability and Complexity of Feedstock: One of the challenges in WtC processes is the variability and complexity of the feedstock. Waste streams can vary significantly in composition, moisture content, and contaminants, which can affect the efficiency and reliability of WtC processes. Furthermore, the complexity of waste feedstock can result in challenges in process design, scale-up, and operation.

Solution: To address this challenge, thorough characterization and pre-treatment of the waste feedstock are essential. Detailed waste composition and properties analysis can help develop tailored processing strategies and optimize process parameters. Pre-treatment techniques such as sorting, shredding, and drying can also be employed to standardize the feedstock and reduce variability, ensuring consistent and reliable processing.

2. Energy Requirements and Environmental Impacts: Another challenge in WtC processes is the energy requirements and environmental impacts of converting waste to chemicals. Some WtC processes require high energy inputs for waste processing and conversion, which can offset the potential environmental benefits.

Solution: One solution is integrating WtC processes with renewable energy sources such as solar, wind, or bioenergy to reduce the overall environmental impact. The process of optimization and heat recovery techniques can also be employed to minimize energy consumption and maximize energy efficiency. Life cycle assessment (LCA) can also be used to evaluate the environmental impacts of WtC processes and guide decision-making towards more sustainable options.

3. Technical Feasibility and Scalability: The technical feasibility and scalability of WtC processes can be challenging due to the complex chemistry involved and the need for specialized equipment and infrastructure. Scaling up from laboratory to pilot or commercial scale can result in technical uncertainties and economic risks.

Solution: Close collaboration between academia, industry, and policymakers is crucial to address the technical challenges and scale-up issues associated with WtC processes. Investment in research and development, pilot-scale testing, and demonstration projects can help validate the technical feasibility and economic viability of WtC processes. Furthermore,

policy support, incentives, and regulations can promote the adoption of WtC technologies and facilitate their scalability.

4. Product Quality and Market Demand: The quality of the chemical products derived from WtC processes can be challenging, as they may need to meet specific standards and market demand. The market for waste-derived chemicals is still evolving, and there may be uncertainties in product pricing, market acceptance, and need.

Solution: Collaborations with end-users, market analysis, and market-oriented product development can help address the challenges associated with product quality and market demand. Engaging with potential customers and understanding their requirements can guide the development of waste-derived chemicals with the desired quality and performance. Diversifying product portfolios and identifying niche markets can also mitigate market risks and uncertainties.

5. Regulatory and Social Acceptance: Regulatory frameworks and social acceptance can pose challenges to WtC processes, as they involve handling and processing waste materials, which may raise concerns about safety, health, and environmental impacts. Obtaining regulatory permits, complying with waste regulations, and gaining social acceptance can be time-consuming and challenging.

Solution: Collaboration with regulators, public engagement, and stakeholder involvement is essential to address regulatory and social acceptance challenges. Demonstrating the safety and environmental benefits of WtC processes through robust risk assessment, monitoring, and communication can help build public trust and gain regulatory approvals.

4. Concept of green chemistry

Green chemistry is defined as the branch of chemistry that deals with the synthesis of eco-friendly chemicals which decrease the rate of environmental pollution, also known as green

chemicals. In this chemistry, the starting materials are less toxic or non-toxic and renewable in origin. The formation of non-hazardous by-products is also the main agenda of green chemistry, leading to less environmental pollution. Nowadays, research is devoted to fabricating new green chemicals and developing green chemicals from pre-existing materials like chemicals, waste materials, etc. (García-Serna et al., 2007). Green chemicals are chemicals that show good functionalities without any harmful impact on the environment or are environmentally friendly throughout their life cycle, known as green chemicals. These green chemicals are designed by considering the twelve principles of green chemistry. For example, green solvents like methanol, ethanol (Capello et al., 2007), water, bio-succinic acid, green plastics, bio-fertilizers, etc. The need for these green chemicals arises due to some misshaping's like Itai-Itai disease (Kubota, 2020), Minamata disease (Aoshima, 2022), Bhopal gas tragedy (Hanley, 2021) etc., which is due to the release of the deadly chemicals.

Further, green chemistry believes in preventing waste despite removing waste materials and producing such chemicals that are not harmful or not toxic for humans, animals, and the environment. Green chemistry has approximately 12 principles, and they are successfully used in various government policies, industry management, the education sector, and technology development worldwide. The 12 principles of green chemistry are briefly explained in **Fig. 8**.

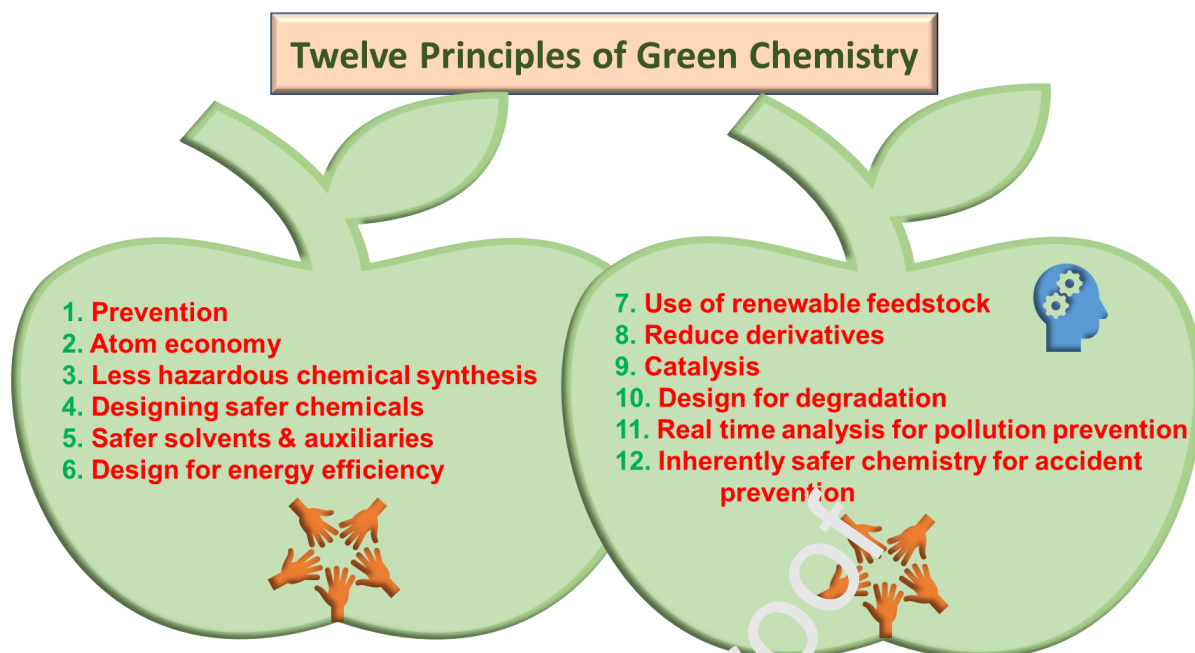


Fig. 8. Twelve principles of green chemistry.

The circular economy aims to maintain the balance among sustainability of the resource, economic growth and protection of the environment, as shown in **Fig. 9**. It also provides a route for sustainable development from the applications of environmental evaluation. It validates the recyclability of novel chemicals (Chen et al., 2020).

