

## Industrial Solid Waste as A Source of Nanomaterial Synthesis

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### ABSTRACT

*There has been an increase in waste resulting from industrialization and urbanization, which directly impacts the environment and human health. Proper utilization of the waste generated by various industries must be initiated to minimize the pollution caused by these industries. To do this, we must adopt a sustainable approach. Nanomaterials can be synthesized from industrial waste as one example of such an approach. An in-depth look at the various methods involved in converting industrial waste into valuable nanomaterials is the focus of this chapter. Waste generated from the steel industry, the plastic industry, the textile industry, the electroplating industry, the mining industry, the paint manufacturing industry, the battery manufacturing industry, the paper and pulp industry, and many others are used as raw materials for manufacturing nanomaterials. Nanomaterials synthesized from industrial waste have been effectively used for wastewater treatment, fluoride removal, environmental pollutant remediation, and carbon nanotubes, among other uses. It is essential to conduct more research to minimize waste generated during production processes and repurpose waste to convert it into wealth.*

**Keywords-** Environment, Ecology, Nanomaterial, Industrial waste, Pollutant, Plastic waste, Carbon Nanotubes Sustainability, No poverty, Zero hunger

### 1. INTRODUCTION

There is an alarming problem relating to environmental pollution caused by industrialization and urbanization, which is considered one of the most significant issues of the 21st Century. Industrialization is one of the most critical aspects of building an uplifting and self-sufficient economy in developing countries. It was reported in a report that about 242Mt (Megatonne) of plastic waste was generated worldwide in 2016 (1, 2). It is estimated that 6.30 billion tons of plastic waste were developed between 1950 and 2015, of which only 9% is recycled, while more than 80% remains in landfills or the natural environment (3). Asia is a significant producer and consumer of plastic. Over 50% of the plastic produced worldwide comes from Asia. From 2013 to 2015, Asia had 131 Megatonnes of plastic. In Asia, plastic waste accounts for 79 and 42 Megatonnes of municipal and industrial solid waste, respectively (4). An estimated 62 million tonnes of municipal solid waste are produced annually in India, including medical, plastic, and E-waste. By the year 2050, India and China will contribute the majority of waste production to the world, with 27 billion tons estimated to be produced worldwide. Steel mills produce steel melting slag and blast furnace slag; thermal power plants have coal ash; copper,

aluminium, and zinc industries generate red mud and tailings; paper and pulp industries generate fertilizer and lime; sugar industries generate press mud and allied industries produce gypsum; these are the primary producers of industrial solid waste. The anaerobic decomposition of solid waste leads to methane production, which contributes to global warming. The average temperature in India during the summer rises to 45 degrees Celsius, which poses challenges due to odor, leachate settling in reservoirs, and uncontrolled waste burning that contributes to respiratory diseases and smog (5). It also indicates an increase in throat and nose infections, inflammation, asthma, breathing difficulties, anaemia, allergies, and reduced immunity (6,7). During the steel production process, a waste product called steel slag is characterized by non-metal oxides, metals, and silicates. This by-product is produced at the rate of more than 15kg/ton of steel produced (6, 8, 9, 10).

Less than 75% of steel slag is reused, as it contains elements that limit its application (11, 12.). Because of this reason, the demand to treat and reuse this waste using less expensive and more sustainable processes is growing (13). Sugarcane bagasse, rice

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husks, palm kernel shells, and bamboo are examples of agro-industry waste sources that contain natural polymers like lignin, cellulose, hemicellulose, and some inorganic substances. There is a large amount of carbon in waste rubber tires (representing about 81.2 wt%) used in various applications to reduce carbon emissions (14). Approximately 1,000 million waste tires are generated worldwide annually (15) (fig.1).

