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Valorization of plastic waste *via* chemical activation and carbonization into activated carbon for functional material applications

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Addressing the complex issue of plastic waste disposal requires a nuanced approach, as no single solution proves universally effective. This review advocates for a comprehensive strategy, combining mechanical recycling and chemical methods to manage plastic waste while emphasizing the transformative potential of carbonization and activation processes specifically. With a focus on chemical activation, this review explores the synthesis of high surface area activated carbon (AC) from diverse plastic sources including polyesters (*e.g.*, polyethylene terephthalate), polyolefins (*e.g.*, polyethylene, polypropylene), and non-recyclable thermoset resins (*e.g.*, epoxy, phenolics). The resulting AC products exhibit notable potential, with high surface areas exceeding 2000 m^2 g^{-1} in some cases. Furthermore, the adsorptive behavior of the plastic derived ACs are discussed with respect to common pollutants such as dyes and CO_2 in addition to emerging pollutants, such as micro/nano-plastics. Overall, this work highlights carbonization and chemical activation as important upcycling methods for plastic wastes that may otherwise end up in landfills or spills into the environment. Given the urgency of plastic waste disposal, it is recommended that the feasibility and scalability of plastic-derived AC production is explored in future work for the potential replacement of conventional AC feedstocks derived from coal or biomass.

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1. Introduction

The use of plastic products has been continuously increasing due to their lightweight, appealing cost structure, ease of processing, durability, and flexibility for various applications.[1] They are mass produced from hydrocarbons refined from petroleum, using coal powered plants resulting in large carbon footprints. Additionally, they do not biodegrade in the natural environment in a reasonable time frame. As a result, greenhouse gas (GHG) emissions from plastic production are rising in conjunction with plastic waste accumulation in landfills and spill to the environment accelerated by the quick disposal of most products after a single use consuming the global carbon budget.[2] Though plastics do not totally degrade in a short time, they can undergo fragmentation due to environmental factors causing the formation of microplastics[3] and even nano-plastics.[4] These highly mobile plastic fragments pollute marine environments, agricultural ecosystems, and other terrestrial and freshwater systems[4,5] which can affect drinking water sources. Therefore, the effective recycling of all plastics and alleviation of this pollution is a major topic of discussion.

Currently, common methods used for plastic waste management include landfilling, incineration, mechanical recycling, chemical recycling, and thermal cracking.[2] Recycling mainly refers to thermo-mechanical recycling, in which plastics are collected, sorted, cleaned, grinded, extruded and pelletized to form new products. This method helps extend the lifetime of plastics, but the resulting decline of product properties limits its continued product value. Both landfilling and incineration are also widely used disposal options but cause burdens on the environment due to the negative effects on soil environments and air pollution respectively. Thermal cracking to form fuels and valuable chemicals is a type of chemical recycling, which has received substantial interest, helps to reutilize plastics while favoring reduced emissions.[2] This review highlights an alternate method of reutilizing plastic waste by controlled carbonization to produce high value carbonaceous products. Carbonization differs from thermal cracking through pyrolysis as it focuses on the production of solid residue with high carbon content[1] as opposed to liquid or volatile fractions which are major pyrolysis products (oil and gas).[6] It can generate valuable products such as carbon nanomaterials, carbon fibers, adsorbents and energy storage devices.[1,2] A particular product of interest in this work is acti-

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vated carbon (AC), which is differentiated through additional activation processes to develop a high surface area.

Because the conversion of polymers to carbonaceous products has drawn attention in recent years, a variety of reviews have covered this topic. Chen *et al.* (2020) provided an overview of the types of carbonizations and the methods used for various plastics in addition to analyzing its feasibility as a plastic waste disposal process.[7] Another review by Gong *et al.* (2019) discussed the conversion of plastic waste to carbon but focused more on the production of carbon nanomaterials,[8] as was also the focus of a separate review by Zhuo *et al.* (2014).[9] Choi *et al.* (2022) covered the upcycling of plastic waste more broadly by addressing processes other than carbonization in addition to the applications of these products.[1] The content of this review is centered around the conversion of plastic into carbon-based products but with a focus specifically on the production of high surface area AC ideal for application as an adsorbent. Unlike the review by Choi *et al.* (2022), this work does not solely speak on the upcycling of plastic to carbon products but also touches on the existing recycling methods and where carbonization lies within this framework.

To highlight the need for alternative treatment options like carbonization, this work begins with a discussion of plastic recycling and upcycling methods in relation to key recycling challenges (section 2). Section 3 focuses on the carbonization of plastics, including the various carbon products obtained from plastic precursors and the pre-treatments necessary for the conversion. This is followed by an overview of the activation of plastics to produce high surface area AC (section 4) and an in-depth review of AC production from common plastics (section 5), with a focus on chemical activation processes. Some key applications of these plastic derived AC adsorbents are also reviewed in section 6 to emphasize the potential impact of these high-capacity products, followed by key future prospectives in section 7.

2. Recycling and upcycling of plastic waste

There are a variety of methods for reutilization of plastic waste, which generally can be categorized into recycling by mechanical methods, chemical methods and incineration for energy recovery. As shown in Fig. 1b, these can also be categorized according to ASTM D5033 definitions of primary, secondary tertiary and quaternary recycling. Primary recycling consists of mechanical recycling of products in a closed loop system, while secondary recycling is mechanical recycling into products with different purposes, often downgraded polymeric materials. Tertiary recycling refers to the use of waste polymers for generation of lower molecular weight materials such as monomers and valuable chemicals.[10] This depolymerization can be carried out by numerous chemical methods such as hydrolysis, ammonolysis, pyrolysis *etc*. For the purpose of this study, chemical recycling was divided into solvolysis methods used for monomer regeneration, and pyrolysis to produce oil and gas. Furthermore, carbonization was identified separately from pyrolysis because the production of carbon materials (mainly activated carbon) will be the focus of this review. Lastly, a final resort is the quaternary recycling of plastics by combustion with recovery of energy.[10]

Based on the breakdown of plastic waste disposal methods in the US (Fig. 1a), only a small proportion (5%) of plastic is recycled, although certain plastics such as PET are recycled at rates as high as 15%. This is due to the challenges associated with recycling, which will be discussed in this section and assessed with respect to the recycling methods outlined in Fig. 1b. Jung *et al.* (2023) outlined factors hindering recycling and upcycling of plastic waste. The major challenges include difficulty in the separation and classification of plastic wastes, variability of additives and coatings in various plastic streams, contaminations with food and other products, and the pres-

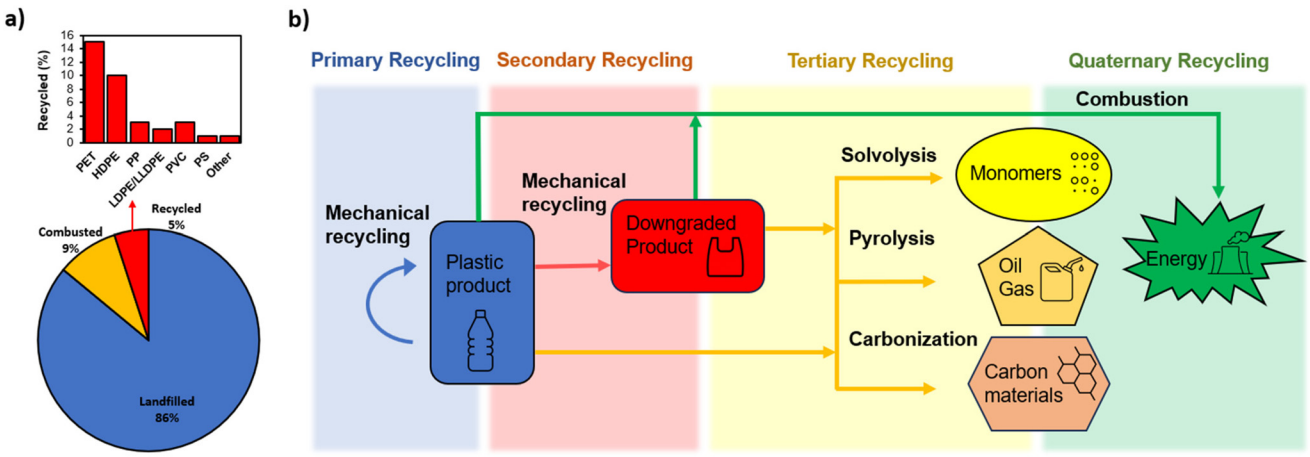


Fig. 1 (a) Breakdown of plastic waste management pathways in the US in 2019. Data obtained from ref. 11; (b) schematic of various plastic recycling methods which are discussed and compared.

ence of thermoset polymers, which are incapable to be melted or dissolved.[12] Therefore, the various recycling methods outlined in this section (Mechanical, solvolysis, pyrolysis, carbonization, and incineration) will be discussed in general and with respect to sorting issues, additives and contamination, and the processing of thermoset materials.

2.1. Mechanical recycling

The most widely employed recycling technique is the mechanical recycling by melt processing of used plastic waste to form new products. This is conducted through sorting, washing and drying, crushing and compounding. It is a relatively simple and economical recycling technique but is limited by various shortcomings. Mainly, the effects of heat, light, oxidation, and mechanical shear lead to degradation of plastic products during their lifetime and during the mechanical reprocessing.[13] Additionally, post consumer plastics are usually laden with contaminants, co-blend partners, additives, and mixed with other plastics or non-plastics (*e.g.*, paper), resulting in the need for additional costly washing, sorting, and separation processes. As a result, mechanical recycling can only be carried out for a few cycles. A very common example is poly (ethylene terephthalate) (PET) bottles, which are usually only recycled once into textiles. A small portion of mechanical recycling consists of primary recycling using the purest and cleanest streams while most mechanical recycling is downcycling.[14] Therefore, the other recycling techniques illustrated in Fig. 1b (tertiary and quaternary) are required as complementary recycling options.

One of the main factors contributing to the difficulty in achieving pure polymer products from mechanical recycling is obstacles associated with plastic waste sorting. Currently, there are methods for sorting different types of plastic such as Near infrared (NIR) and X-ray fluorescence based identification and sorting technology, which can identify polymers based on their unique spectrum leading to the subsequent separation process. There are also techniques to sort plastic granules based on their specific density in air (air sorting) and in fluid (sink float sorting). Electrostatic methods are employed to separate plastics according to their triboelectric charge in addition to melting of polymers with varying melting temperatures.[15] Despite these techniques, they all have their limitations, such as NIR being ineffective for dark plastics,[16] X-ray fluorescence being constrained to polymers that fluoresce and applied for the identification of limited polymers, such as PVC.[17] Other challenges include the difficulty in controlling and maintaining the purity of density sorting techniques due to overlapping density ranges,[18] the inability to sort coarse granules by triboelectrostatic methods,[19] and the applicability of melt separation to two plastics of varying melt temperatures such as mixtures of polypropylene (T_m = 160 °C) and poly (ethylene terephthalate) (T_m = 260 °C).[20] Therefore, sorting remains a challenging and time-consuming aspect of recycling.

For mechanical recycling, there is potential to produce blend polymers in systems where complete sorting is not possible.[10] However, many polymers are immiscible and incompatible, such as polyolefins (PO) with polystyrene (PS) and must be compatibilized to produce stable blends. Compatibilization is commonly achieved using hydrogenated styrene butadiene rubber copolymers (*e.g.* SEBS), and other more cost-effective alternatives, such as styrene butadiene block copolymers, isotactic polybutene among others. For example, SEBS and PP grafted with styrene,[21] styrene butadiene styrene (SBS),[21] and ethylene-propylene-diene terpolymer (EPDM)-*g*-maleic anhydride and SEBS-*g*-MAH[22] were used to stabilize mixed waste blends of plastics including PS, PP, PE, and PVC. Additionally, fillers are often required to maintain the physical properties including elongation, young's modulus and impact strength of recycled plastics and blends. For example, organic fillers such as starch, cellulose, lignin, chitin *etc*. are used as compatibilizers in blends.[23] Other common fillers are cheap materials like glass fibre, $CaCO_3$, and talc,[24] in addition to nanoparticles, most notably modified montmorillonite clay.[25–27]

An important consideration when employing polymer blends to retain value from incomplete plastic sorting is that reprocessing is often not addressed. For this reason, the complete investigation of polymer blend degradation mechanisms and the influence of polymer blends on waste management systems is necessary.[28] Secondly, not all plastics can be blended due to extreme incompatibility or variation in processing parameters. For example, PET and PVC can not be processed together because the high temperatures required for PET processing accelerates the dehydrochlorination degradation of PVC.[29] This also means that mechanical recycling cannot be used for treatment of multilayer packaging materials due to the chemically incompatible layers.[30]

Next, additives are a big issue in mechanical recycling since most plastic products contain additives (*e.g.*, impact modifiers, plasticizers, compatibilizers, pigments) to enhance material properties, such as stiffness, flexibility, thermal stability, and barrier properties.[31,32] Additionally, fillers and other performance or processing enhancing additives are incorporated during the recycling process to overcome the reduced physical properties of recycled materials.[13,33] However, the use of filler and additives must be planned cautiously because their presence can increase the processing viscosity, causing increased risk to equipment and greater energy requirements. In some cases, the filler may even need to be removed before recycling due to differing recyclability of filler compared to the polymer.[28]

Contamination also complicates the recycling process and decrease the final product quality. For example, pigments can accelerate plastic degradation during extrusion, ink components from labels introduce volatile components, and lubricants used on plastic bags can produce unwanted odors.[34–36] The effects of these contaminants are often combatted by introducing virgin polymer into the recycling stream, which is employed for PET bottles with a virgin to recyclate ratio of 70/30.[37] Other methods to improve the quality of recycled PET is through molecular weight improvement using solid state post condensation[38] and chain extenders.[39]

Additives and contaminants may also be dealt with extraction or dissolution and precipitation methods. During extraction, the waste plastic is washed by an appropriate solvent or supercritical fluid, while the dissolution/precipitation method consists of dissolving the polymer to separate it from insoluble impurities followed by precipitation in antisolvents.[14] Despite these existing techniques, the reduction in quality due to additives, inks and remaining traces of incompatible polymer is an inevitable occurrence. This contributes to the stream of plastic waste that must be downgraded to products of less demanding quality (plastic containers, wood plastic composites for fences, agricultural applications, such as silage wraps and mulch films),[34] as shown by the secondary recycling in Fig. 1b.