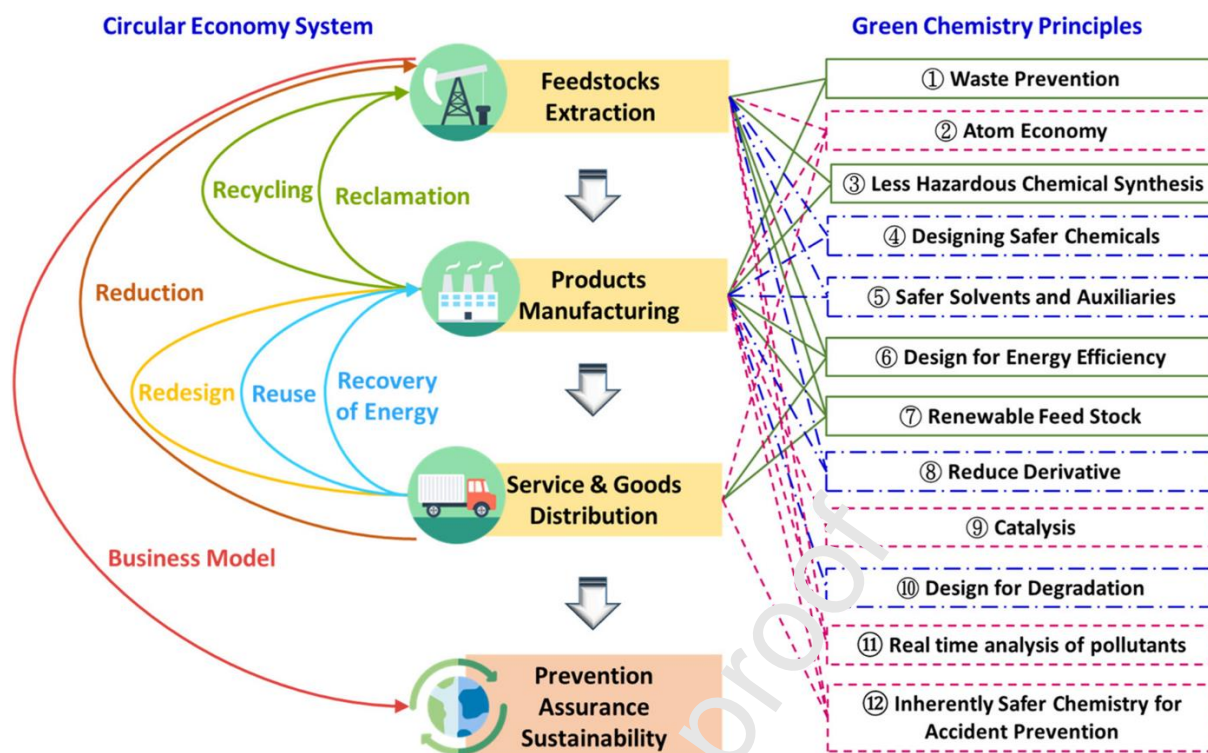


Fig. 9. The structure framework of circular economy and green chemistry principle in the whole life cycle. Reprinted with permission from Ref. (Chen et al., 2020).

Going through all these concepts, we have a huge waste management problem. Keep it in mind, further relating it with green chemistry. Additionally, we will discuss converting waste materials into green chemicals through a circular economy. This will also be useful in bioeconomy markets.

5. Conversion of waste into chemicals

In today's developing era, due to human activities, waste increases which badly affects the ecosystem and human health. Therefore, everyone must safely dispose of waste materials by recycling them or converting them into biodegradable materials. The quality of the environment is degraded day by day. To solve this situation, researchers work day and night to convert these waste materials into value-added products by recycling them and using clean methods by integrating waste materials to return to nature. There is no doubt that using waste materials not only solves the waste disposal problem but is also helpful in solving problems

related to environmental pollution (Siwal et al., 2023). Awareness regarding waste management is improving day by day globally for ecological sustainability and conservation. Only the help of green chemistry can do this. Much more expenses are required to commercialise these technologies. However, implementing it can solve many environmental and human health problems by providing future dimensions (Zainudin et al., 2022). In contributing toward green chemistry and keeping this in mind, the more relevant procedure is converting waste into chemicals. This technology deals with the practical use of the carbon content of MSW or other waste materials, providing an excellent chance to manufacture and distribute chemicals with low carbon content. This also helps reduce fossil resources as raw materials (Iaquaniello et al., 2018). In this manner, waste management occurs through the production of green chemicals.

5.1. Waste to biofuels

As the world's energy consumption increases daily, this leads to decreased fossil fuel. On the other hand, fossil fuel combustion releases toxic substances into the environment. Primary emission of carbon dioxide increases global warming. In this manner, there is a need to develop renewable and sustainable energy sources. Bioethanol, biogas, and biodiesel have been considered the most prominent alternative to fossil fuels as they act as carbon-neutral fuels. Biogas is produced from organic waste materials as raw materials, leading to waste management (Mishra et al., 2023).

Further, sugarcane bagasse, paddy straw, and other edible crop straw are used to produce biodiesel and bioethanol. The production of bioethanol is also done by cattle manure. The overall production of biofuels from organic waste materials and livestock is shown in **Fig. 10** (Jung et al., 2021).

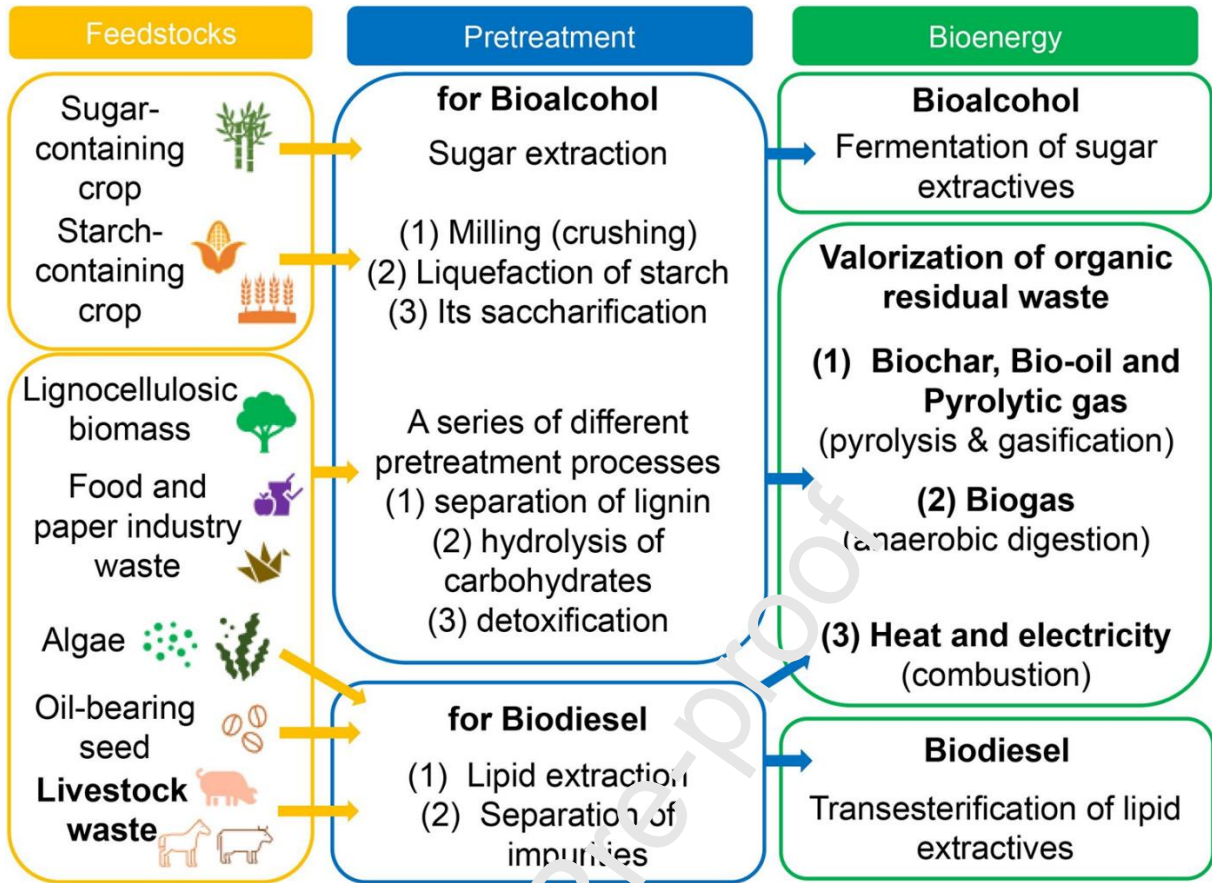


Fig. 10. Production of biofuels from organic waste materials and livestock. Reprinted with permission from Ref. (Jung et al., 2021).

On the other, the accumulation of plastic waste also increases day by day. Thus, the disposal of plastic waste nowadays has become a challenge. Other solid biomass is also much more abundant and more affluent in energy. The mixture of this solid biomass and plastic waste can be converted into biofuel and some other value-added products by the co-pyrolysis process. In this manner, these products can be used as chemicals and sorbents of pollutants. In this manner, they act as an eco-friendly substitute for waste management and sustainability (Wang et al., 2021). The fast co-pyrolysis of paulownia wood and polyethylene terephthalate (PET) was studied by Chen *et al.* (Chen et al., 2017a) and observed synergistic behaviour in thermal nature and gas product. The increase in biochar is observed in mixing.