**Fig. 1: Solid Waste in India**



*Source: Adopted from available review and literature*

As China alone produces over 50 million waste lead batteries each year, recycling these batteries is necessary to prevent ecological and public health issues (16). China manufactures 15 billion Zn-manganese batteries annually (17). The toxic effects of Zn on humans and other organisms can include metabolic deficiencies and impaired calcium uptake (18). Industry negligence and a lack of infrastructure contribute to problems related to industrial solid waste disposal. Industrial waste is treated through incineration, curing, landfilling, and stabilization. Incineration reduces waste volume and causes air pollution, soil and groundwater contamination from landfill leakage, and high costs for waste stabilization. The 3R rules (Reduce, Reuse, Recycle) emphasize finding a method for adequately utilizing industrial waste (19). Nanomaterial synthesis from industrial waste is considered the most effective way to recycle industrial waste, as very little waste is generated. The waste generated by various industries can be used as raw material, thereby reducing the cost of production and promoting environmental sustainability. Many nanomaterials have been made from waste and are used in reducing pollution, wastewater treatment, fluoride removal, carbon nanotube synthesis, and many other uses. However, more research is needed to improve the recovery process and manage the toxic gases and by-products created during nanomaterial synthesis.

### 1.1. Pretreatment of Industrial Waste

Pretreatment of industrial waste is the most critical step in synthesizing nanomaterials from industrial waste—several methods for preparing industrial waste samples depending on their composition and type. Pretreatment methods can be classified into physical, chemical, and combined processes. Nanomaterials synthesized from waste can be influenced by their treatment and chemical composition (20). Chemical activation, treatment with acids, and temperature are all factors that affect nanomaterial synthesis (21). Initially, industrial waste was used directly as a catalyst without Pretreatment (22). However, physical and chemical activation later enhanced the activity (23).

### 1.2. Physical Pretreatment for Nanomaterial Synthesis

In physical Pretreatment, chemicals are not used. Grinding and milling are ubiquitous and easy processes. Mechanical energy can be produced and transferred to the reactants using mortar and pestle. Milling describes the process in the ball mill (24). Ball milling of industrial waste reduces the particle size to obtain a homogenous mixture for further applications (25). Preparing Pb nanoparticles from cathode ray tube funnel glass waste is also possible. The glass waste is first ground into smaller pieces of 10 mm. Wet scrubbing and ultrasonic cleaning were used to remove the coatings on the glass. The glass particles are then ball-milled, sieved through a 200 mesh (74 m) channel, and dried for 24 hours at 105 °C (26). From waste rubber tires, Zn nanoparticles are synthesized by the ball milling technique. A slow-speed shredder removes metal wire from scrap, followed by a narrow blade shredder that reduces the particle size to 6 cm. Particles are ground to a smaller size using rolling mills and then sieved through stainless sieves to separate particles of 1000 and 100 micrometres (27).

### 1.3. Chemical Pretreatment for Nanomaterial Synthesis

Removal of contaminants from the waste sample is the primary aim of the chemical pretreatment method. This can be achieved by making them soluble by heating or treating them with chemicals. One of the chemical pretreatment methods is strong acid hydrolysis, where concentrated strong acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> are commonly used for treating waste materials. However, the limitations of concentrated acids are their necessity to recycle, corrosive nature, and neutralization of acids. The commercial process of strong acid hydrolysis is available for microbial fermentation (28). Adding toxic chemicals such as sulphuric acid, lime, or ammonia which adds cost to the process, is not required if Pretreatment is done using water.

### 1.4 Combined Pretreatment for Nanomaterial Synthesis

The combined method of Pretreatment includes both physical and chemical processes of Pretreatment. Sugarcane waste or bagasse was a precursor in synthesizing Nano-activated carbons (NACs). Bagasse was washed, sundried, and heated in a muffle furnace for 5 hours at 300°C. Later it is soaked for 18-20 hours in a CaCl<sub>2</sub> solution. After that, waste is washed with double distilled water and oven dried at 110°C before it is used in nanomaterial production.

## 2. Synthesis of Nanomaterials

For the synthesis of nanomaterials from waste material, various techniques were used. The following are some of the designs. Table 1 shows the methods of nanoparticle synthesis.

### 2.1. Chemical/Thermal activation method

The waste material (e.g., sugarcane waste) is mixed with the chemical reagent at a particular ratio in a glass container. Various activating agents such as ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, KOH, CaCl<sub>2</sub>, FeCl<sub>3</sub>.6H<sub>2</sub>O, CO<sub>2</sub>, and KCl have been used. The mixture is stirred and heated once the distilled water is added, forming a homogenized and impregnated mixture. Mixing is done at a fixed temperature until it becomes a thick homogeneous paste. Then the wet paste is weighed and placed in the reactor on top of a metal mesh filter. For this purpose, a U-shaped stainless steel reactor is commonly used. The reactor has both inlet and outlet gas pipes. Removal of gaseous by-products is done by using the latter. An inert gas such as N<sub>2</sub> can be passed through the reactor to eliminate air. For sample activation, the reactor is placed in

the muffle furnace for a fixed time and heated to the required temperature. Chemical impregnation of sugarcane waste was done with concentrated sulphuric acid, followed by heating at 600-800°C for 24 h to produce activated carbon. Sugarcane waste is used to prepare Nano activated carbons (NACs) via chemical/thermal activation.