Lastly, the processing of thermoset plastic wastes must be discussed. Thermoset plastics such as epoxies, polyurethanes, silicones, and polyesters account for around 12% of the global plastic production and is projected to grow over time.[40] However, they cannot undergo melt processing due to the covalent bond between the thermoset chains leading to most thermoset wastes being incinerated, sent to landfills or grinded for use as filler.[41,42] With respect to mechanical recycling, the only method that can be employed for thermoset plastics is pulverization into powder to be used as fillers in thermoplastic and thermoset polymers.[43] Although the thermoset waste must be cleaned and sorted before processing, this method is economical and therefore being used commercially albeit as a small scale.[44] Overall, recycling of thermoset plastic waste by mechanical recycling is extremely limited and therefore requires chemical methods for full reutilization. An example of a successful commercial recycling technology for thermoset wastes is the devulcanization of waste tires by critical CO_2, introduced by Tyromer in Canada.[45]

2.2. Chemical recycling (solvolysis)

Because mechanical recycling can only be used for a fraction of plastic markets, chemical recycling is necessary in cases where mechanical recycling can not deliver the required mechanical performance or purity. As shown in Fig. 2a, some plastics are more easily depolymerized into monomers while others can only be cracked through the more intense pyrolysis process to form hydrocarbon materials. In this mapping adapted from Lange (2021), the horizontal axis identifies the plastics which are easy to depolymerize based on heat of polymerization while the vertical axis indicates the incentive to recover the monomer based on the mass of resources consumed for its production.[14] Resultingly, the condensation polymers, such as PET and polyamides (PA) in the upper left quadrant are recommended to be depolymerized into monomers through various solvent methods (solvolysis).

These condensation polymers in the upper left quadrant of Fig. 2a consist of monomers connected through bonds, such as ester, amide, urethane linkages *etc*., which are susceptible to chain-scission through various reactions. In Fig. 2b select chemical approaches are illustrated for the depolymerization of PET, polyurethane (PUR), and PC. PET, which is often chemically recycled, can be depolymerized using various methods including methanolysis, glycolysis, hydrolysis, aminolysis, *etc*. depending on the chemical used.[13] However, glycolysis is the simplest method and is practiced by many large companies, such as DuPont, DOW Chemical Company, and Goodyear.[46] PURs can also be depolymerized through similar methods (alcoholysis, glycolysis, and hydrolysis) but rather than yielding its original monomers it results in high molecular weight polyols and aromatic oligomers.[14] For PC, these methods are used to break the carbonate bonds and regenerate BPA monomers in addition to organic carbonates, urea (ammonolysis) and methanol (hydrogenolysis).[47]

For chemical recycling, waste sorting is an important operation, since high purity monomers are desired. For the chemical recycling of PET, it is generally kept as a pure mono stream with only around 16 ppm PVC and 29 ppm of other contaminants.[48] In other cases, solvolysis can be used to separate different plastic constituents. For example, PLA can be separated from PET through hydrolysis which can selectively depolymerize the PLA component followed by glycolysis to depolymerize the PET.[14] Polymers can also be selectively dissolved from a mixture such as polyolefin dissolution in hydrocarbons, which has been commercialized in multiple processes (*e.g.*, Newcycling process, CreaSolv process) in Europe and Asia.[48,49] For the separation of components from multilayer films, Walker *et al.* (2020) reported a method for separation of PET, PVOH and PE from real films using solvent targeted recovery.[50] The authors reported that targeted selective dissolution and precipitation process was able to separate polymers from a commercial multilayer film with a reasonable cost, and close to 100% material efficiency, and high material quality.

Next, the effects of additives and contamination must be considered as well. Compared to mechanical recycling, the cleaning process may not be as consequential, as solvolysis can remove additives and foreign polymers. However, it may add significantly to the cost and complexity of the process if the purification stages must remove high proportions of additives and comonomers.[14] With respect to the components added during the recycling process, only catalysts may be required. Resultingly, difficulties in catalyst separation can limit the monomer purity and direct usability, as has been an issue for BHET obtained from PET glycolysis.[51,52]

Lastly, chemical recycling can provide disposal options for thermoset plastics. Due to the inability to mechanically recycle thermoset plastics, a common approach is to apply solvolysis methods to break the crosslinked bonds. Although solvent processes in general are difficult to scale, this method can recover unaltered fillers from thermoset composites. This is important because some reinforcing agents and fillers used in thermosets, such as carbon fiber reinforced resin materials are often used as substitutes for metals in a variety of industries (construction, energy, transportation),[44,53] and it is of interest to recover these filler materials without degrading their physical properties. Solvolysis methods can be performed on thermoset plastics due to the presence of degradable functional groups such as esters,[53–55] carbonates,[56] acetal,[57–59] sulfur groups,[60–62] and furans and maleimides[63–65] which have been

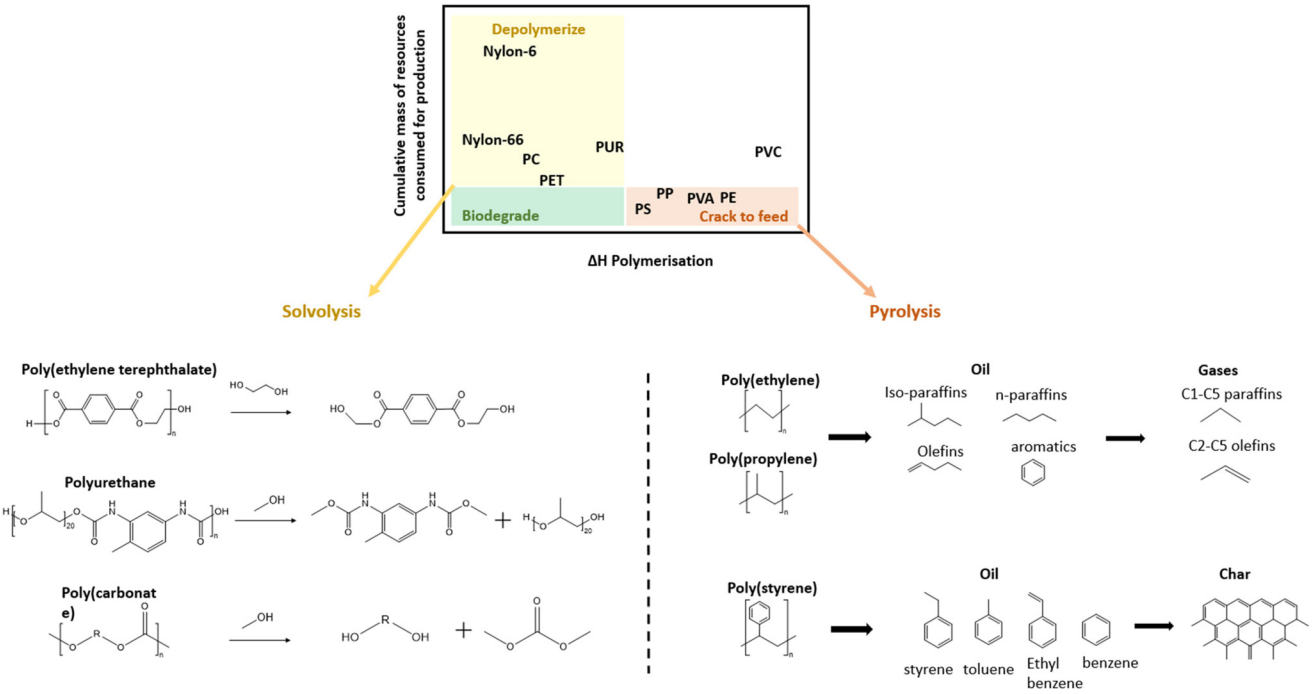


Fig. 2 (a) Mapping of the recommended chemical recycling technique for different plastics;[14] (b) schematic of the glycolysis of PET and methanolysis of PUR and PC; (c) general pyrolysis products of PE, PP and PS.

degraded under generally mild conditions.[66] Therefore, solvolysis is used as a commercially feasible method for recycling carbon fiber reinforced plastic composites to recover filler materials.[67] For these reinforced materials, various chemicals, such as ethanol,[68] supercritical methanol[69] and even water[70,71] have been used for degradation. Although the resin portion of the composites undergo degradation, this method generally focuses on the recovery of reinforcing fiber rather than the recycling of the thermoset matrix.

2.3. Pyrolysis based chemical recycling

As illustrated in Fig. 2a, the chemical recycling of most polyolefins must also consider pyrolysis as a suitable alternative due to the strength of the constituent hydrocarbon bonds. Pyrolysis is a tertiary recycling method which converts high molecular weight polymers into oil, gases and char by high temperature decomposition under an inert atmosphere.[72] The oil and gas products are desirable since they are used as precursors to valuable fuels and chemicals. A recent study by Wang *et al.* (2023) also showed that the oil and gas products of plastic waste pyrolysis can be converted to valuable hydrogen and solid carbon products through subsequent thermolysis.[73] The produced hydrogen fuel can generate clean electricity and the solid carbon has many applications including the investigated use as a reinforcing agent.

In the pyrolysis of polyethylene, it is understood that degradation occurs by free radical initiation, random scission, followed by recombination of various chains through termination.[74,75] The pyrolysis results in gas products consisting of C1–C4 olefins and oil products consisting of C5–C20 olefins and aromatics.[76] Das and Tiwari (2018) reported similar pyrolysis products after slow pyrolysis of PE and PP plastics, which consist of paraffins, olefins and some aromatics. However, the proportion of branched paraffins (isoparaffin) was higher in PP compared to PE. The gaseous products consisted of light paraffins and olefins, mainly propylene, ethane, methane *etc.*[77]

For PS, the degradation is also known to occur through free radical reactions.[78,79] The pyrolysis results in complete conversion to oil products at 350 °C, but as temperature is increased char production is promoted with very small proportions of gas (max 2.5 wt%). Therefore, the products are mainly oil (toluene, ethylbenzene, benzene, and styrene) and char due to the predominant presence of aromatic degradation products leading to char formation by condensation of aromatic rings. In comparison, LDPE began degradation at 450 °C, but increasing pyrolysis temperature promoted conversion to gases rather than char.[80] This phenomenon is shown in Fig. 2c, in which the pyrolysis oils and following gaseous products are illustrated for the pyrolysis of PE and PP, while the aromatic oil products and following char at increased temperature are illustrated for the pyrolysis of PS.

One of the key obstacles is that mixed plastics complicate the pyrolysis process compared to individual plastics due to the unique product compositions for each type of plastic. As mentioned previously, the pyrolysis of PE and PP produces oil/wax, light hydrocarbon gas, and negligible char, while polystyrene produces an aromatic oil product[81,82] and char at high temperature.[80] On the contrary, PVC pyrolysis produces hydro-

gen chloride, along with aromatic oil and char,[81,82] and PET pyrolysis yields CO_2, CO and char.[81,83] As a result, the pyrolysis products obtained from mixed plastic wastes are expected to vary greatly depending on composition. Furthermore, the compositions of pyrolysis products from mixed plastics have been reported to deviate from what is expected based on individual plastic pyrolysis data likely due to complex reactions during the process. For example, Williams and Williams (1998) reported that introducing PS to other common plastics resulted in a significantly greater gas yield than would be expected.[84] It has also been reported that PS reduces the time required to produce maximum oil yield from PE.[85] Generally, Wenning (1993) has reported variations in product compositions of 40–55 wt% oil/wax, 30–50 wt% gas, and 5–15 wt% char from pyrolysis of different plastic mixtures of PE, PP, PVC, PET and PA.[86] Therefore, if plastic wastes cannot be sorted properly, it is close to impossible to understand the expected product yields from mixed pyrolysis processes.

Next, additives are somewhat of a concern because pigments and by-products in plastic waste can lead to issues in pyrolysis oil.[87] Therefore, there can be a need for removal of contaminants by pre-treatments and washing before pyrolysis similar to mechanical recycling. Additionally, the presence of chlorine from PVC and other halogens that can be introduced from pigments and coatings[88,89] can result in many harmful products (dioxins, HCl).[87] This issue necessitates that the chlorine content in the oil product must be reduced below 10 ppm through post-treatment before use as a feedstock.[87]

With respect to the cleaning process, Genuino *et al.* (2023) has investigated the effects of washing on the pyrolysis of a mixed plastic waste stream containing PE, PP, PET, PS, acrylonitrile butadiene styrene (ABS), paper and aluminum laminates. Washing using a combination of cold and hot water resulted in significant cleaning (11.7 wt% reduction) which mainly affected the ash content in the pyrolysis product. The washed and unwashed batches produced similar wax and oil yields (66–69%), with the difference in the solid product aligning exactly with the ash removal by cleaning.[90] Therefore, washing of plastic waste before pyrolysis is very helpful for reducing the ash content caused by inorganic contaminants.