Further co-pyrolysis of PET with solid biomass like a stalk of cotton, sunflower residue, hazelnut shells and *Euphorbia rigida* was done in a fixed bed reactor, and it was found that some products in the form of gas, liquid and char were obtained (Çepelioğullar and Pütün, 2014). Chen *et al.* (Chen et al., 2016) reported co-pyrolysis of waste newspaper and high-density polyethene to know the synergistic behaviour from oil characterization and improved yields of alcohols and hydrocarbons (Chen et al., 2017b). Biofuels are the source of energy. The techniques which convert waste materials into fuels are known as waste-to-energy (WTE) technologies. WTE technology produces biogas (carbon dioxide, methane), liquid biofuels (biodiesel, ethanol), syngas ($\text{CO}+\text{H}_2$), etc., from waste which is further converted into electricity (Fatih Demirbas et al., 2011). Several processes are used in the WTE process for converting waste into chemicals, as shown in Fig 11.

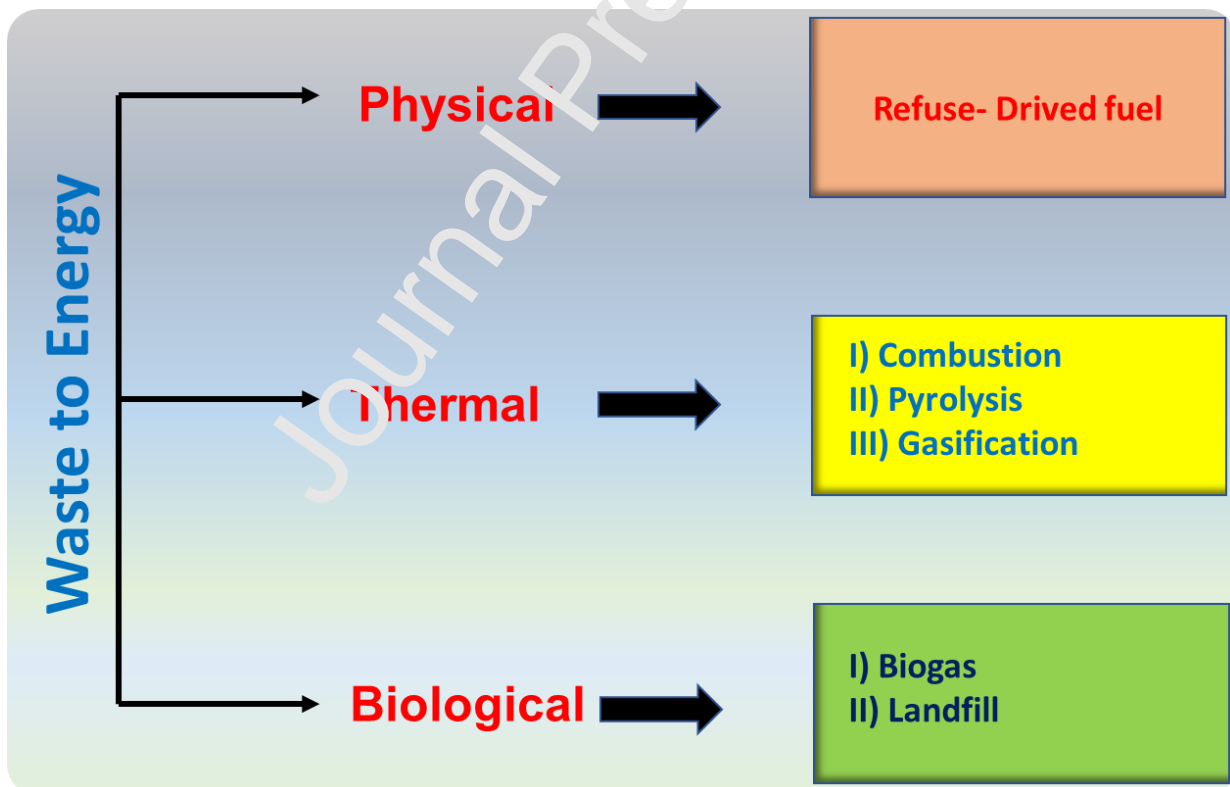


Fig. 11. Various WTE technologies.

As we know that liquid biofuels are classified into many categories, one is biodiesel, and another is vegetable oil, bio-alcohols etc. (Demirbas, 2009b). Generally, biodiesel is manufactured by the transesterification process. Using an acid-catalysed transesterification reaction, Wang *et al.* (Wang et al., 2006) prepared bio-methanol from waste cooking oil. In this process, H_2SO_4 act as a catalyst. During the procedure, 97.22% of free fatty acid from waste cooking oil was converted into fatty acid methyl ester. Similarly, in another study, using a supercritical methanol transesterification process and KOH as a catalyst, 99.6% pure fatty acid methyl ester is prepared from waste cooking oil (Demirbas, 2009a). By the hydrolysis of agricultural waste like rice straw, bagasse etc., as raw material, acetone-butanol-ethanol is synthesized by using *Clostridium beijerinckii* P260 (Qureshi et al., 2007) and *Clostridium saccharoperbutylacetonicum* (Soni et al., 1982).

Biogas can also be obtained by anaerobic digestion of organic substances of MSW. In this process landfill process of MSW is used. Landfill mainly contains methane and carbon dioxide gas (Demirbas, 2006). The cost of biodiesel with its separation process was minimized by using heterogeneous catalysts during biodiesel production. A novel heterogeneous catalyst, ZnCuO/N-doped graphene, was fabricated using a straightforward mechanochemical approach. This catalyst prepared biodiesel via waste cooking oil (WCO) transesterification in methanol. The WCO transesterification was highly accelerated by ZnCuO/(30 %)NDG catalyst up to 97.1%. The reaction time is 8 hours at 180 °C with 10 wt% catalysts, and the molar ratio of methanol and water in this reaction is 15:1. The main advantage of this experiment is that catalyst is recovered and reused for up to six cycles without loss in activity. The complete process of heterogeneous catalyst-based transesterification of WCO to produce biodiesel is shown in **Fig. 12** (Kuniyil et al., 2021).

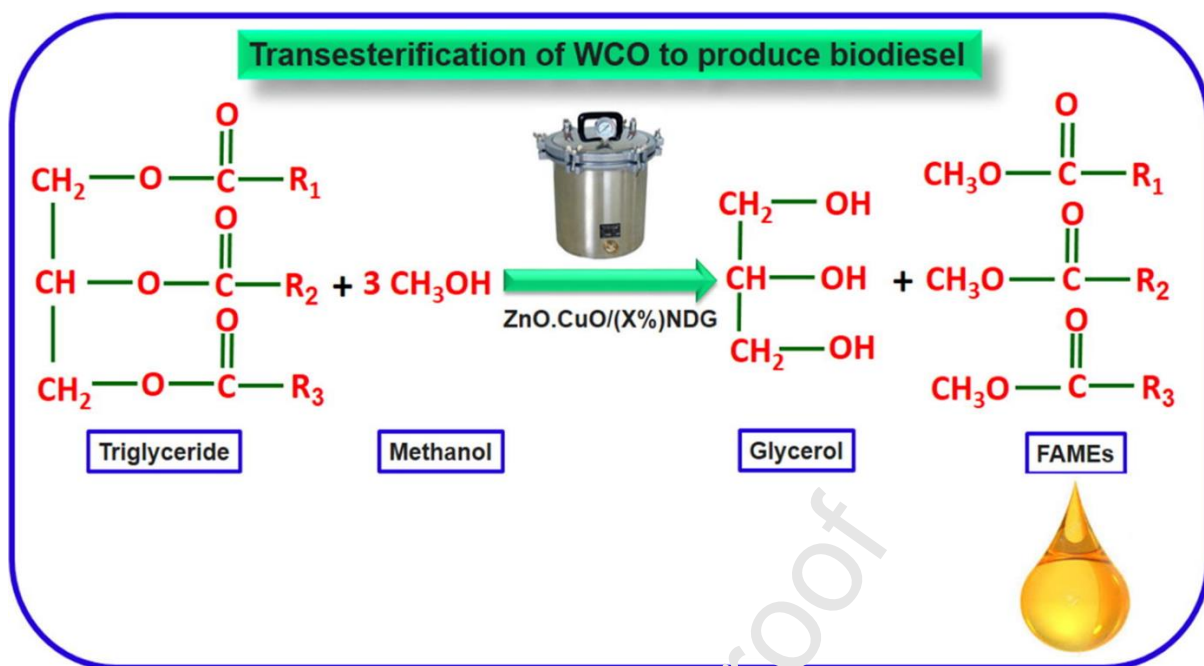


Fig. 12. Diagrammatic representation of WCO transesterification using heterogeneous catalyst ZnCuO/(X%) NDG to form biodiesel. Reprinted with permission from Ref. (Kuniyil et al., 2021).