## 2.2. Electric arc discharge method

Generally, the electric arc discharge method utilizes a very high temperature (17000°C) to synthesize CNTs. Compared to other methods, this method characteristically yields CNTs with fewer structural defects. In the rotating cathode arc discharge setup, a hollow graphite rod with a definite diameter, length, and density is used as an anode. The experiment is conducted at a pressure of 500 Torr for 1 min and under an N<sub>2</sub> atmosphere. In the hole of the anode, the waste materials are packed tightly and arced continually for 1 min. The anode is cut into several pieces of equal length from the arcing tip after arcing and then divided into different portions. The soot inside cut pieces is scraped, analyzed, and used to prepare CNTs via the arc discharge technique. The potential and ability to produce a large number of CNTs is the advantage of this technique, while comparatively less control over the alignment of generated CNTs is the main drawback of this technique (Table 1).

**Table 1: Formation Methods of Nanoparticles**

Nanoparticle	Recyclable waste	Method	Advantages	Disadvantages
Iron oxide	Iron oxide	Wet ball milling	No use of toxic chemicals, pure, uniform size and shape	High cost, exposure to radiation, high temperature, less productivity
Mn Fe <sub>2</sub> O <sub>4</sub>	Pickling waste liquor	Co-precipitation	Cost-effective, highly versatile, high yielding, controllable, stable	Low purity, use of toxic chemicals, hazardous to human beings and animals
Fe <sub>3</sub> O <sub>4</sub>	Steel pickling	Co-precipitation	Cost-effective, highly versatile, high yielding, controllable, stable	Low purity, use of toxic chemicals, hazardous to human beings and animals
Zn Fe <sub>2</sub> O <sub>4</sub>	Electroplating sludge	Calcination	No use of toxic chemicals, pure, uniform size and shape	High cost, exposure to radiation, high temperature, less productivity
Zero valance iron	Steel waste	Precipitation	Simple and inexpensive, less instrumentation, low temperature	Low purity, use of toxic chemicals, hazardous to human beings and animals
Aluminium oxide	Alum sludge	Calcination	No use of toxic chemicals, pure, uniform size and shape	High cost, exposure to radiation, high temperature, less productivity
Titanium oxide	Fly ash	Washed and TiO <sub>2</sub> coated	Cost-effective, highly versatile, high yielding, controllable, stable	Low purity, use of toxic chemicals, hazardous to human beings and animals
Tea waste	Tea factory waste	Co-precipitation	Cost-effective, highly versatile, high yielding, controllable, stable	Low purity, use of toxic chemicals, hazardous to human beings and animals
Iron oxide nanocomposite	Papermill sludge	Calcination	No use of toxic chemicals, pure, uniform size, and shape	High cost, exposure to radiation, high temperature, less productivity
Zeolite	Fly ash	Washed with acid	Cost-effective, highly versatile, high yielding, controllable, stable	Use of toxic chemicals hazardous to human beings and animals
Fly ash nanocomposite	Fly ash	Hydrothermal	No use of toxic chemicals, pure, uniform size and shape, Simple and inexpensive, less instrumentation,	High cost, exposure to radiation, high temperature, less productivity
Composite adsorbents	Waste sludge	Pyrolysis	No use of toxic chemicals, pure, uniform size and shape, Simple and	High exposure to radiation, high temperature, less productivity