Lastly, one of the major advantages of pyrolysis is that it can be easily employed for thermoset plastics. For the treatment of filler reinforced thermosets, the polymer portion is decomposed to form liquids and gases while the filler portion can be separated and reused.[91] However, to ensure that the filler is not significantly damaged the processing conditions must be considered. At very low temperatures (<300 °C) the resin component does not degrade properly, while at high temperatures (>600 °C) the reinforcing fibres are degraded.[92] To overcome this issue, a two-stage process has been reported for glass fiber recovery from thermoset plastic which led to improved tensile strength of glass fibers.[93] In terms of carbon reinforced thermosets, pyrolysis is more suitable. At the lowest temperature of 400 °C, the tensile strength reduction of recycled carbon fibres is much less (5–20%) compared to that of glass fibers (>50%).[94]

2.4. Carbonization chemical recycling

The carbonization of plastic waste is considered a distinct treatment compared with pyrolysis, because it is specific to the production of value-added carbon materials rather than fuels and chemicals. For carbonization processes, a slow heating rate is employed to promote the production of solid products containing maximum carbon content from the precursor. This slow heating rate leads to a more sequential conversion of the feedstock into a carbonized material through many reactions. Additionally, higher temperatures of 600–1200 °C are used in carbonization compared to pyrolysis for oil products generation, which occurs at temperatures around 500 °C.[1] During carbonization, the plastic is heat treated at high temperature under an inert atmosphere to produce carbon material through aromatization, while some gases (H_2O, CO_2, CH_4, NH_3 *etc.*) are released through decomposition of the plastic constituents.[2]

Carbonization at different conditions (catalysts, templates, and pressures) can result in varying carbon products. As a result, different structures are obtained, including activated carbon, carbon fibres, carbon nanotubes, carbon spheres, and graphene.[95] In terms of the plastic precursors, polyolefins such as PP and PE are ideal for producing carbon nanotubes, carbon spheres, and graphene because they form light hydrocarbons, which are catalyzed to form these structures during the carbonization process.[95,96] This can be achieved using combined catalysts, which act as both degradation and carbonization catalysts. The degradation catalyst helps to promote the formation of the required low molecular weight compounds, while the carbonization catalyst facilitates the degradation process such that carbon materials can be formed.[97] Templates may also be employed, in which a removable mold is used to create controlled voids in the material. Some materials used as rigid templates include silica, clays, MgO and $CaCO_3$.[98]

During the carbonization of PET and PS containing benzene rings in their structure, aromatics and oil products are formed which then lead to the formation of amorphous carbon.[95] This is due the occurrence of cyclization, aromatization and crosslinking rather than degradation into small molecules.[96] As a result, polyolefins, such as PP and PE are considered non-charring while aromatic plastics such as PET and PC are considered charring plastics, as shown in Fig. 3. Non-charring plastics are beneficial for producing ordered carbon materials (graphene, carbon nanotubes *etc.*) through catalysis while charring plastics can produce amorphous carbon material. Activation by chemical or physical methods can then be used to enhance the surface area and porosity of the products.

Sorting of plastic waste prior to carbonization is an important consideration because of the variation in products that can be obtained based on the type of plastic. For example, PET plastic is the most frequently used feedstock to produce porous carbon, but this is aided by the already established systems in place for collection and recycling of PET bottles and

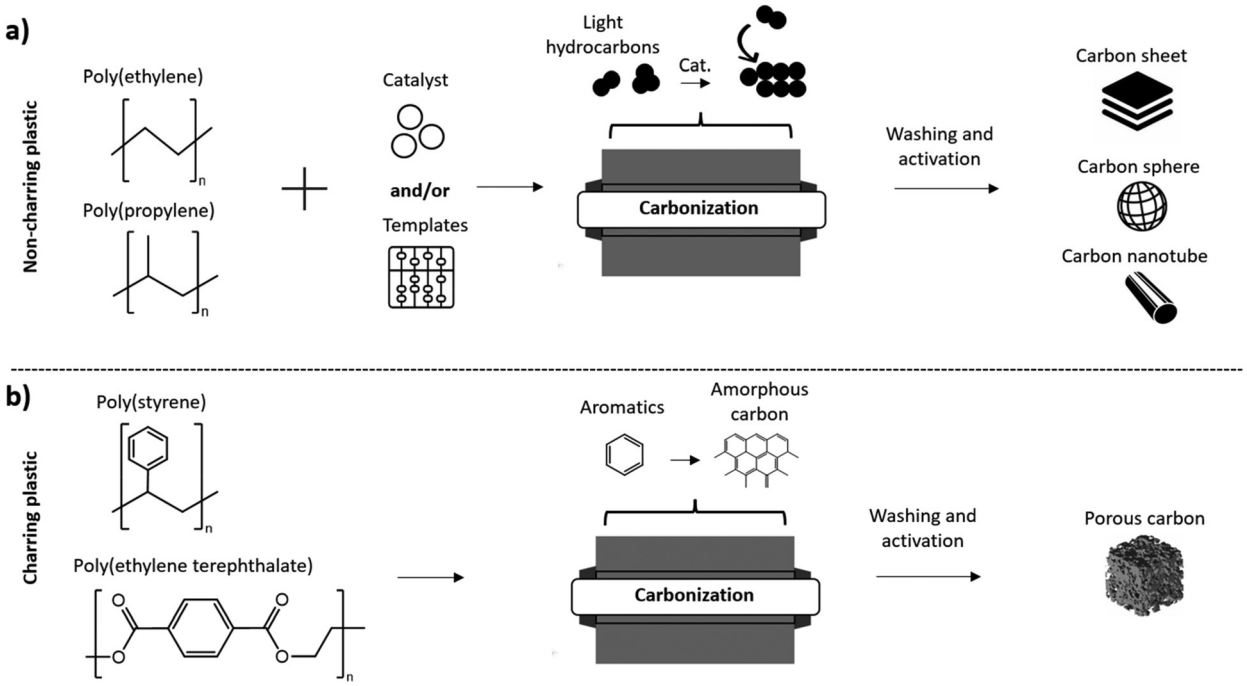


Fig. 3 (a) Carbonization of non-charring plastics to produce carbon sheets/carbon spheres/carbon nanotubes; (b) carbonization of charring plastics to produce porous carbon.

other products.[99] On the other hand, the low fixed carbon content of polyolefins doesn't allow for porous carbon to be produced from these common waste plastics.[100] Pretreatments of polyolefins enabling the production of porous carbon will be discussed in the following section, but still require different procedures compared to charring plastics. Therefore, sorting must be performed before carbonization processes to ensure the feed consists of the appropriate type of plastic for the intended product such as porous carbon.

It has been reported that mixed waste plastics containing polyolefins can be used to produce carbon sheets and spheres through template methods employing organically modified montmorillonite (OMMT). The acidic sites on OMMT promote dehydrogenation and aromatization of plastics and catalyzes the carbonization such that graphene or carbon spheres can be grown on its surface.[8] Using this template, mixed plastics have been converted into hollow carbon spheres[101] and porous carbon nanosheets[102,103] by incorporating a final activation step. Plastic mixtures have also been used to produce carbon nanosheets on magnesium oxide[104] and carbon nanotubes on silicone, glass, and carbon paper substrates[105] and over a Co–Mo–MgO catalyst.[106] However, it remains a challenge to directly produce porous carbon products from polyolefins without the use of template or catalyst methods, limiting the production of porous carbon from mixed wastes.

Next, the consideration of additives and contamination is relevant to the production of carbon nanomaterials such as nanosheets and nanotubes, as these impurities can interfere with the catalytic process of carbon growth.[8] Therefore, cleaning pretreatments may produce higher quality products. With respect to general carbonization, most research has neglected the impact of impurities like plasticizers, metals, antioxidants *etc*. This area should be investigated further since additives may affect the carbon conversion process.[96] However, it is expected that the effects of washing on carbonization would be similar to that of pyrolysis, in which the ash content is reduced greatly.

Lastly, carbonization technology has the advantage of being able to process thermoset plastics by conversion into carbon material. Specifically, phenolic formaldehyde resin (PFR) is the most used resin for producing amorphous carbon and exhibits a high carbon yield (61.8%).[107] Another area of research is in the conversion of epoxy resin to carbon materials, as it is used in many products including electronics (circuit boards) and composite materials (windmills, aircrafts). The production of high surface area activated carbon has been reported using physical[108] and chemical activation[109] of the epoxy resin component in waste circuit boards. Additionally, the conversion of cured epoxy to activated carbon has been investigated and applied as an adsorbent material[110] and for supercapacitors.[111] The upcycling of thermoset waste to high value carbon materials is a promising area, but more work is required to investigate more precursors and conversion methods. One prominent concern with respect to epoxy waste, is the separation of the metal component in waste circuit boards before treatment.

2.5. Energy recovery

Lastly, energy recovery through combustion is a common method used to deal with large quantities of plastic waste. As

illustrated in Fig. 1b, combustion for energy recovery is a quaternary recycling method that used as a last resort for producing value from unutilized waste streams. It takes advantage of the high energy density of plastic waste, which can supply large amounts of thermal and electric power (*e.g.* PE: 43 MJ kg^{-1}).[10] It is a simple and inexpensive method of disposing plastic waste; however, it results in large emissions of harmful chemicals (dioxins, furans, greenhouse gases *etc.*).[2] Still, combustion is a very useful alternative to landfilling plastics which are difficult to recycle.

It is known that various plastics have different calorific values. For example, PVC, PET and PA have much lower carlorific energy than PP, PE and PS, which are similar to conventional fuels. Therefore, some plastics are not as suitable for an incineration process due to their efficiency.[112] As a result, variations in compositions can cause significant fluctuations in energy output, making it ideal for sorting operations to be applied before treatment.[10] However, combustion is still used for disposing mixed wastes which would otherwise be landfilled.

Next, the incineration of materials containing additives may contribute to the ash content in the product. This may pose concerns if the waste contains heavy metals, because these can be released into the environment upon incineration.[2] Regardless, incineration is known to release toxic emissions, which is why it is used as a last resort and the impact of additives and extraneous agents need to be considered.

Lastly, combustion can be a last resort option for disposal of hard to recycle thermosets. It is specifically helpful in the recovery of precious metals from electronic wastes, because of the difficulty in removing the plastic resin portions. Therefore, the metals are extracted by incineration of the resin, or alternatively by using solvent methods,[12] as discussed previously for the removal of reinforcing agents in epoxy.

3. Anoxic pyrolysis carbonization of plastics

With respect to the various disposal methods, the carbonization route is a very promising method for producing both amorphous and graphitic carbon. To better understand the application of this technology, the effect of plastic composition should be further investigated. In section 2.4., it was outlined that non-charring polyolefin plastics required catalytic conversion to produce structured carbon materials while aromatic plastics can be directly converted to amorphous carbon (Fig. 3). This section focuses on anoxic pyrolysis carbonization, which refers to the direct heat treatment of plastics under an inert atmosphere rather than the catalytic carbonization of polyolefins for producing nanomaterials.[2] Although polyolefin plastics (PP, PE) produce light hydrocarbons upon heat treatment, there are stabilization treatments that allow these non-charring plastics to undergo anoxic pyrolysis carbonization. Additionally, the subsequent activation of carbon materials to produce high surface area activated carbon from plastic precursors will be discussed in the next section (section 4).

3.1. Stabilization pre-treatments

It is generally known that carbonization of aromatic plastics leads to the formation of oils and aromatics which enhance char formation.[95] However, the oxygen content in the polymer also plays an important role in its conversion to carbon material. Plastic which contains oxygen, such as PET and epoxy resins, are more easily carbonized through heat treatment, while non-oxygen containing plastics may require a stabilization pre-treatment. The preliminary treatment allows for an increased yield of carbon residues rather than gaseous organic molecules.[2] Therefore, polyolefins can be converted into amorphous carbons (*e.g.* activated carbon, carbon fibres) if a stabilization through oxidation or other chemical treatment is preformed before carbonization.

In terms of stabilization treatments, sulfonation and oxidation treatments are commonly used. For LLDPE, Choi *et al.* (2017) has shown that oxidation in air introduces C=O bonds and C–O bonds, which occur in the main chain and as ether bonds bridging chains. As temperature increases, the linear chains are converted to a crosslinked structure with an increasing composition of oxygen. The cyclized structure can then be carbonized at higher temperature under inert atmosphere to yield a carbonaceous product.[113] Alternatively, PE can be sulfonated using sulfuric acid to result in sulfonic acid groups among other sulfur containing groups (sultones, sulfates). Subsequently during carbonization, unsaturated polyolefin is obtained through release of sulfur and oxygen, and carbonized material can then be achieved. The sulfonation mechanism is investigated in detail by Younker *et al.* (2013).[114] The general mechanism of the oxidation and sulfonation pre-treatments are illustrated in Fig. 4a.