The sustainability of manufacturing biodiesel requires proper survey or observation because it is the appropriate multi-purpose solution for the establishment of energy security, encouraging a circular economy, and also reducing pollution of the environment with food safety (Zhao et al., 2021). Further, the waste materials, mainly agricultural and industrial also used to produce bioethanol. Lignocellulose is present primarily in these types of wastes which contain cellulose, lignin and hemicellulose. In the future, lignocellulose will be the primary raw material for bioethanol production. Bioethanol production by lignocellulosic biomass mainly depends on the complex enzyme degrades the lignocellulose. The composition of used raw material significantly affects the production of bioethanol with micro-organism variety and fermentation conditions (Balat, 2011). In various developing countries like India, Indonesia etc., biogas production using animal waste is the most effective method to achieve the goals of sustainable energy development. In this way, waste-to-energy technology is also implemented. It was reported that in Indonesia, there are many

techniques developed by which waste of animals can be converted into biogas, and it was about 9597.4 Mm³/year of biogas. This hugely produced biogas from animal waste is used in producing electricity up to 1.7×10^6 KWh/year. The overview of this concept is shown in **Fig. 13** (Khalil et al., 2019).

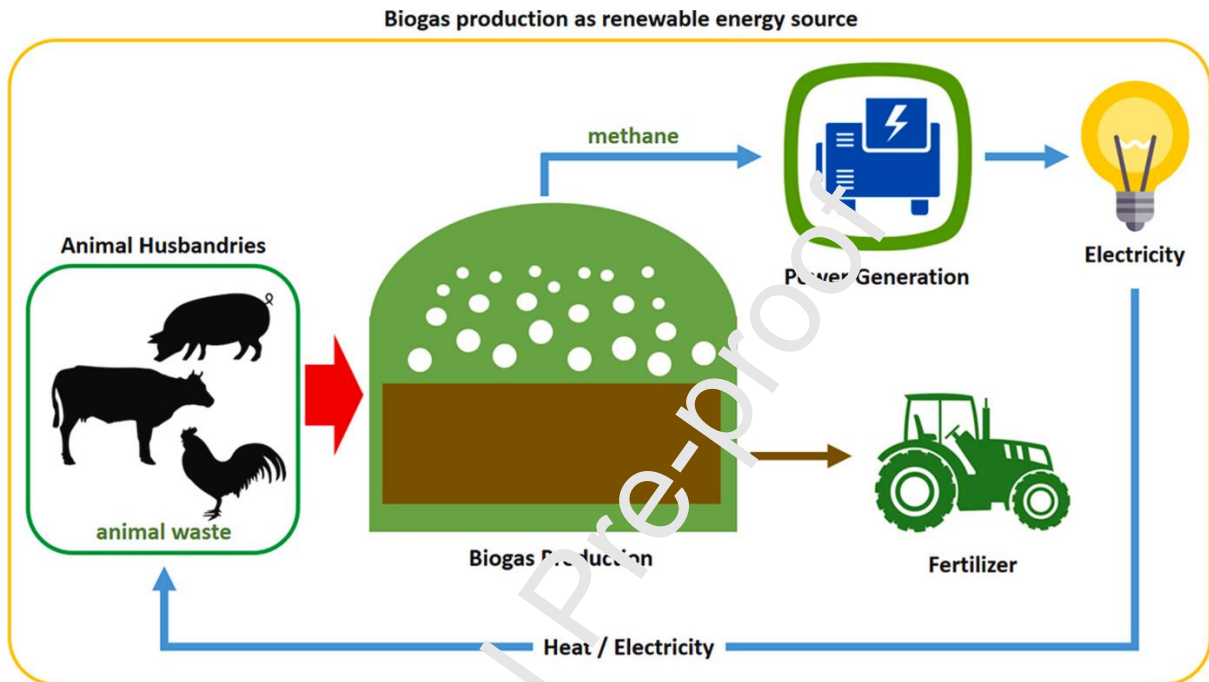


Fig. 13. Schematic representation of biogas production from animal waste. Reprinted with permission from Ref. (Khalil et al., 2019).

5.2. Waste to biofertilizer

The increasing use of chemical fertilizers for a long time has created many environmental complications with adverse impacts on animals and humans. It is come to know that about 10% of total greenhouse gas emission is due to these chemical fertilizers. Chemical fertilizers also spoil the quality of soil and crop productivity. Nowadays, biofertilizers are a suitable alternative in place of chemical fertilizers, which give sustainable products and contribute to bioeconomic markets due to less cost and easy availability. Biofertilizers consist of living micro-organisms that provide the required nutrient to the soil for crop growth without adversely affecting the environment.

Moreover, many researchers continuously work on producing and commercializing biofertilizers based on waste materials. For this purpose, organic materials are used; in this manner, the method becomes eco-friendly, and integrated waste management occurs. These organic waste materials are less costly and renewable (Sartori et al., 2021). The biofertilizers are classified on behalf of the micro-organisms they contain (Puglia et al., 2021). The micro-organisms like *Rhizobium*, *Azospirillum*, *Azotobacter*, Blue-green algae, and *Azolla* that fix atmospheric nitrogen for plants present in a biofertilizer known as Nitrogen biofertilizers (Sun et al., 2020). Kang *et al.* (Kang et al., 2011) advised that to avoid the environmental hazards related to P added to manure, it is significant to consider the disintegration of organic ingredients and the competition between P and dissolved organic C for the adsorption of anions. The micro-organisms that make P-soluble are shown mainly through *Pseudomonas* and *Bacillus*; fungi can proficiently convert insoluble P into soluble forms to make it readily available to plants by secreting organic and inorganic acids that modify rock phosphate and tricalcium phosphate in the soil. Moreover, various waste materials from Industry, animals, food and agriculture are used to prepare biofertilizers, but we need a reliable technique to make biofertilizers less expensive (Sun et al., 2020). Replacing chemical fertilizers with biofertilizers is the most appropriate method to recover nutrients from waste. This approach also reduces 30% the use of non-renewable resources (Mikula et al., 2020).

The primary source of lignocellulosic biomass is the plant and forest residue incorporated into a matrix of polylactic acid, while nitrogen is obtained from the manure of animals like pigs, poultry and cattle etc. these materials improve the fertility of the soil and hence increase the production of crop or help in the recovery of many substrates using anaerobic digestion (Chojnacka et al., 2020; Spiridon et al., 2018). The biogas CH_4 and CO_2 are mainly produced by the anaerobic digestion of agricultural waste and other organic waste and, as a by-product, produce digestate. This digestate is left behind rich in nutrients and used as a biofertilizer by

adding nutrition to crops (Alburquerque et al., 2012; Pezzolla et al., 2012). Over the Mediterranean area, olives are cultivated, so these areas are rich in olive mining waste. Olive mining waste contains a considerable number of organic materials. These organic materials are used to recover micro and macronutrients to get biofertilizers by composting (Gigliotti et al., 2012). The obtained compost of olive milling waste contains organic materials that are less soluble in water, lipidic, and phenolic compounds.