*Source: Adopted by authors based on review and literature*

## 2.3. Vacuum Evaporation and Inert Gas Condensation Method

In vacuum evaporation, a solid is deposited on a heated surface via chemical reactions, a commonly used method for synthesizing nanomaterials. The thermal process leads to vaporization. A vacuum level of 75006.2 to 750.062 Torr and a pressure of less than 0.0008 Torr are generally required to perform this procedure. Heating causes the evaporation temperature to rise. The atoms/molecules leave the source surface and come into contact with another character in the chamber as they evaporate. As a result of the lower surface temperature compared to the starting temperature, molecules lose their energy and condense. The vapour pressure is higher at the elevated temperature than the previous temperature of the surface; hence they will stick to the surface and will not re-evaporate. A reasonable deposition rate can be achieved if the vaporization rate is sufficiently high, e.g., 1.3 Pa or 0.01 Torr. Gas condensation was first used in the synthesis of metallic nanocrystals. The metallic component or inorganic material is vaporized in a 1-50 bar atmosphere using a thermal evaporation source. High residual gas pressure is responsible for the generation of NPs by gas phase collisions. For example, in a helium (He) gas atmosphere, Fe is evaporated to synthesize Fe-NPs. Collisions with Helium atoms cause Fe atoms to lose kinetic energy and condense into tiny crystals that become loose nanopowder. The vacuum separation and inert gas condensation methods were used to recover zinc and prepare zinc nanoparticles from battery waste.



#### 2.4. Sodium Borohydride Reduction Method

Metallic nanoparticles are commonly synthesized using sodium borohydride reduction. A sodium borohydride solution is rapidly added to waste material to produce NPs via reduction. After NPS production, excess sodium borohydride was repeatedly removed by rinsing with deoxygenated water and ethanol solution.

#### 2.5. Solvent thermal method

Using the solvent, the thermal method to synthesize metallic nanoparticles or nanocrystals is standard practice. In this process, solvents present in closed vessels undergo chemical reactions. Hydrothermal processes use water as a solvent. To ensure that waste materials undergo optimal thermal treatment, the waste materials are mixed with suitable solvents and heated at a particular temperature. Afterwards, the mixture is cooled, washed, and dried to form the final NPS product. This technique is used to prepare Pb NPs from spent lead battery waste.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NPs were prepared via solvent thermal method using ethanol as a solvent and heating the mixture for two h at 1500C to produce NPs (fig. 2).