Sulfonation can also be used for PS, as was reported by Hines *et al.* (2004) to produce porous carbon.[115] Additionally, PS can be stabilized by the Friedel–Crafts reaction in which crosslinking occurs through carbonyl bridging using a carbon tetrachloride reagent and Lewis acid catalyst (Fig. 4b). This leads to enhanced carbonization due to the crosslinked structure and increased oxygen content.[116] In the case of PVC, stabilization usually occurs through heat treatment in air, during which oxygen functional groups are introduced during this treatment, leading to crosslinking and aromatization.[117] A list of various carbon materials obtained from plastic precursors with or without pre-treatments is presented in Table 1. Evidently, the sulfonation of PE is a very common method, especially to produce carbon fibers.[114,118,119] Carbon fibres are often used in polymer composites reinforcement as alternatives to heavier construction materials like steel and are mainly produced from poly(acrylonitrile) (PAN) by melt spinning and oxidation pre-treatment.[118] Alternatives like PE are of interest due to the costs of PAN precursor and conversion yield, which limit the applications in industries requiring lower cost products.[118]

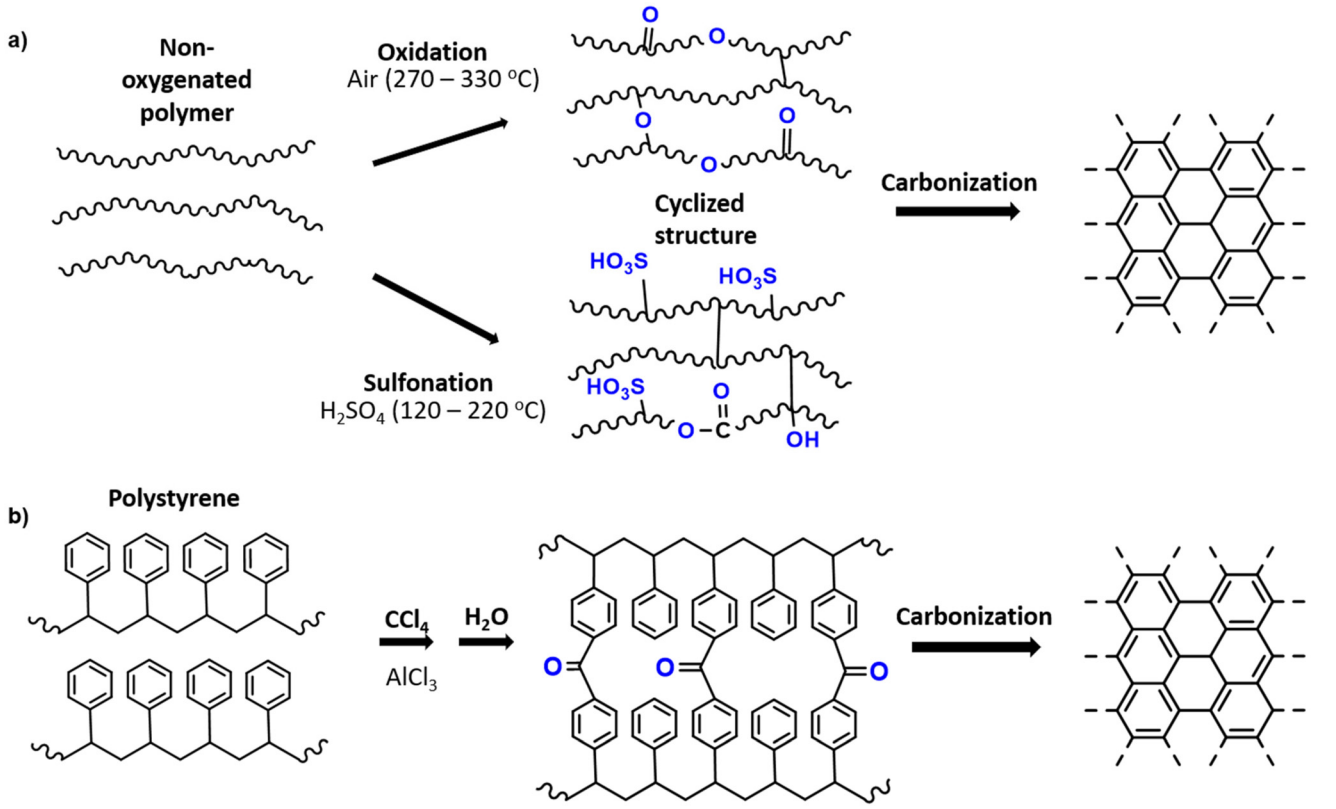


Fig. 4 (a) General schematic of oxidation and sulfonation pretreatments for carbonization of plastics based on the mechanisms of PE stabilizations;[2] (b) Friedel–Crafts reaction as a pretreatment for polystyrene carbonization.[116]

Table 1 List of carbon products obtained through anoxic pyrolysis of plastic precursors with or without stabilization pre-treatments

Precursor	Stabilization treatment	Carbon product	Ref.
LLDPE	Oxidation	Graphitic carbon	113
LLDPE	Chlorosulfonation	Carbon fiber	119
LDPE	Sulfonation	Carbon scaffold	120
PS	Sulfonation	Porous carbon	115
PS	Crosslinking (Friedel–Crafts)	Porous carbon	116–121
PE	Sulfonation	Carbon fiber	114–118
PE	Sulfonation	Porous carbon	122
PE	Sulfonation	Amorphous carbon chips	123
PVC	Oxidation	Porous carbon	124
PVC	—	Char	125 and 126

4. Activation of plastics

4.1. Activation methods

As seen in the previous section, porous carbons are often produced from plastic precursors (Table 1). These products are very valuable due to their high surface area (SA) and pore volume, which allow them to be used as high-capacity adsorbents. However, activation processes are often used to further improve the SA of the carbonized materials to produce activated carbons (ACs), which are defined by large SA, porosity, and adsorption capacity.[127] The activation process involves reactions between carbon and an activating agent to produce new pores and open existing pores in the carbon structure through physical or chemical methods. The specific SAs of commercial ACs are in the range of 500–1500 $m^2\ g^{-1}$,[128] which is determined by the Brunauer–Emmett–Teller (BET) method of SA analysis through N_2 adsorption.

Physical activation involves heat treatment with an oxidizing gas such as O_2, CO_2 or steam at high temperature (800–1200 °C). This takes place after carbonization of the material under an inert atmosphere, such that a two-stage process is required.[129] It can be considered a more environmentally friendly approach due to the lack of chemicals, but it has the downsides of long activation times and high energy consumption.[130] Chemical activation on the other hand involves impregnation of the precursor with an oxidizing and dehydrating chemical, heat treatment at temperatures between 400 to 900 °C, and subsequent washing (*e.g.*, HCl) to remove the chemical. In this case, the carbonization and activation can occur simultaneously such that a single stage process can be employed.[130] However, many studies also employ carbonization prior to activation, using a lower temperature of around 600 °C for carbonization where most mass loss occurs, followed by chemical activation at temperatures from 400 to 1000 °C.[127] This two-stage chemical activation is illustrated in comparison to physical activation in Fig. 5a.

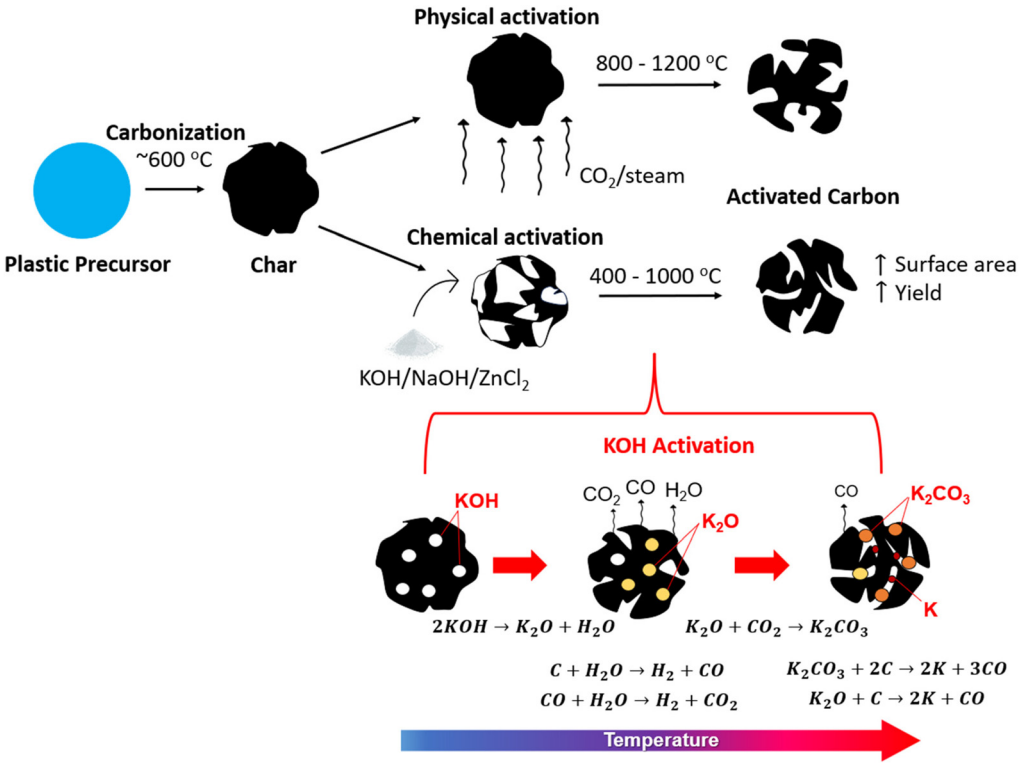


Fig. 5 (a) Illustration of activated carbon production through physical *versus* chemical activation; (b) KOH activation mechanism adapted from ref. 110.

The main parameters affecting activation include the activating agent, treatment temperature, time, and the impregnation ratio (IR), which is the mass ratio of chemical activating agent to precursor in the case of chemical activation. In general, chemical activation is preferred compared to physical activation due to the advantages of lower activation times and temperatures, generation of high specific SAs, and high carbon yield.[131] The most used chemical activating agents include alkaline chemicals, such as KOH, NaOH and K_2CO_3, acidic chemicals such as H_3PO_4 and H_2SO_4, and metal salts such as $ZnCl_2$.[130] Of all activating agents, KOH is known to be the most effective due to its capacity to produce high SAs in AC.[129] As a result, much of the work that will be explored has focused on activation using KOH.

With respect to the feedstock, commercial AC is mainly produced from charcoal, lignite, wood, peat shells and coconut, but any carbonaceous organic material are viable precursors.[130] Therefore, plastics are an enticing option for AC feedstocks since they possess high carbon content, and the utilization of plastic waste is of high concern. Currently, the production of AC from plastic waste has not been commercialized, although it is under ongoing investigation. For example, an Australian company called ByGen has reported the success in converting plastics including PET into AC,[132] although they do not yet produce any AC products at full scale. Therefore, this section will reflect on the current understanding of AC production from plastics based on the relevant research studies.

4.2. Chemical activation mechanisms

First, the activation mechanism of KOH will be outlined in detail, as it is the most well studied chemical activating agent. The mechanism of pore formation using KOH activation occurs through physical activation by the evolved CO_2 and H_2O, redox reactions between potassium compounds and carbon, and through the formation of potassium metal at high temperatures,[133] as illustrated in Fig. 6b. Gases such as CO and CO_2 are formed through the reaction of carbon with surface and internally bound water (eqn (1) and (2)), and water is released through the dehydration of KOH (eqn (3)). As the decomposition continues, K_2CO_3 is produced due to the transformation of K_2O (eqn (4)). At high temperatures exceeding 700 °C, metallic potassium is formed through the reduction of K_2O and K_2CO_3 (eqn (5) and (6)).[129,133,134] The potassium metal is important for the continued pore formation due to its ability to penetrate and expand the carbon structure. It also helps to form more active sites for reaction with carbon and improves the wettability of the surface. These effects are unique and can not be achieved through activation by acidic or neutral activating agents.[129] This is why strong alkali activating agents are very effective, especially KOH.

$$C + H_2O \rightarrow H_2 + CO \quad (1)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (2)$$

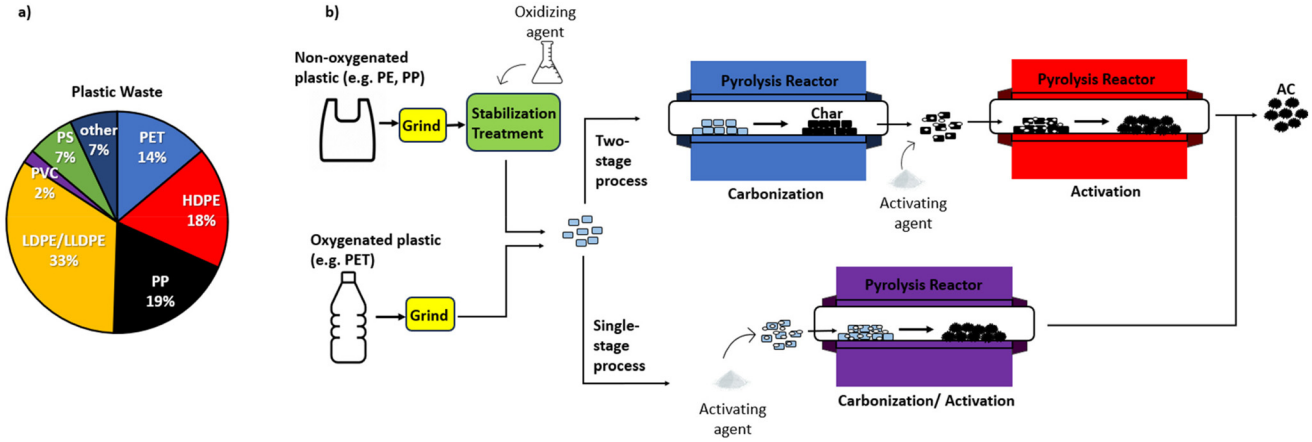


Fig. 6 (a) Composition of plastic waste managed in the US in 2019. Data obtained from ref. 11; (b) illustration of various pathways for the chemical activation of oxygenated and non-oxygenated plastics.

$$2KOH \rightarrow K_2O + H_2O \quad (3)$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \quad (4)$$

$$K_2O + C \rightarrow 2K + CO \quad (5)$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \quad (6)$$

Although KOH is most well-known, there are other activating agents which also are effective in producing high SA products. These chemicals include NaOH, K_2CO_3, $ZnCl_2$ and acids such as H_3PO_4, which are all employed in some of the studies referenced in section 5. Firstly, NaOH is a common alternative to KOH, as it is another alkaline hydroxide that can melt without decomposition at high temperature, allowing reaction with carbon at high temperature.[135] The NaOH activation mechanism follows the same global activation mechanism (eqn (7)) at high temperature, in which M refers to either K or Na.[135,136] Although the activation mechanisms are very similar, KOH is seen to have a greater activation effect due to the lower temperatures required for reactions to occur in the case of KOH.[136]

$$6MOH + 2C \rightarrow 2M + 3H_2 + 2M_2CO_3 \quad M = Na, K \quad (7)$$

Another well-known activating agent is K_2CO_3, as it has a high activating effect and is a non-harmful alternative to the corrosive metal hydroxides. It has a powerful activating agent because it is the effective activating agent in the KOH activation mechanism at high temperatures,[137] based on eqn (6). At lower temperatures the K_2CO_3 activator does not participate in any reactions as it is stable below 700 °C during activation.[137] This makes K_2CO_3 very effective in SA development because it only participates in high temperature activation reactions; however, the lack interaction with the feedstock at low temperature can lead to low carbon yield, as was reported in the case of Epoxy activation.[110]

Acidic activating agents such as H_3PO_4 are also employed due to its multiple activation effects outlined by Gao *et al.* (2020).[129] Firstly, H_3PO_4 acts as a dehydrating agent to draw out hydrogen and oxygen in the form of water rather than carbon volatiles. Secondly, it diffuses into the starting material to produce a homogenous incorporation that enables uniform heating during activation, acts as a framework for the carbon network, and lowers the carbonization temperature due to the higher thermal conductivity of H_3PO_4 compared to the alternative heating media (air, water or CO_2). Above 200 °C polyphosphoric acid is produced, which facilitates oxidation and carbonization of volatile components. Additionally, polycondensation, cross-linking and cyclization reactions lead to the formation of a polycondensation structure with the organic material. With increasing temperature, these polyphosphate esters and polyphosphoric acids are also converted into P_2O_5, which contributes to the pore development through its reaction with carbon to form C–O–P structures.