A less expensive phosphorous-rich biofertilizer was obtained using *Aspergillus niger* 1107, a phosphate-soluble fungus. For this purpose, the waste materials like cobs of corn, husks of wheat with perlite, peat, and composed manure of cattle are used by sterilizing it with gamma rays. During the experiment, 5.6×10^6 spores of *A. niger* were present in the soil before harvesting of Chinese cabbage when applied to it. The growth of cabbage plants accelerated by using this biofertilizer with the increase in the phosphorous amount in the soil (Wang et al., 2015). Tsai *et al.* (Tsai et al., 2007) convert waste of food materials into biofertilizers by using thermophilic and lipolytic microbes. The inoculation of microbes was increased by the breakdown of food waste, resulting in increased nitrogen amount with alfalfa seed germination. On the other hand, inoculation decreases the maturity period by improving biofertilizer quality. When the waste food is inoculated for 28 days with *Brevibacillus borstelensis* SH168, the amount of nitrogen and ash increases while crude fat with the C/N ratio decreases. The solid-state approach, also known as solid-state fermentation, is used to produce microbial metabolites by fermentation. In this process, the surface of the solid substrate having low moisture content is used, also the solid matrix absorbs the required water, providing oxygen to the growing micro-organisms. In the solid-state approach, the substrate may be sugarcane bagasse, rice hulls, rice and wheat straw, corn cobs, etc. (Srivastava et al., 2019). Solid-state fermentation is a heterogeneous process in three phases, i.e., solid, liquid and gas and eco-friendly in nature as it uses agricultural waste as a solid

substrate. This process converts agro-industrial waste into valuable products like biofuels, biofertilizers, enzymes, etc. (Costa et al., 2018). The solid-state approach to synthesizing useful products is shown in Fig. 14.

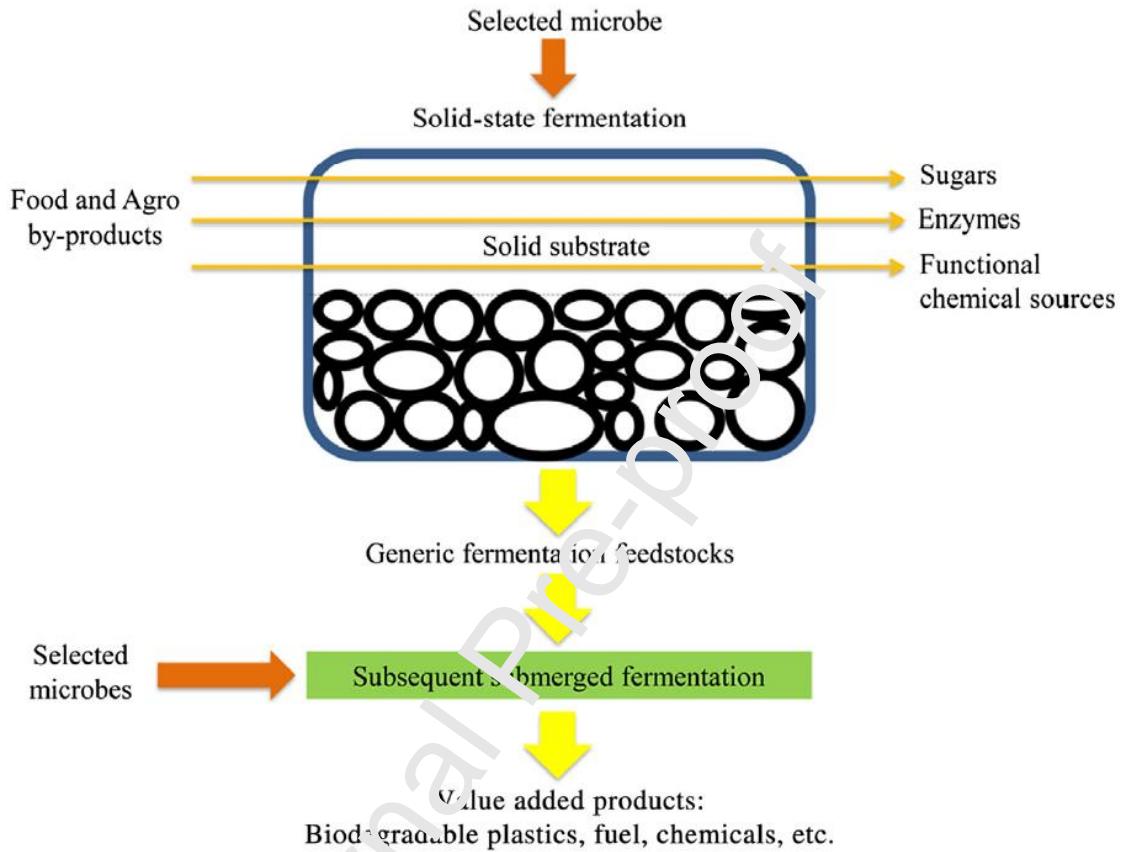


Fig. 14. Solid-state approach for the synthesis of value-added products. Reprinted with permission from Ref. (Srivastava et al., 2019).

Agricultural waste materials like pineapple, banana, watermelon, orange and papaya were fermented by solid-state approach to obtain biofertilizer. For the process, 500 g of waste was placed in a 2.5 L polyethene bag in 500 ml water. The above settle material is put at 298 K temperature; when the soluble product is formed, it is filtered. The filtrate is known as a biofertilizer. This is used as an accelerator for the next batch of fermentation. Of all the above-formed biofertilizers, banana biofertilizer has more potassium, about 3.932 g K/L. While papaya biofertilizer has 2.245, and watermelon, it is 1.529 g K/L potassium. Orange biofertilizer has a lesser potassium amount of 0.472 g K/L. These natural biofertilizers are

much more effective in increasing crop yield and are more economical. The weight of grains also increases with biofertilizers (Lim and Matu, 2015). The various applications of biofertilizers are shown in **Fig. 15** (Sartori et al., 2021).

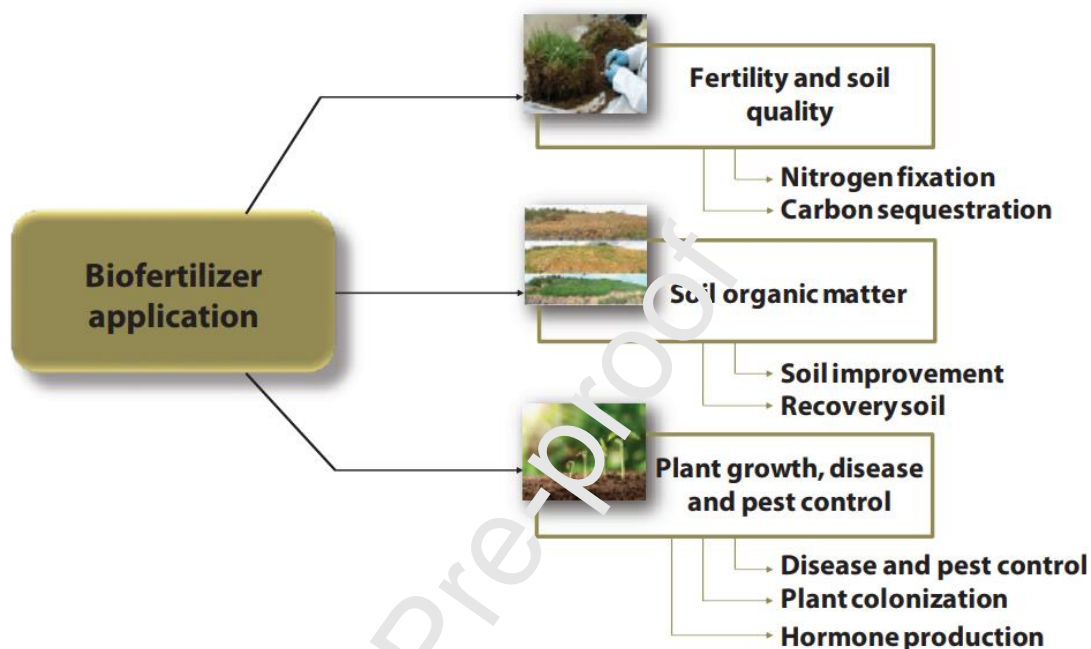


Fig. 15. The various applications of biofertilizers. Reprinted with permission from Ref. (Sartori et al., 2021).

5.3. Waste to green solvent*

Solvents define a significant part of the environmental performance of processes in the chemical industry also impact cost, safety and health issues. The idea of “green” solvents expresses the goal of minimizing the environmental impact resulting from the use of solvents in chemical production. The framework combines the assessment of substance-specific hazards with the quantification of emissions and resource use over the entire life cycle of a solvent (Capello et al., 2007). Green solvents are non-poisonous, not easily converted into vapours, biodegradable and recyclable. The synthesis of green solvents also needs less energy (Das et al., 2017).