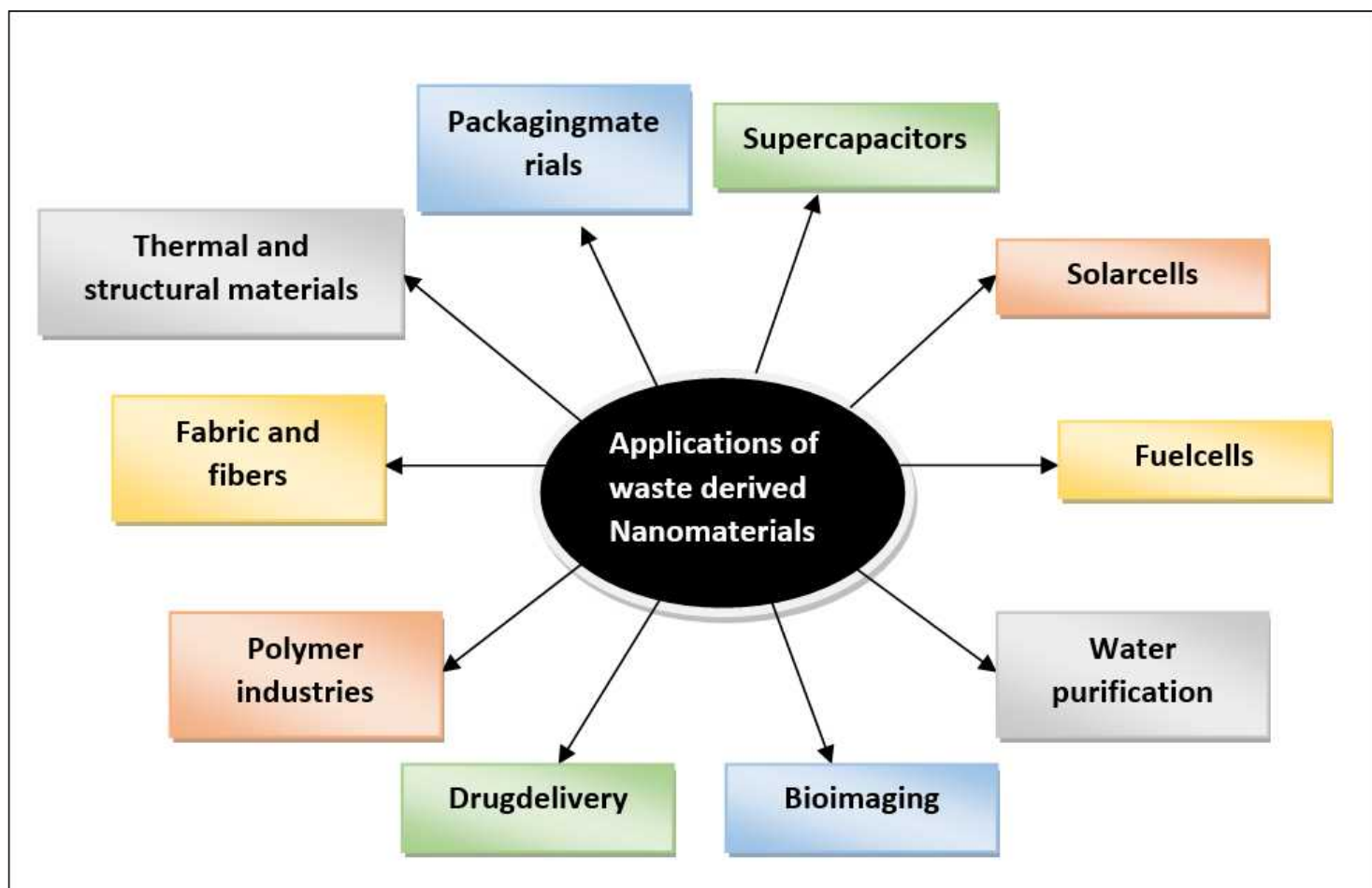


Fig. 2: Schematic representation of the application of waste-derived Nanomaterials

### 3. Application of Waste-Derived Nanomaterials in Environmental Pollution Remediation

Nanomaterials synthesized from industrial waste using physical-chemical methods have broad applications in environmental pollution remediation. Nanomaterials produced from industrial waste include CuO, MgCr<sub>2</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, and MFe<sub>2</sub>O (M-Cu, Mn, Ag, and Zn), copper ferrite, magnetic biochar, etc., among these iron-rich waste, is proved effective and widely used in pollutant removal by adsorption method, Fenton degradation, and photocatalytic degradation. Besides their application in pollution remediation, it is essential to study the hazards which may be caused by the by-products produced during the reaction or leaching back of the original pollutant (fig.2). The steel slag waste (SSW) obtained from the steel slag industrial solid waste is used in the synthesis of Al-Cu oxide nanoparticles for the efficient removal of fluoride from aqueous solutions. The SSW/Al-Cu Nanocomposite was synthesized by

using the chemical reduction method. The steel slag was crushed, sieved through 20 and 40 meshes, washed with distilled water for 24 h, decanted, dried, and stored to synthesize nanocomposite SSW/Al-Cu. On the other hand, steel slag was used as a low-cost sorbent for the removal of Ni (II), Pb(II), Co(II), and Cd(II) ions from the aqueous solutions in the presence of the chelating agent.

#### 3.1. Production of Nanofiber Gels and Paper From Sugar Beet Waste using Enzymatic Pretreatment

Sugar beet pulp is the primary waste product obtained from the sugar industry. It constitutes a potential source of biopolymers. Some pulp is used as fodder for animals, but a significant portion is discarded. The leftover sugar beet pulp roughly consists of 30% hemicellulose, 20-30% cellulose, and 30% pectin. The cellulose fraction can be utilized in producing paper, gels or as a reinforcing agent in composites.

## 4. Methods for Nanomaterial Synthesis with Advantages & Disadvantages

It is possible to synthesize nanoparticles from industrial wastes using various methods. Synthesis of nanoparticles requires multiple chemical and thermal methods (31, 32). Nanoparticles are modified to remove different types of pollutants from industrial waste (33, 34). Following are the various methods and techniques to form nanoparticles:

**4.1. Co-precipitation method:** Chemical methods synthesize nanoparticles from industrial waste. This method helps obtain a high yield of nanoparticles because it is efficient and straightforward (35). All industrial waste is treated with acid to leach down its metal content. The acids used for leaching are HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, etc. After acid wash, it is treated with some alkali salts, including NaOH and MgO, which helps increase the pH to 12 (35, 36). Different parameters that determine the size and shape of nanoparticles include extractant type, metal type, reaction temperature, leaching liquid, pH, rate of stirring, and reaction speed (36). In the co-precipitation method, silica precipitation occurs to synthesize the nanomaterials. Base extraction and acid wash of waste to maintain its pH up to 7, followed by ageing for 12hrs at 100°C temperature (37). Precipitation of silica from biomass fly ash ranges from 44.42 to 93.63% and determines the purity of nanoparticle synthesis. The main disadvantage of this method is that the material obtained is less pure than the material synthesized by other methods.