Lastly, $ZnCl_2$ is often employed as an activating agent, especially for cellulosic feedstocks.[130] It is considered as a neutral activating agent, which generally performs through the reduction reactions between the positive ion (*e.g.* Zn^{2+}) and carbon.[129] This consumes the carbon to leave behind pores containing carbon bonded components to be removed during the washing process. The metal species may also play a role in the catalysis of CO_2 and CO release, as were observed by neutral activators $FeCl_3$ [138] and $KMnO_4$.[139] This process contributes to surface area development by the additional physical activation.

5. Progress in plastic conversion to AC

The conversion of plastics to AC can occur through various methods. As discussed previously, the composition of the plastic can necessitate preliminary stabilization treatments (section 3.1) and the activation process itself can follow

various paths. In this section, the conversion process for common plastics will be reviewed, with a focus on chemical activation methods. The BET SAs are investigated as the main indication of AC quality due to the wide range of applications in the investigated works. The SAs achieved in ACs through activation of various thermoplastics (Table 2), chemical activation of PET (Table 3), and chemical activation of thermosets (Table 4) have been tabulated in the following sections. Based on these tables, it is evident that most research focuses on KOH activation of plastics in both single stage and two stage carbonization/activation processes. The various process pathways utilized in these works have been illustrated in Fig. 6b to showcase the combination of steps required to produce chemically activated AC from plastics.

The plastic precursors investigated in this study were chosen based on the abundance in waste streams as represented in Fig. 6a in addition to thermoset plastics, which are non-recyclable. With respect to the relevant thermoplastics, each possess differing structures and properties, prompting their high demand for specific industrial applications. To provide some background of the importance of these plastics leading to their usage and disposal, the structures and applications of the commodity thermoplastics outlined in Fig. 6a are presented in Table 2.

Polyethylene (PE), which is available in both high density (HDPE) and low density (LDPE) grades, has a very linear structure with a low degree of branching. It can be easily processed into a variety of forms including films, and blow-moulded con-

Table 2 Structure and applications of commodity thermoplastics[140–143]

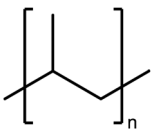
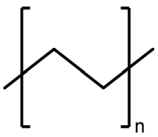
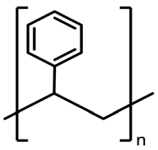
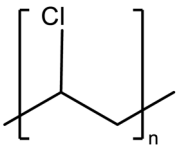
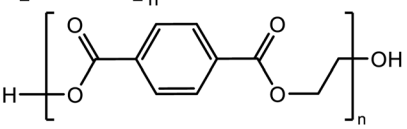
Plastic	Structure	Properties	Applications
Poly(propylene)		Stiff, resistant to heat distortion, good fatigue strength	Barrier film pouches, caps/lids, thin-walled containers, blow-moulded bottles
Poly(ethylene)		Tough, flexible, low strength, poor resistance to weathering, electrical resistance	Blow moulded containers, plastic bags, cling wrap
Poly(styrene)		Good thermal and dimensional stability, low density, good electrical properties	Insulating medium, mouldable packaging material, cups/trays
Poly(vinyl chloride)		Rigid, abrasion resistant, susceptible to heat distortion	Piping, buildings, furniture
Poly(ethylene terephthalate)		Strong, stiff, good fatigue and tear strength, resistance to humidity, acids, solvents, low gas permeation	Beverage containers, clothing (textile fibre)

Table 3 List of activated carbon BET SAs produced from various thermoplastics with or without stabilization pre-treatments

Precursor	Stabilization treatment	Activation type	Activating agent	AC surface area ($m^2\ g^{-1}$)	Ref.
PE	Sulfonation	Chemical	KOH	156–1803	148
PVC	Oxidation	Physical	Steam	1096–2096	153
PVC	Oxidation	Physical	CO_2	528–1211	117
PVC	Oxidation	Chemical	KOH	4–2507	158
PVC	—	Chemical	KOH	2666	155
PS	Sulfonation	Physical	Air, steam	567, 842	149
PS	—	Chemical	KOH	2109–2712	152
PS	—	Chemical	KOH	393–1250	151
PS	Crosslinking (Friedel–Crafts)	Chemical	KOH	2637	150
PC	—	Chemical	KOH	Max. 2098.7	156
PC	—	Chemical	NaOH	348–815	157

Table 4 List of the ranges in activated carbon BET surface areas produced through chemical activation of PET plastic

Carbonization conditions	Activating agent	IR	Activation conditions	AC surface area (m^2 g^{-1})	Ref.
—	$ZnCl_2$	1	500 °C 2 h	700	169
—	K_2CO_3	0.25–1	800 °C 2 h	680–1390	
—	K_2CO_3	2	800 °C	1439	170
	KOH			1206	
—	$ZnCl_2$	1	400 °C 1 h then 800 °C 1 h	682	171
	H_3PO_4			1223	
	H_2SO_4			583	
	KOH			1338	
—	KOH	1	700–800 °C 1–2 h	625–1214	159
—	KOH	2	700 °C 30 min	1418	176
—	KOH	2	700 °C	1334	177
—	KOH	2	700–850 °C 1 h	566–1002	165
			800 °C 0.25–2 h	666–844	
—	KOH	1–5	800 °C 1 h	817–1889	172
—	KOH	5	900–1100 °C 1 h	1092–1808	173
600 °C 1 h	KOH	2	850 °C 1.5 h	2831	155
600 °C 2 h	KOH	2	700–1000 °C 1 h	1689–2006	168
	NaOH			1926–2060	
600 °C 1 h	KOH	2	600–1000 °C 1 h	1636–1937	174
		1–3	700 °C 1 h	736–2650	
700 °C 2 h	KOH	1–4	700 °C 2 h	591–1690	178

tainers.[141] Polypropylene (PP) also has very good processability but exhibits increased hardness due to the methyl group in its repeating structure. It also has improved temperature resistance, leading to its usage in containers and bottles.[144] In comparison, polystyrene exhibits a phenyl group in place of the methyl in polypropylene, leading it to an amorphous and clear plastic when extruded.[145] However, most PS products are expanded PS, a lightweight material ideal for insulation and foam products such as cups/trays.[141,146] Polyvinyl chloride (PVC) is different from other thermoplastics due to its chlorine content. This makes PVC non combustible and suitable for use in buildings and furniture.[141] Lastly, poly(ethylene terephthalate) (PET) is a semi-crystalline polyester leading to a balance of properties including strength and stiffness in addition to resistance to gas and water permeation.[141,147] These properties combined with its transparency has led it to become the main containment material for beverages including water and carbonated drinks. These plastics are reviewed with respect to their conversion into activated carbon due to their high consumption. Additionally, polycarbonate (PC), a strong thermoplastic containing carbonate groups was also investigated, as it is a good precursor for carbonization due to its oxygen content.

5.1. Polypropylene (PP) and polyethylene (PE)

In terms of carbon materials, PP waste is mainly transformed into carbon nanotubes.[1] As discussed in section 2.4, polypropylene decomposes into light hydrocarbon gases which can be used as building blocks for carbon nanomaterials through a catalyzed process. Although PE also produces similar pyrolysis products, stabilization pre-treatments have been heavily investigated for the successful anoxic pyrolysis carbonization of PE. As shown in Table 1, sulfonation of PE is often employed to produce a variety of carbon materials such as carbon fibres and porous carbon. PP and PE are not often used to produce activated carbon; however, Yang *et al.* (2022) reported the subsequent activation of sulfonated PE using a 1 : 4 KOH IR and an activation temperature of 900 °C.[148] The ACs exhibited a maximum SA of 1803 m^2 g^{-1} using a carbonization temperature of 900 °C, which decreased upon further increases in carbonization temperature up to 2400 °C.

5.2. Polystyrene

To produce carbon materials from polystyrene (PS) chemical stabilizations can be performed prior to carbonization, but direct carbonization/activation has also been reported in the production of AC (Table 3). Gonsalvesh *et al.* (2016) employed sulfonation of PS using sulfuric acid prior to carbonization (at 600 °C) and activation using air or steam.[149] The capacity of the steam activated AC based on iodine number increased with temperature. However, 850 °C was determined as optimal due to the decreasing carbon yield with respect to temperature. For activation in air, a temperature of 350 °C was used due to the significant decrease in iodine number beyond this temperature. The steam activation was more effective, as it produced a greater SA (842 m^2 g^{-1}) compared to the air activated AC (567 m^2 g^{-1}).

Stabilization of PS by Friedel–Crafts reaction was also employed by Gatti *et al.* (2019) prior to carbonization at 600 °C and activation by KOH using an IR of 1 : 3.[150] Activation at 800 °C for 1 h resulted in a very large increase in SA from 739 m^2 g^{-1} to 2637 m^2 g^{-1}. Based on these studies, the Friedel–Crafts reaction combined with KOH activation was more effective for producing AC, as the carbonized PS had a much greater SA (739 m^2 g^{-1}) compared to the sulfonated PS (267 m^2 g^{-1}) under the same carbonization temperature. Additionally, a much greater increase in SA was achieved through KOH activation compared to the physical activation at the same temperature (800 °C).

Although stabilization treatments of PS improve the carbonization, it is not completely necessary due to its aromatic structure which can aid char formation. For example, Deka *et al.* (2020) produced AC from PS through direct chemical activation using KOH.[151] Using an IR of 1 : 3, it was observed that the SA increased from 393 $m^2 g^{-1}$ to 1250 $m^2 g^{-1}$ alongside increases in activation temperature from 600 °C–800 °C. Additionally, de Paula *et al.* (2018) investigated KOH activation of PS after carbonization at 10 bar and 530 °C for 5 h.[152] Under the same activation temperatures as the previous study and an IR of 1 : 4, the ACs exhibited higher SAs in the range of 2109–2712 $m^2 g^{-1}$. This large difference is likely attributed to the separation of carbonization and activation stages in the study by Paula *et al.* (2018). However, the carbon yield and cost of such a process must be considered as well.

5.3. Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) is not often upcycled to carbonaceous products,[1] but it has been reported to produce porous carbons using a stabilization pre-treatment[124] and char in the absence of pretreatment.[125,126] Activation of carbonized PVC has been investigated to produce AC fibres through carbonization and activation of melt spun PVC.[117,153] Both studies utilized a two-stage heat treatment to produce spinnable PVC pitch, which was then stabilized in air up to 320 °C prior to carbonization and activation. Qiao *et al.* (2004) utilized steam activation at 900 °C and found that the resulting AC SA increased from 1096 $m^2 g^{-1}$ to 2096 $m^2 g^{-1}$ as activation time increased from 30 to 90 min.[153] Their later study using CO_2 as an activating agent reported lower AC SAs of 528 $m^2 g^{-1}$ to 1211 $m^2 g^{-1}$ using greater temperatures of 900 °C to 1000 °C and an activation time of 1 h.[117] PVC has also been chemically activated by KOH after stabilization in air. Liu *et al.* (2022) reported a maximum SA of 2507 $m^2 g^{-1}$ under activation conditions of 800 °C for 1 h and a KOH IR of 3 : 1.[154] A similarly high SA of 2666 $m^2 g^{-1}$ was achieved by Lian *et al.* (2012) using a lower KOH IR of 2 : 1 and elevated activation conditions of 850 °C for 1.5 h.[155] At these conditions, it was also shown that a higher SA AC (2831 $m^2 g^{-1}$) was achieved using PET as a precursor while the PVC AC displayed a narrower pore distribution. Based on these studies, it seems that the chemical activation of PVC by KOH can produce higher SAs while using lower activation temperatures compared to the physical activation processes.