Green solvents are classified into four groups i.e., supercritical fluids (SCFs) involving CO₂ and water, neoteric containing ionic liquids (ILs) and deep eutectic solvents (DESs), bio-based solvents like alcohol, ether etc. and supramolecular solvents. The classification of these green solvents is summarized in **Fig. 16**.

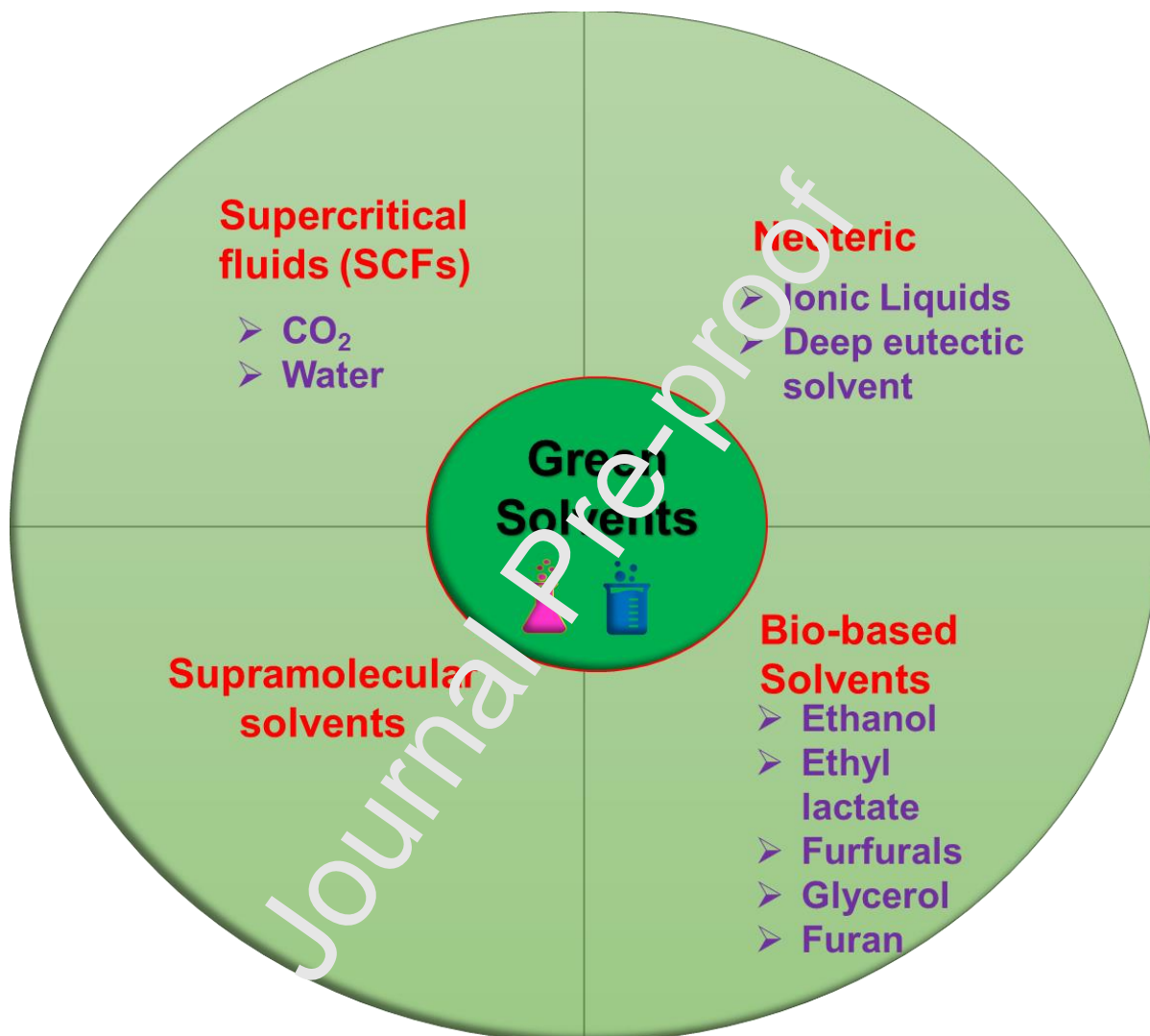


Fig. 16. Classification of various types of green solvents.

For SCFs, the temperature and pressure are more than their critical values (Cabeza et al., 2017; Knez et al., 2014). SCFs have properties like liquids (viscosity and diffusion) and gas (density and solvation). They are used in industry and scientific research to dye fibres, analyse polluted soil, product separation, micro and nano-sized powder production and various chemical reactions as solvents in place of organic solvents with biofuel production.

Out of CO₂ and water, water is more in use. Supercritical water and supercritical CO₂ are used for safety purposes and resolving health issues. These solvents are used in the extraction of various bioactive materials from waste, like phenolic compounds from grape seeds (Pérez et al., 2015), passion fruit seeds (Oliveira et al., 2017), and papaya seeds (Castro-Vargas et al., 2019) essential oil from orange peel (Xhaxhiu and Wenclawiak, 2015), phytochemical complexes from soya bean expeller (Alvarez et al., 2019), phenols from olive oil mill waste (Lafka et al., 2011), limonoid glucosides from grapefruit molasses (Yu et al., 2006), phytosterol from roselle seeds (Nyam et al., 2010), solanescrol from the waste of tobacco (Wang and Gu, 2018), and saponins from Agave salmiana bagasse (Santos-Zea et al., 2019).

Neoteric solvents have a completely new structure and unique physical and chemical properties that can be changed according to the application in which they are used by changing their chemical composition (Gutiérrez-Arnillas et al., 2016). ILs, DESs, and fluoruous solvents are paying more attention to this category. Fluorinated compounds like perfluoro hexane, perfluoro decalin, perfluoropolyether, etc., are the main constituents in fluoruous solvents (Matsuda et al., 2012). They are not mixed with water and organic solvents, hence known as the third liquid phase, and are used in various separation applications. Generally, ILs are made up of different cations and anions with melting points less than 100 °C (Henderson et al., 2011). ILs have unique properties like high chemical and thermal stability, minute vapour pressure, and the ability to dissolve inorganic, organic and organometallic materials with expansive electrochemical potential windows. ILs are used to extract various bioactive materials from agricultural and food waste like reducing sugar from the stalk of corn, and soybean hulls (Li et al., 2008), levulinic acid from the husk of rice (Khan et al., 2018), cellulose from husk of coconut (Zahari et al., 2018), lactic acid from wheat straw (Grewal and Khare, 2018), cotton seed cake and sugarcane bagasse tyrosol from olive mill wastewater (Larriba et al., 2016; Saha et al., 2017).

ILs sometimes cause environmental problems; to overcome this, DESs are used. In properties, they are similar to the ILs but more stable and accessible to prepare than ILs. DESs are eco-friendly and highly economical (Sattlewal et al., 2018; Zhang et al., 2012). DESs are mainly eutectic mixtures of Lewis or Bronsted acids and bases that contain various anionic and/or cationic moieties (Smith et al., 2014). They are generally formed by the complexation of a quaternary ammonium salt and a metal salt or hydrogen bond donor. DSEs have a lower melting point and lattice energy due to charge delocalization by hydrogen bonding. DESs used for extraction of biomaterials from organic waste like tools from crude palm oil (Abdul Hadi et al., 2015), genistin, genistein and apigenin from Pigeon pea roots (Cui et al., 2015), anthocyanins from wine (Bosiljkov et al., 2017; Radošević et al., 2016), and lignin from rice straw (Hou et al., 2018; Kumar et al., 2016) and anthocyanins from grape pomace (Panić et al., 2019).

Bio-based solvents are a type of solvent that are produced from renewable biomass sources like energy crops, aquatic biomass, products of forests and waste materials (Naidu et al., 2018). They are manufactured in a biorefinery (Vovers et al., 2017), targeting the highest recovery and manufacturing of high-added-value products. The most commonly used bio-based solvents are ethanol, ethyl lactate, furfurals, glycerol, furan, terpenes, levulinic acid etc. (Li et al., 2016). Firstly, bio-based ethanol was obtained from organic materials like sugar, vegetable oil, starch, animal fat etc. (Pandiyan et al., 2019). Yeasts like *Saccharomyces cerevisiae*, *Kluyveromyces marxianus* and *Wickerhamomyces anomalus* can change sugar into ethyl acetate (Kruis et al., 2017). In place of chlorinated hydrocarbons, ethyl lactate is used as a green solvent (Pighin et al., 2017). Bio-based solvents also utilize to obtain rosmarinic and caffeic acids from basil wastewater (Pagano et al., 2018a; Pagano et al., 2018b), polyphenols, ellagic acid, anthocyanins and flavonoids from peel of pomegranate (Masci et al., 2016), carotenoids and phenols from waste of tomato (Silva et al., 2019; Strati

and Oreopoulou, 2016), phenolic compounds, flavonoids and sinapine from rapeseed, mustard crambe and sunflower (Matthäus, 2002), oil from the bran of rice (Liu and Mamidipally, 2005), and volatile products from Cooperage woods for making of wine (Alañón et al., 2017).

Supramolecular solvents have nanostructures produced in colloidal suspensions of amphiphiles by natural, sequential phenomena of self-aggregation and coacervation (Caballo et al., 2017). Coacervation is a process in which “the differentiation into two liquid phases occurs in colloidal systems. Withdrawal of polyphenols from wine sludge (Chatzilazarou et al., 2010), saponins from sisal (*Agave sisalana*) waste (Kibiro et al., 2015), betaine from beet molasses (Mohammadzadeh et al., 2018), and anthraquinones from aloe peel (Tan et al., 2012).

6. Green chemistry toward sustainable development goals (SDG)

Sustainable development goals (SDGs) were projected for balanced development in the future; this aim is highly comprised of the idea of a circular economy, which can be completed using green chemistry principles (GCPs). Designing chemicals, manufacturing, and applications may be harmful and produce waste, which the GCPs aim to stop; for this purpose, the chemical development of materials and substances must be sustainable (Burgman et al., 2018). Green chemistry is also very economical to decrease the cost of storage and treatment with various environmental benefits (de Marco et al., 2019). Green chemistry also recommends sustainably obtained and renewable inputs, meaning ethical harvesting approaches and transparent origins. Green chemicals break down into harmless products or are converted into materials that can be used further to fulfil SDGs 6, 9, 12, and 14. The introduction of green chemistry livings, i.e., plants and animals are protected from toxic environmental chemicals, leading to SDGs 12, 15. SDGs also concentrate on the lesser potential for global warming, ozone depletion, and smog formation that are relevant to SDGs

number 11, 13, and 14, lesser or no chemical disruption of ecosystems that are relevant to SDGs number 12, 14, 15) and fewer use of landfills, mainly dangerous waste landfills related to SDGs 11, 12. The sustainable design consists of GCPs 4, which are directed to designing safer chemicals; GCPs 6, i.e., design for energy efficiency; and GCPs 10, which focus on design for degradation. The goods proposal should advance to remanufacturing, breakdown, and subsequent waste eradication (Robèrt et al., 2002). The environmental aspect is also responsible for the quantity of waste produced by dividing the total produced waste by the product mass (Mulvihill et al., 2011). These tools can also show the degree to which green chemistry helps attain exact SDGs. For the point of economy and business, SDG claims more product for chemical reactions that use a lesser quantity of feedstock to get equal yield relevant to SDGs number 9, 12.

7. Importance of green chemistry in the bioeconomic market

A new model was proposed for the economy in 2015, collaborating with “closing the loop- An EU action plan for a circular economy” (Mhatre et al., 2021). Now a day, the challenging aim is how to enhance the value of waste by using it in another sector and producing valuable materials. The main requirement for the growth of this proposed model to get a circular chain was finalized in which products with high value were produced from agricultural waste, co-products and by-products. The main objective is to use waste materials as raw materials and substrates and to give innovative value-added products (Diacono et al., 2019).

Bioeconomy is also toward the process of the low carbon economy. Nowadays, various industries work on the waste obtained from agriculture, forest, household, and SMW to convert them into valuable products and contribute to an economy based on biomass, extending the term bioeconomy. The bioeconomy mainly focuses on three aspects: i) much investment is made in research, innovation and skill, ii) strengthening of policy interaction,

iii) robustness in markets and competition in bioeconomy (Scarlat et al., 2015). An approach that uses organic waste as industrial raw material will move forward toward the era of bioeconomy. Further, circular economy helps in the expansion of markets that are based on green products. The food waste is converted into many products like antioxidants (Lima et al., 2022), microbial oil, biofertilizers and biogas (Haouas et al., 2022; Saba et al., 2023), enzymes, bioplastics (Sharma et al., 2021), pectin, biodiesel (Mahmoud et al., 2022) as shown in **Fig. 17** and contributes majorly to the bio-economy (Maina et al., 2017).

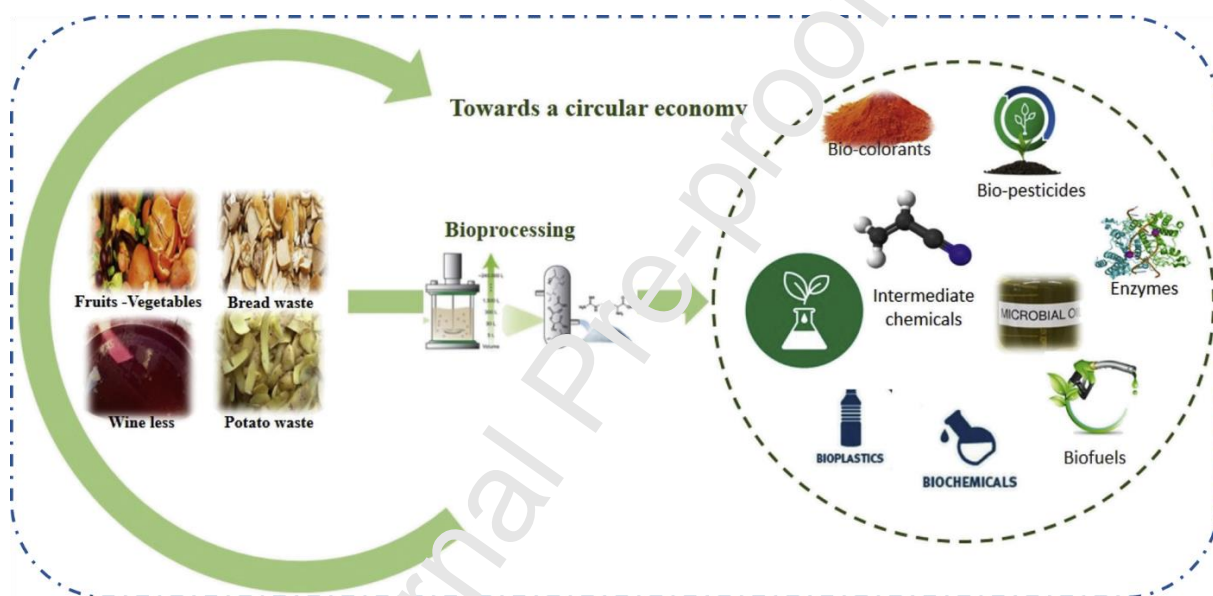


Fig. 17. Schematic representation of various obtained products from food waste. Reprinted with permission from Ref. (Maina et al., 2017).

The waste obtained from a lemon also contributes toward bioeconomy as it is used for the production of pectin as value added substance. Pectin is a natural hydrocolloid used in pharmaceuticals and food beverages as raw materials. Pectin is extracted from lemon peel through a microwave-assisted process utilizing green chemistry (Ciriminna et al., 2020). The bioeconomy is moving daily with bottom-up and top-down initiatives not only by one factor but also the mutual contribution and interaction among industries, science, society and stakeholders, as shown in **Fig. 18** (Wohlgemuth, 2021).