5.4. Polycarbonate

Polycarbonate (PC) has also been reported as a feedstock to produce AC without the need for stabilization pre-treatment. The KOH activation of PC has been used to achieve AC with SAs as high as 2098 $m^2 g^{-1}$ and with yields of greater than 40%.[156] As an alternative to KOH, NaOH was also investigated due to its lower cost and corrosivity. Li *et al.* (2014) investigated NaOH activation of PC at 500 °C using a central composite design and produced ACs with a maximum SA of 815 $m^2 g^{-1}$ using an IR of 1 : 4 and 150 min activation treatment.[157] Evidently, the NaOH activator was not as effective in developing SA as KOH but may be preferred in some applications as a less corrosive/hazardous option.

5.5. Poly(ethylene terephthalate)

Poly(ethylene terephthalate) (PET) plastic is a special example because it is the most researched plastic feedstock for AC production. PET is an ideal precursor to AC due to its aromatic and oxygenated structure, high carbon content (> 60 wt%) and high char yield compared to other waste plastics.[159] Most studies have employed chemical activation for the synthesis of PET AC, which is the focus of this section. The various carbonization conditions, chemical activation conditions, and resulting AC SAs have been summarized in Table 4, and the trends with respect to operational conditions will be discussed.

5.5.1. Physical activation. Despite the large number of studies and focus on chemical activation of PET (Table 4), it should be noted that the physical activation has also been explored using CO_2[160–164] and steam[165–167] as activating agents. For CO_2 activation, Esfandiari *et al.* (2012) found optimal conditions of 975 °C for 240 min to produce ACs with a SA of 790 $m^2 g^{-1}$.[163] Compared to much of the chemical activation results presented in Table 4, the CO_2 activation requires a higher temperature and longer treatment time to produce a product of lesser SA. Mandoza-Carrasco *et al.* (2016) compared steam activation (8.33 mL min^{-1}) of PET to KOH activation at an IR of 2.[165] It was found that KOH activation caused an optimal SA (1002 $m^2 g^{-1}$) at 850 °C, while steam activation resulted in a higher SA (1235 $m^2 g^{-1}$) at 800 °C under the same treatment time of 1 h. Although the results are influenced by the levels of activating agent used, this showcases that steam activation can produce similar SAs as KOH at a reasonable IR of 2.

5.5.2. Alternatives to KOH. In terms of the chemical activation of PET, a number of studies have investigated chemical activators other than the widely used KOH activator. For example, NaOH activation was found to produce very similar SAs to that of KOH using a two-stage carbonization/activation process.[168] Both activating agents (IR = 2) produced maximum SAs of ~2000 $m^2 g^{-1}$ at 850 °C (KOH activation) and as low as 800 °C (NaOH activation). de Castro *et al.* (2018) investigated K_2CO_3 activation at 800 °C and $ZnCl_2$ activation at 500 °C.[169] Through analysis of the K_2CO_3 IR, it was found that an optimal SA of 1390 $m^2 g^{-1}$ was achieved at a relatively low IR of 0.5. In a separate study, a greater SA of 1439 $m^2 g^{-1}$ was achieved using a K_2CO_3 IR of 2, which was greater than that of the equivalent KOH activation (1206 $m^2 g^{-1}$).[170] However, $ZnCl_2$ activation at 500 °C was not as effective as it produced an AC of 700 $m^2 g^{-1}$ using an IR of 1.[169] Adibfar *et al.* also achieved a similar SA (682 $m^2 g^{-1}$) by $ZnCl_2$ activation up to a temperature of 800 °C,[171] indicating that an increased activation temperature did not improve the SA development. This study also emphasized the significance of KOH activation, because it reported that KOH produced the highest SA compared to H_3PO_4, H_2SO_4 and $ZnCl_2$ activators under the same conditions.

5.5.3. Single-stage KOH activation. The operational conditions during KOH activation can be analyzed in more detail than other activators due to the increased number of studies performed. As shown in Table 4, the most prevalent process used is the single stage KOH activation. Blanchard & Mekonnen (2022) reported that increasing KOH activation (IR = 1) temperature from 700 to 800 °C and time from 1 to 2 h caused increases in SA to a maximum of 1214 $m^2 g^{-1}$ (800 °C 2 h).[159] The activation temperature and time were also investigated by Mendoza-Carrasco *et al.* (2016) at an IR of 2, in which activation at 800 °C was found to be optimal at 1 h (SA = 844 $m^2 g^{-1}$) due to the decreased SA upon further increases in time.[165] Additionally, increasing temperature to 850 °C caused the highest SA of 1002 $m^2 g^{-1}$. Another key factor is the IR, which was investigated by Sarici-Ozdemir and Onal (2018) in the IR range of 1–5.[172] At the standard activation conditions of 800 °C for 1 h, the SA continuously increased with IR up to 1889 $m^2 g^{-1}$ at an IR of 5. A second study employing this high IR at even higher temperatures of 900 to 1100 °C, produced ACs with a maximum SA of 1808 $m^2 g^{-1}$ at 900 °C.[173] Evidently, an elevated IR may be necessary to achieve SAs as high as 1800 $m^2 g^{-1}$ but increasing temperature beyond 800 °C does not seem to be worthwhile.

5.5.4. Two-stage KOH activation. Despite the ease of implementing a single stage carbonization/activation process, it is evident from Table 4 that the separation of carbonization and activation can result in the highest PET AC surface areas reaching greater than 2000 $m^2 g^{-1}$. This may be attributed to the interaction of activating agent solely with carbon rather than uncarbonized precursor. Using a 600 °C carbonization step and a KOH IR of 2, two studies have found optimal surface areas of 2006 $m^2 g^{-1}$ (ref. 168) and 1937 $m^2 g^{-1}$ (ref. 174) at an activation temperature of 800 °C. The decrease in SA as activation temperature is increased beyond this point results from pore expansion due to excessive activation. Based on the latter study of Yuan *et al.* (2020), a higher IR was necessary to further increase the SA to a superior value of 2650 $m^2 g^{-1}$ at only 700 °C.[174] A separate study employing a higher carbonization temperature of 700 °C found that an IR of 3 was optimal for activation at 700 °C. However, a comparatively lower surface area of 1690 $m^2 g^{-1}$ was achieved in this study.[175] Therefore, the carbonization conditions may also play a significant role in the final AC properties due to the differences observed in these two studies.

5.6. Thermoset resins

Another important category of plastic precursors is thermoset plastics, which are often found in composite materials. Thermosetting resins are used as a matrix to hold a structural filler in place and are chemically cross-linked such that they cannot be reprocessed or reshaped after curing. Therefore, conversion of thermoset resins to carbon is a promising treatment as they cannot be recycled by the conventional thermomechanical process. Some examples of AC production from commonly used phenolic and epoxy resins are summarized in Table 5.

Phenolic resin (PR) is an example of thermosetting resin material which is commonly used to make fiber reinforced composites.[2] It is a good candidate for carbonization due to its complex structure of phenol and aldehydes that facilitate high carbon yield.[179] Dong *et al.* investigated the production of PR derived AC for application in supercapacitors using K_2FeO_4 as both an activating and graphitization agent.[179] An activation temperature of 950 °C was required to produce an electrode material with a SA above 1000 $m^2 g^{-1}$; however, this was not the only parameter of importance given its application. With respect to SA development alone, KOH has been shown to be most effective compared to K_2CO_3 and $ZnCl_2$ in the activation of phenol–melamine–formaldehyde resin.[180] Within this study, the benefit of PR was also apparent due to the excellent SA of 2376 $m^2 g^{-1}$ achieved, which is superior to that of PET ACs synthesized using similar single-stage activation conditions (Table 4). Additionally, Zheng & Gao (2011) produced a PR derived AC of even higher SA (2653 $m^2 g^{-1}$) using an increased IR of 5.[181] Similar to PET, PRs do not require a stabilization step; however, the impact of an oxidative pretreatment was investigated by Teng & Wang (2000). Oxidation after impregnation was found to increase the carbon yield and enhance SA but only at high KOH levels (IR = 4).[182]

Epoxy resin is another very commonly used thermosetting plastic. In addition to its application in composite materials it is also a large component of electronics, specifically printed

Table 5 List of the ranges in activated carbon BET SAs produced through chemical activation of various thermoset plastics

Precursor	Stabilization treatment	Carbonization conditions	Activating agent	IR	Activation conditions	AC surface area ($m^2 g^{-1}$)	Ref.
Epoxy	—	500 °C 1 h	KOH	3	600 °C 3 h	1353.78	183
Epoxy (PCB)	—	650 °C 2.5 h	KOH	3	800 °C 1 h	2573	109
Epoxy	—	—	KOH	1–2	600–800 °C 2 h	788.1–1728.5	110
Phenolic resin	—	—	K_2FeO_4	19.8	750–950 °C 1 h	416–1086	179
Phenol formaldehyde resin	—	—	KOH	5	750 °C 1 h	2653	181
Phenol–melamine–formaldehyde resin	—	—	KOH	2	800 °C 1 h	2376	180
			K_2CO_3		800 °C 1 h	1610	
			$ZnCl_2$		700 °C 1 h	1296	
Phenol formaldehyde resin	Oxidation (pre-impregnation)	—	KOH	1–4	700 °C 2 h	960–2800	182
	—					1200–2200	

circuit boards (PCBs). The non-metallic portions of PCBs, which comprise 70% of the material, are mainly composed of epoxy resin (~60%).[108] Therefore, it has been of interest to convert the non-metallic portions of waste PCBs to high SA AC using KOH activation[109] and steam activation.[108] Both studies employed carbonization prior to activation at 800 °C. However, the KOH activation (IR = 3) produced a much higher SA (2573 m^2 g^{-1}) using a shorter treatment time of 1 h compared to steam activation, which required 1.5 h to produce ACs of SA = 803 m^2 g^{-1}. Epoxy ACs were also produced for application in supercapacitors using a similar two-stage process with the same proportion of KOH.[183] However, a lower SA of 1353 m^2 g^{-1} was reported, likely due to the lower activation temperature of 600 °C. A single-stage KOH activation process was also investigated by Blanchard & Mekonnen (2023) with increases in IR from 1 to 2 and activation temperature from 600 to 800 °C.[110] This resulted in a maximum SA of 1728 m^2 g^{-1}, which is lower compared to the two-stage KOH activation processes but still comparable and takes advantage of a much simpler process design.

6. Applications of plastic derived AC

Activated carbon (AC) is mainly used as an adsorbent for a variety of pollutant molecules. At its origins in ancient Egypt (1500 BC) it was used for water purifications, and during the first world war it was implemented in gas masks to remove toxic gases.[184] In recent times, AC is often applied for purification of air and color removal from industrial wastes. For many applications, the most important property of the AC adsorbent is the specific surface area, which refers to the total internal and external surface area (SA) of the material per unit mass. Other parameters affecting adsorption include the pore structure, surface functional groups and elemental composition.[185] However, it is also dependent on the treatment conditions and the specific mechanism of adsorption.

Various adsorption isotherm models are used to describe the adsorption process, specifically the relationship between adsorbate concentration (liquid phase) or pressure (gas phase) and the resulting equilibrium adsorption (mg adsorption/g adsorbent). For example, it is generally known that the equilibrium adsorption of dyes increases with dye concentration until the binding sites are filled and the adsorbent is saturated with dye.[186] This adsorption point is called the monolayer capacity (q_m) and is a relevant parameter in many adsorption models, such as the Langmuir model, which is a very popular isotherm describing the adsorption of a single layer of solute on an adsorbent surface (Fig. 7). It is a very simple model assuming adsorption onto homogenous surfaces but can accurately predict the adsorption behavior of a wide variety of molecules. As shown in Tables 6 and 7 outlining various plastic derived AC adsorption capacities, most plastic derived ACs exhibit adsorption behaviors which have been described by the Langmuir model. Additionally, the adsorption of key solutes methylene blue and CO_2 surpass that of commercial ACs in all relevant studies.

6.1. Dye adsorption

One very large application of AC is in the treatment of dye contaminated wastewater produced from textile industries. For this application an additional process consideration is the pH due to its effect on the ionization degree of the adsorbate dye in addition to the chemical state of the AC.[186] This is important because textile dyes are often charged molecules, so electrostatic interaction with the AC plays a large role in the adsorption process. For example, the adsorption of a cationic dye such as methylene blue (MB) is enhanced by a negatively

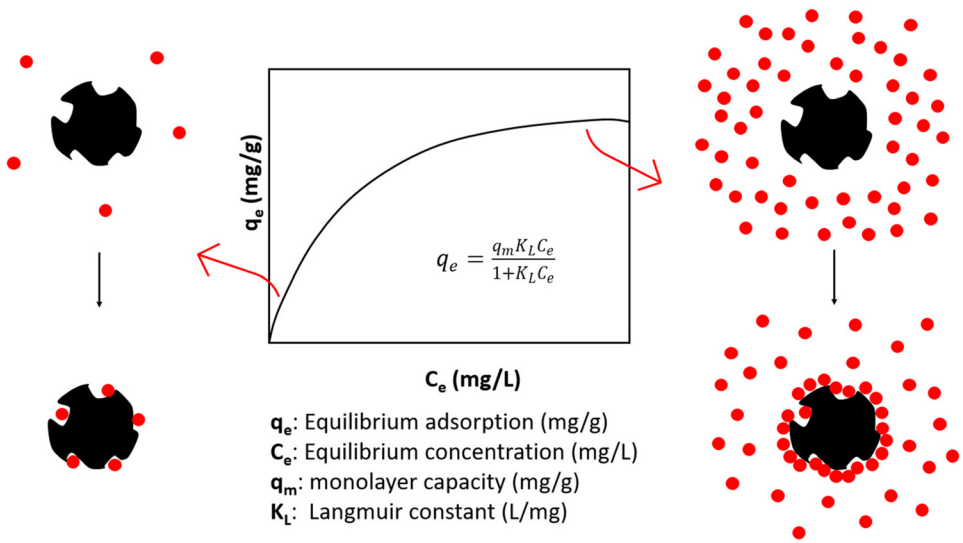


Fig. 7 Langmuir adsorption isotherm and corresponding illustrations of adsorption onto AC at low and high solute concentrations.[187]

Table 6 Tabulated BET surface areas and monolayer adsorption capacities (q_m) exhibited by plastic derived ACs during the adsorption of various pollutants in liquid phase

Precursor	Activating agent	Adsorbate	AC surface area ($m^2\ g^{-1}$)	q_m ($mg\ g^{-1}$)	Isotherm model	Ref.
PVC	KOH	Trichloroethylene	2666	1418.9	Polanyi-Dubinin-Manes	155
		Dichlorobenzene		1308.3		
		Dinitrobenzene		1193.6		
		Hexachlorocyclohexane		2326.5		
PET		Trichloroethylene	2831	1510.9		
		Dichlorobenzene		1381.8		
		Dinitrobenzene		1277.6		
		Hexachlorocyclohexane		2471.9		
PS	Steam	Ni(II)	842	40.82	Langmuir	149
PET	KOH	Methylene blue	1334	326.2	Langmuir	177
		Chloromethylphenoxyacetic acid		298.9		
PET	K_2CO_3	Methylene blue	1390	625	Langmuir	169
		Victoria blue		137		
	$ZnCl_2$	Methylene Blue	700	333		
		Victoria blue		196		
PET	KOH	Methylene blue	1124	335	Langmuir	159
PET	KOH	Phenol	1418	207	Langmuir	176
		Nitrophenol		278		
Epoxy	KOH	Methylene blue	2572	737.19	Langmuir	109
Epoxy	KOH	PET nano-plastic	1705	325	AD-Langmuir	110
Commercial AC		**Methylene Blue**	**900**	**303**	**Langmuir**	169

Table 7 Tabulated BET surface areas and monolayer adsorption capacities (q_m) exhibited by plastic derived ACs during the adsorption of various gases

Precursor	Activating agent	Adsorbate	Surface area ($m^2\ g^{-1}$)	Monolayer capacity ($mmol\ g^{-1}$)		Isotherm model	Ref.
PET	KOH	CO_2	1338	8.65		Langmuir	171
		CH_4		5.60			
	H_3PO_4	CO_2	1223	8.50			
		CH_4		5.30			
	$ZnCl_2$	CO_2	682	5.73			
		CH_4		3.38			
	H_2SO_4	CO_2	583	4.80			
		CH_4		2.94			
PET	KOH	CO_2	1812	10.32		Langmuir	168
	NaOH		1707	8.18			
PET	KOH	CF_4	1771	6.76		Langmuir	174
PET	KOH	CO_2	1690	3.81		Langmuir	178
PVC	KOH	CO_2	2507	Site A	21.36	Dual-site Langmuir	158
				Site B	0.78		
Commercial AC		**CO_2**	**856**	**4.50**		**Langmuir**	194

charged AC surface.[159] As shown in Fig. 8b, a basic pH improves MB adsorption as explained by the development of negative charge on AC through deprotonation of acidic functional groups such as hydroxyls (Fig. 8a). Therefore, not only does the pH influence the electrostatic interaction with charged dyes but also the amount and types of AC surface functional groups. Kuang *et al.* (2020) reported increased MB adsorption onto AC modified by anionic surfactants, while AC modified by a cationic surfactant reduced MB adsorption (Fig. 8d).[188] The effect of dye type as it relates to charge is exemplified in Fig. 8c in which PET ACs selectively adsorb cationic MB dye over anionic methyl orange (MO) dye (Fig. 8c). The monolayer capacity (q_m) of MB dye and other aqueous pollutants by plastic derived ACs can be seen in Table 5 alongside their corresponding AC surface areas.

6.2. Carbon dioxide adsorption

AC is also commonly used for the adsorption of gas molecules such as volatile organic compounds (VOCs)[189] and CO_2,[190] especially considering the increasing concerns related to climate change. The adsorption process primarily occurs through physical adsorption, which is influenced heavily by the AC surface functional groups. AC can be comprised of various functional groups such as carboxylic acid, phenolic and lactone groups,[190] but they also may be imparted through treatments with ammonia, nitric acid, metal hydroxides *etc.*[189] For CO_2 adsorption specifically, the introduction of nitrogen[191] and oxygen[192] functional groups are known to enhance the adsorption. Both elements are more electronegative than the surrounding carbon and can pull electrons to increase the

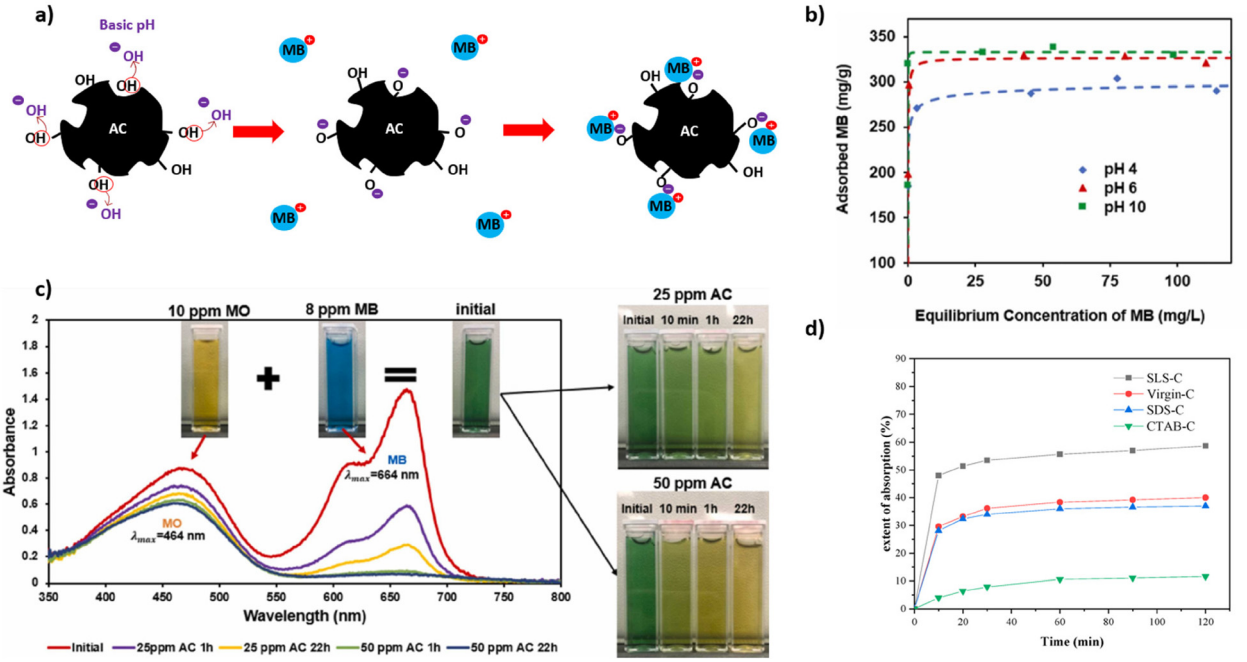


Fig. 8 (a) Adsorption of methylene blue (MB) by AC in basic solution with hydroxyls as representative surface functional groups facilitating electrostatic interactions; (b) adsorption isotherms of MB onto PET AC (1 : 1 KOH IR, 800 °C) under various solution pHs; (c) UV-vis spectra of a mixed dye solution containing methyl orange (MO) and MB over time after treatment with PET AC (1 : 1 KOH IR, 800 °C) and corresponding solution images. Adapted from ref. 159 with permission from Elsevier. Copyright ©2022; (d) adsorption isotherm of MB onto unmodified AC (Virgin-C), and AC modified with anionic sodium lauryl sulfate (SLS-C), anionic sodium dodecyl sulfonate (SDS-C), and cationic hexadecyl trimethyl ammonium bromide (CTAB-C). Adapted from ref. 188.

polarity and attract CO_2 molecules[192] through dipole–dipole forces, as shown by the red hashed bonds in Fig. 9a. Additionally, Yuan *et al.* (2020) found that the pore size plays a large role in CO_2 adsorption by PET ACs.[168] As displayed in Fig. 9c, the pore volume of narrow pores (<0.8 nm) was correlated closely with CO_2 uptake rather than total pore volume. Therefore, the trend in CO_2 adsorption with increasing activation temperature (Fig. 9d) did not align with the BET surface area which was optimal at 800 °C. On the other hand, PET ACs produced at 700 °C followed CO_2 adsorption trends aligning with the overall textural properties (BET SA, pore volume) which were maximized at an IR of 3 (Fig. 9b).[178] The q_m of CO_2 and other gaseous pollutants by plastic derived ACs can be seen in Table 6 alongside their corresponding AC surface areas.

6.3. Micro- and nano-plastic adsorption

Another noteworthy application of AC is in the adsorption of micro- and nano-plastic (NP) pollution from wastewater. This waste is caused by human activities such as laundering and exfoliant products which introduce small plastic particles into wastewater effluents.[4] These particles breakdown into microplastics (MPs) and further into nano-plastics (NPs), which can escape wastewater treatment operations much more easily.[195] With respect to MPs, various studies have investigated biochar within columns[196–198] and AC filters.[199] Similarly, the adsorption of the more difficult to treat NPs using biochar[200,201] and commercial AC[202] have been studied using batch mixing experiments. Recently, a plastic epoxy precursor has been activated and investigated for NP adsorption.[110] Unlike the other studies which employed charged PS NPs as the adsorbate, this work used neutrally charged PET NPs. Due to the surface charges, the PS NPs followed monolayer adsorption which was described well by the Langmuir model (Fig. 10a and b), while the more neutral PET NPs could form multiple layers on the AC which was described best by the multilayer AD-Langmuir adsorption isotherm model (Fig. 10c).

The NP adsorption capacity of the various carbonaceous adsorbents and the maximum percentage recovery of NPs are reported in Table 8. Based on the monolayer capacities, the Epoxy AC clearly has a much higher capacity for adsorption of NPs, which may be attributed to its high surface area of 1705 $m^2\ g^{-1}$. However, the NP recoveries (%) at low NP concentration are important to discuss as it is relevant to its application in wastewater treatment. While the epoxy AC showed superior adsorption under relatively high NP concentrations (100–350 mg L^{-1}), it struggled to achieve percentage recoveries above 95% as was observed for biochar[200] and commercial AC[202] at lower NP concentrations. This may be attributed to the oppositely charged NP and adsorbent combinations in these studies (Table 8), which enhance the adsorption even at low solute concentrations. Therefore, adsorbents derived from plastics like epoxy have good potential for applications in NP recovery but may require surface treatments and further process optimization to improve their interaction with neutral plastic particles.

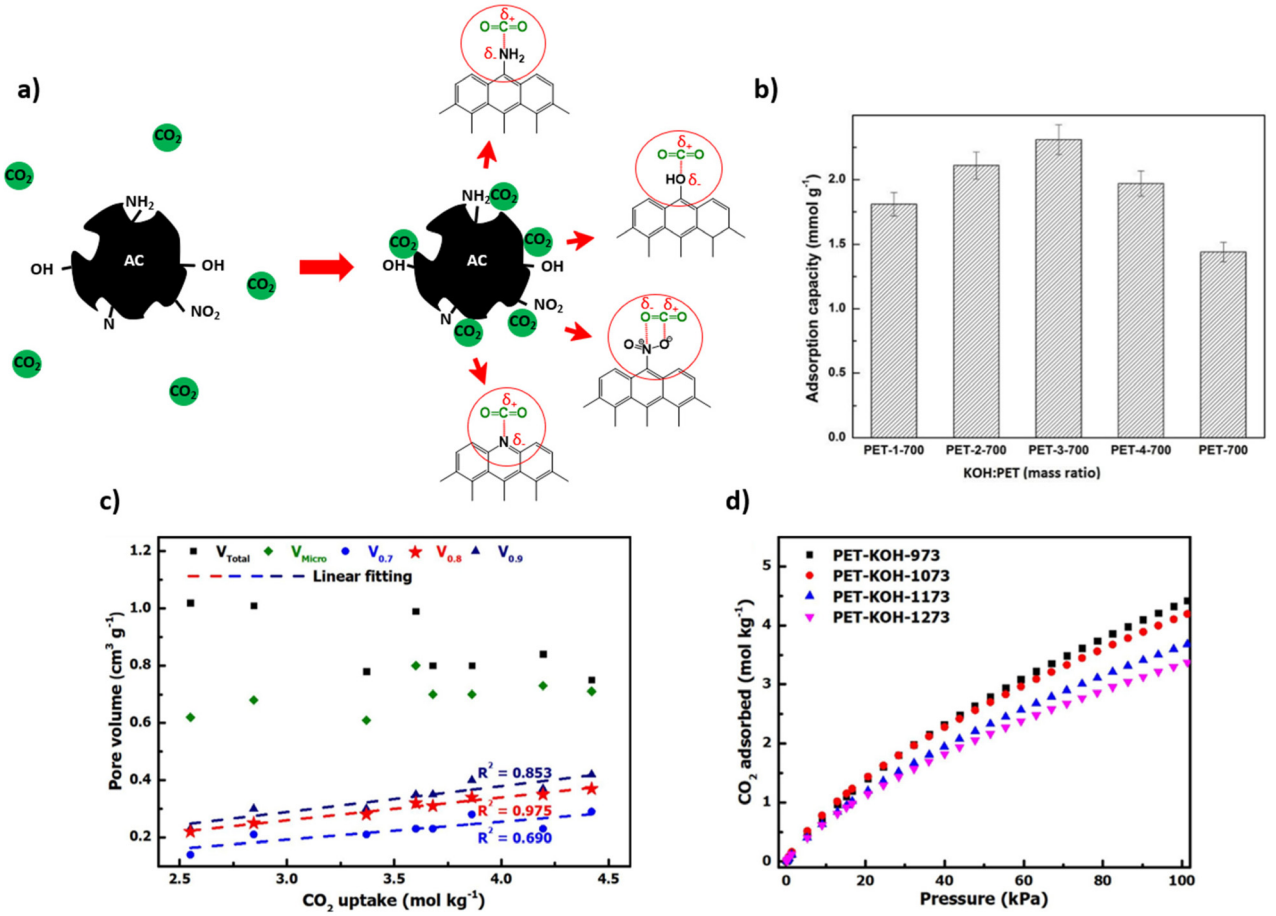


Fig. 9 (a) Adsorption of CO_2 on AC with oxygen and nitrogen surface functional groups facilitating polar interactions (red hashed bonds);[193] (b) adsorption capacities of PET ACs prepared at 700 °C using varying KOH IRs. Adapted from ref. 175 with permission from Elsevier. Copyright ©2019; (c) CO_2 uptake in relation to pore volumes of PET AC prepared using a KOH IR of 2 and (d) the CO_2 adsorption isotherms using AC of various activation temperatures. Adapted from ref. 168 with permission from Elsevier. Copyright ©2020.