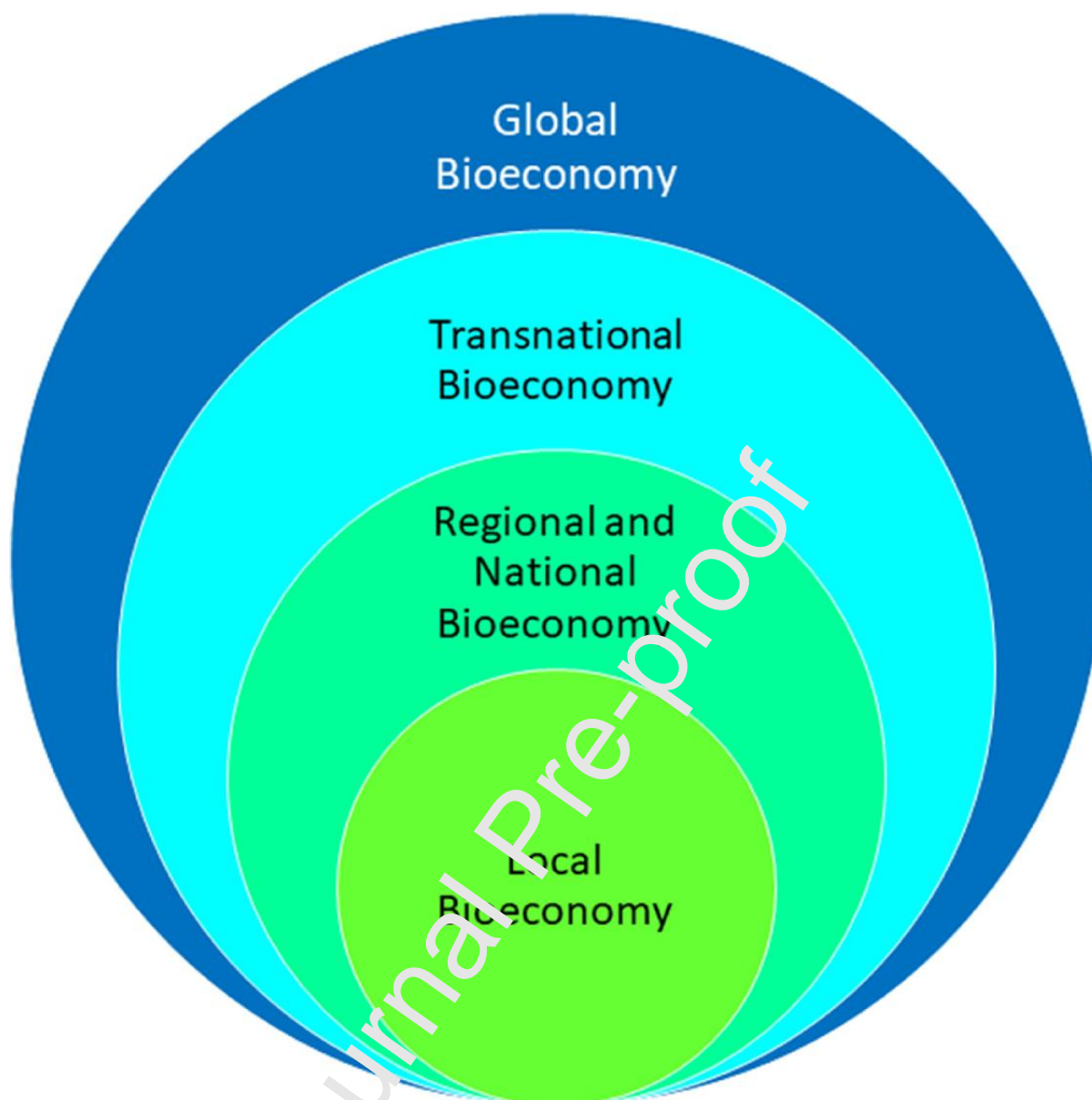


Fig. 18. The growth of the bioeconomy shows step by step. Reprinted with permission from Ref. (Wohlgemuth, 2021).

8. Conclusions and future outlook

In today's scenario, the human population increases, resulting in an increase in waste materials from their daily activities. Therefore, we need proper disposal methods of these waste materials using eco-friendly processes. There is another problem that creates environmental concern, i.e., the release of chemicals which are also harmful to the ecosystem. Green chemicals and chemistry are the best suitable option for overcoming these problems.

Using these waste materials to generate green chemicals contributes to the economy. For the safety of the human community, the safe recycling of this agro-agricultural waste is required. These include their conversion into energy, compost, bio-chemicals etc. Waste materials based on agriculture are the best suitable option to fulfil the needs of today's population without any compromise for our future generation. The present article deals with the detailed introduction of green chemicals and various waste materials used to prepare green chemicals, introducing green chemistry with waste management. The role of bioeconomy market in sustainable development is also discussed in this review article. More emphasis was given to producing biofertilizers, biodiesel, biogas, bio alcohols, antioxidants etc., from obtained waste materials. These green materials are eco-friendly and low in cost. The management of waste by producing green chemicals is the best suitable option. This is possible because waste materials are rich in nutrients as well as in carbon-based compounds. However, the waste materials obtained from various sources are not directly used for processing; they require pre-treatment. The pre-treatment methods of waste materials are very costly nowadays and use much energy. Thus, to implement or commercialize these techniques, we must discover cheap ways to treat waste materials so that the production cost is low. Further, converting materials obtained from agri-food production into valuable products is our long-term goal based on circular bio-economy and upcycling principles. This review article mainly focuses on recycling abundant waste materials and their diverse applications. This review also concludes that converting waste materials into valuable products solves the problem related to waste disposal and environmental pollution. Processing waste materials into useful products open a new gate for researchers and help decrease ecological concerns. For the first time, this article deals with converting waste into biochemicals based on the 12 principles of green chemistry. The role of the bioeconomic market in sustainable development is also discussed in this review, which opens a new door to research.

Declaration of competing interest

The authors declare no conflict of interest.

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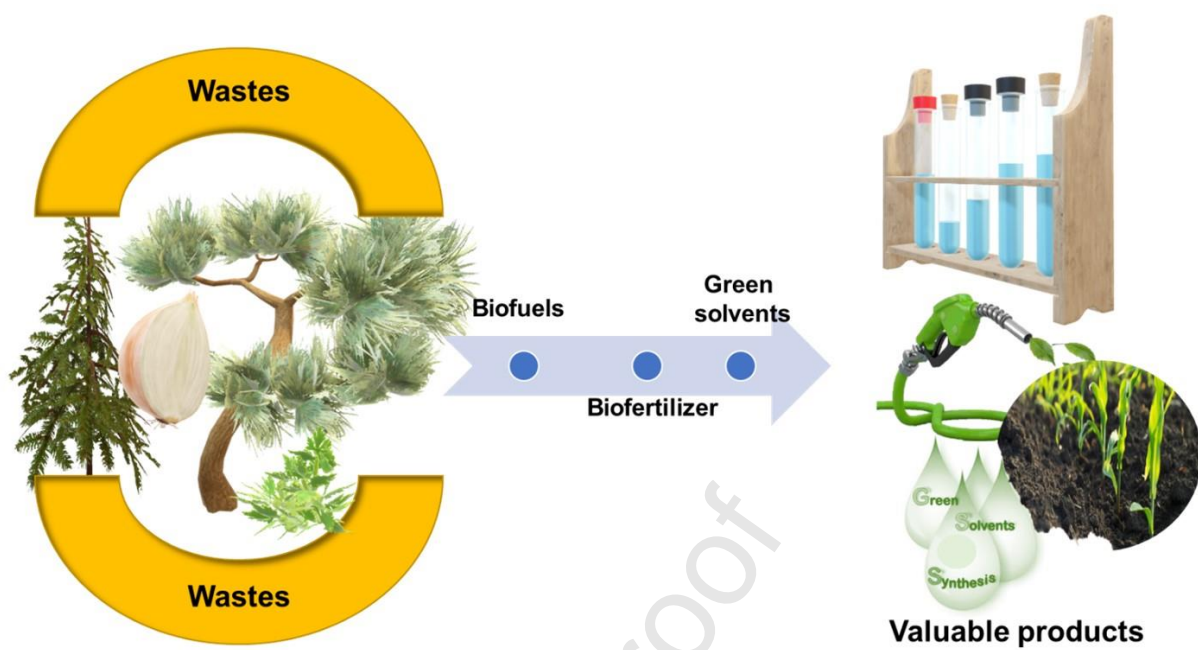
Credit authorship contribution statement

Kirti Mishra: Conceptualization, Methodology, Visualization, Writing - Original Draft.

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Journal Pre-proof



Graphical abstract

Highlights:

- The importance of waste to valuable products has been discussed more preciously.
- The role of the circular economy in green chemistry is discussed.
- The formation of various green value-added products is discussed.
- The contribution of waste materials in bioeconomy market is explained in detail.

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