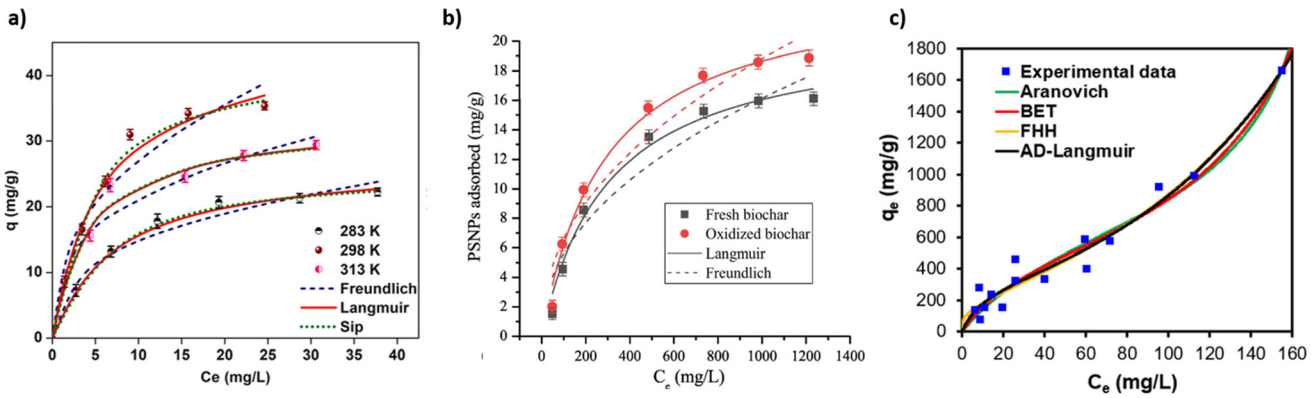


Fig. 10 Adsorption isotherm curves of (a) PS NPs onto sugarcane Bagasse biochar at varying adsorption temperatures. Adapted from ref. 200 with permission from Elsevier. Copyright ©2021; (b) PS NPs onto oxidized and non-oxidized corncob biochar. Adapted from ref. 201 with permission from Elsevier. Copyright ©2021; and (c) PET NPs onto epoxy AC. Adapted from ref. 110 with permission from Elsevier. Copyright ©2023.

6.4. Comparison to existing products

The capacities of other activated products were also compiled to contextualize the properties of the plastic derived ACs. Activated products of various feedstocks are compared in Table 9 with respect to their surface areas and methylene blue adsorption. Methylene blue (MB) was chosen as a reference adsorbate because it is a common parameter for measuring

Table 8 Comparison of NP adsorption capacities and recovery using various carbon-based adsorbents

NP type	Adsorbent type	Adsorbent surface area ($m^2\ g^{-1}$)	[NP] ($mg\ L^{-1}$)	pH	NP zeta potential (mV)	AC zeta potential (mV)	Monolayer capacity ($mg\ g^{-1}$)	Isotherm model	Maximum NP recovery (%)	Ref.
PS	Bagasse biochar	540.36	10–50	5.5	−39.8	+2.85	44.9	Langmuir	>99	200
PS	Corncob biochar	36.3	50–1000	7	−48	−45.1	20.89	Langmuir	—	201
PS	Commercial AC	1150	5–40	7.4	∼(+40)	∼(−28)	2.15	Langmuir	98	202
PET	Epoxy AC	1705	100–350	7	−0.074	−33.8	325	AD-Langmuir	94	110

Table 9 Surface area and methylene blue adsorption capacities of AC products from various sources

AC source	AC surface area ($m^2\ g^{-1}$)	Langmuir monolayer capacity ($mg\ g^{-1}$)	Ref.
Commercial AC (Filtrasorb)	1050	299	203
Commercial AC	950–1050	355	204
Commercial AC (DARCO)	900	303	169
Commercial AC (Merck)	950	200	205
Peach stone	1298	412	206
Bamboo dust	—	143	207
Coconut shell	—	278	
Groundnut shell	—	165	
Rice husk	—	344	
Straw	—	472	
Oil palm shell	596	244	208
Tire char	602	227	209
Rubber seed coat	1225	227	210
Desert plant	1178	130	205
Cola nut shell	648	87	211
Pea shell	—	270	212
Tea seed shell	1530	325	213
Chitosan flakes	318	144	214

adsorptive capacity. The most common methods include the iodine adsorption for indication of small pore (<2 nm) adsorption and molasses adsorption for indication of large pore (>50 nm), while MB adsorption is related to both mesopore and macropore adsorption.[203] Therefore, MB adsorption data is available for many commercial and synthesized AC products, which can be compared to the aqueous adsorption data obtained for plastic derived ACs (Table 6) containing mainly MB studies.

When comparing Tables 9–6 it can be stated that plastic derived ACs have very similar SA and MB capacities to the commercial AC products. In terms of the alternative products, there is a range of adsorption capacities generally between 100–400 $mg\ g^{-1}$. However, most of these values are also in line with commercial ACs which are observed to be ≥200 $mg\ g^{-1}$. As observed in Table 9, the products of lower adsorption capacities are not necessarily explained by the trends in SA due to the effect of the initial feedstock on the final AC surface chemistry. In comparison, the consistently high MB adsorption capacities of the plastic derived products in Table 6 (∼300–700 $mg\ g^{-1}$) indicate that these products may exhibit a more acidic surface property, as was reported for PET activated by solid KOH.[159,215] This means that the AC surface may contain oxygenated groups with acidic characteristics (*e.g.* Hydroxyl) which can become deprotonated to produce negative surface charge for better interaction with cationic MB dye.[159] Therefore, not only do the plastic derived ACs exhibit competitive SAs with commercial products, but there is also indication of significant oxygen functionalities which can generally improve interaction with polar molecules.

7. Future prospectives

Although research has shown significant potential for the conversion of both thermoplastic and thermoset plastic to activated carbon with substantial adsorption capabilities, there are challenges which have inhibited the implementation of full-scale production. These issues are outlined in Fig. 11. To begin, the first barrier to production of AC from plastics involves the already existing challenges for plastics recycling including sorting, cleaning, and additives. Waste segregation is specifically important due to the concerns surrounding carbonization of mixed plastic streams as mentioned in section 2.4. Therefore, the upcycling of plastic waste will likely begin with plastic that are more easily separated, such as PET bottles which are one of the first plastic wastes to be recycled at high levels.[216] PET is also one of the best plastic feedstocks for a carbonization process, with the most amount of research available on its conversion to activated carbon, as compiled in section 5.5.

With respect to the conversion process itself, the main factor limiting the large-scale production of AC is the cost.[217] Therefore, proper optimization of activation temperatures and times are important to reduce the amount of energy required while producing a product of highest quality and value.[184] Additionally, it is vital to address the typically low production yield for the conversion of plastic to AC. For example, the mass yield of carbon material from PET is only around 17%.[159,171] This can be improved by doping the plastic precursor with chemicals such as increased levels of chemical activating agents, which has shown to inhibit volatilization during heat treatment.[110,159] Lastly, there are environmental concerns surrounding the potential release of hazardous volatile compounds during the carbonization process, such as benzoic and terephthalic acids in the case of PET.[218] This issue reinforces the need to improve AC yield such that gaseous emissions are minimized. Overall, upcycling plastic waste into AC would be a very helpful waste diversion method; however, the feasibility

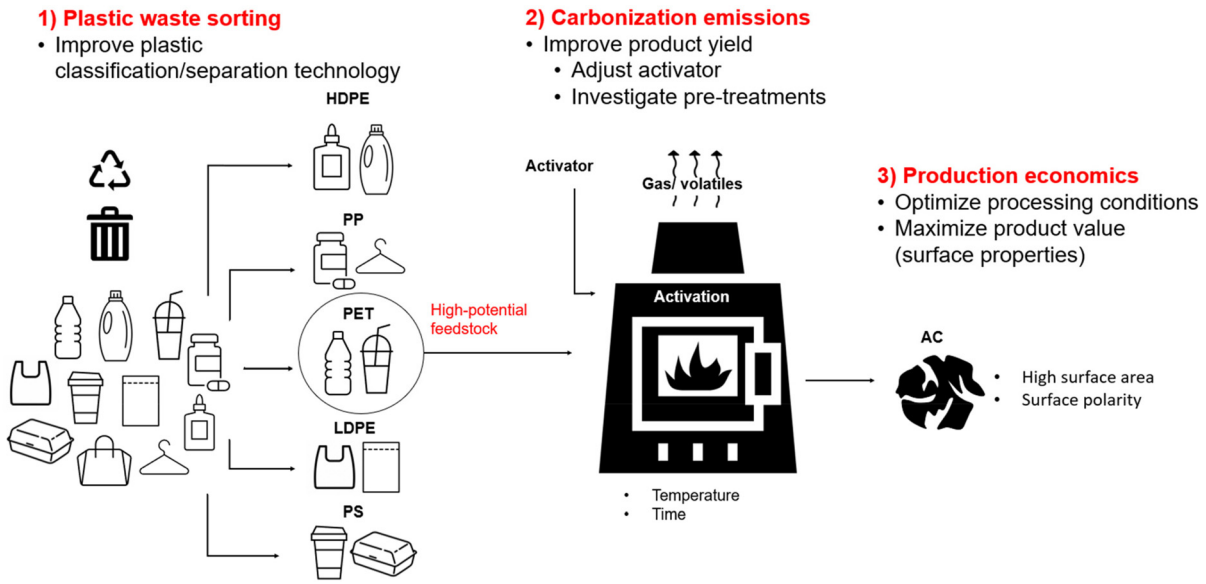


Fig. 11 Key challenges in producing AC from waste plastic and the areas of future investigation.

must be fully investigated based on the supply of segregated waste streams, energy requirements, and the resulting product value and yield.

8. Conclusions

There is no single solution to the plastic waste issue, as this waste may vary in its composition and each disposal option has its advantages and disadvantages. Relying solely on mechanical recycling proves insufficient, yielding recycled products of limited quality and offering no remedy for thermoset plastics. To address this challenge, a combination of chemical recycling and mechanical recycling is imperative. In addition to the depolymerization of plastics into monomers, it is essential to integrate upcycling methods such as pyrolysis processes to extract value from underutilized waste streams. Notably, this study underscores the significance of carbonization, akin to pyrolysis but tailored to optimize carbon material synthesis. Both pyrolysis and carbonization processes must overcome key recycling issues, such as accommodating mixed waste streams and contamination. However, they offer viable solutions for recycling thermoset waste, which are notoriously challenging to recycle. Furthermore, carbonization processes exhibit the potential to yield high-value products like nanomaterials, carbon fibers, and specifically activated carbon (AC), achievable by introducing an activating agent during carbonization.

This review discussed the current progress in the conversion of plastics to AC, with a specific focus on chemical activation. It was evident that KOH is by far the most common activating agent and produced very high surface area ACs. Although many studies successfully produce high surface area ACs through simultaneous carbonization and activation processes, the use of two separate process stages resulted in extremely high surface areas surpassing 2000 m^2 g^{-1}. It was also seen that there is much more research available on the production of AC from PET plastic among all other commercial plastics. PET is a good AC precursor as it is a charring plastic due to its aromatic structure and does not require stabilization pre-treatments due to the presence of oxygen. Other plastics like polyolefins do require stabilization treatments but produce similarly high surface area ACs through activation. Thermoset resins are also very good precursors due to their aromatic and oxygenated structure, in addition to the greater need for disposal of these non-recyclable plastics. Both epoxy and phenolic resin have shown good potential for producing ACs with application in supercapacitors, CO_2 adsorption and even nano-plastic adsorption.

A very important aspect of the carbonization and activation conversion processes is the value of the resulting AC product. It was shown that plastic derived ACs exhibit very high surface areas, which translates into substantial capacities for the adsorption of pollutants, such as dyes and CO_2. There is also potential for these ACs to treat a wider range of pollutants including micro and nano-plastics, which are an increasing pollution concern. However, more research investigating this area is necessary, especially with respect to plastic derived ACs. Overall, this work communicates that alternative plastic waste disposal options such as carbonization can potentially divert a portion of plastic waste from landfilling or incineration. It displayed the success in converting many types of plastics to high surface AC and their application in various adsorption processes. The feasibility of employing these carbonization and activation processes should be considered in detail in future analyses. However, due to the dire need to dispose of plastic wastes, they should not be overlooked as precursors to AC products that are conventionally produced from coal or biomass sources.

Conflicts of 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.

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