**4.2. Hydrothermal method:** The method involves heating industrial waste at 120-550 C and 20-150 bar, respectively, at high temperatures and pressures. Industrial waste can be converted into value-added products by heating some inert gases, such as oxygen or nitrogen, at high temperatures and pressures (38). In addition to hydrothermal heating, solvothermal heating uses different solvents instead of water (39). The product obtained from this method contains other oxygen-containing carbon compounds in which C=O generate oxygen species, which help degrade organic pollutants and convert the carbon-rich waste into Nano products (40). Nano products formed by this hydrothermal process include ferrite catalysts, sludge carbon/TiO<sub>2</sub>, TiO<sub>2</sub>-FA nanocomposites, and tungsten oxide-FA nanocomposites. This method is very suitable for treating wet solid waste rich in carbon as it has more benefits than high-temperature pyrolysis. Maintaining the raw material's moisture content is unnecessary because the energy consumption rate is shallow, and the reaction process is mild. Similarly, there is no need to dry the waste before starting the process of hydrothermal (41). The hydrothermal method has many advantages as it can control the size of the particle, morphology, and surface chemistry as it controls the temperature and pressure, and this is its disadvantage, too, as it requires high temperature and pressure to conduct the reaction (42).

**4.3. Microwave-assisted synthesis:** It is one of the methods used to synthesize a wide variety of inorganic materials such as nanoparticles, semiconductors, and non-porous materials. During this process, the synthesis of nanoparticles is carried out through the interaction of the molecular and ion structure of the different agents because microwave energy strikes the material through these interactions (43). These radiations decontaminate the sediment sludge and metal ions from various

toxic compounds. This process is one of the most efficient ways to create nanoparticles because it has significant benefits over other techniques, such as quick heating, quick reactions, high yields, and excellent thermal stability (44). Using a microwave chemical reactor, Duan et al. 2017 produced magnetic biochar from iron sludge and cotton stalk to remove Cr (VI). The successfully manufactured hydroxyapatite nanoparticles from phosphogypsum waste generated by phosphorus fertilizer factories to test its effectiveness in removing fluoride from aqueous solutions (45). This approach is superior to previous synthesis techniques because it produces crystalline nanomaterials quickly and operates at low temperatures (46).

**4.4. Pyrolysis:** One of the most efficient processes for producing materials with a sufficient surface area, a stable structure, a high ion exchange capacity, and value-added surface functional groups is pyrolysis (47). The temperature and length of the reaction during pyrolysis significantly impact how the material's surface chemistry changes. It alters the surface's ability to absorb water, a crucial element in the adsorption reaction. In research by Badosz (48), surface pH increased as temperature increased from 650 to 950°C. Thus, altering the pyrolysis conditions can change the surface attributes such as porosity, selectivity, or catalytic activity. The novel surface chemistry produced by solid-state reactions during pyrolysis directly affects the product's catalytic activity. Toxic gas emissions during the material synthesis process and significant energy usage are drawbacks of this approach (49).

**4.5. Sol-Gel method:** It is an ancient method that is used in different scientific and engineering fields for the production of materials for chemical sensors, fibres, membranes, etc. In this method, the hydrolysis of particles occurs to form a colloidal suspension. As a result of different processes like polycondensation, ageing, thermal decomposition, and drying a colloidal solution was prepared to begin the nanoparticles. The nanoparticles which are synthesized by this method are primarily crystalline. The size of these crystals is small compared to the particles created by other processes like hydrothermal or pyrolysis (50). The precursors primarily used in this method are organic metal compounds and inorganic metal salts. The factors that affect the formation of the gel from colloidal suspension are the type of solution and solvent, acid and base content for treatment, water, and temperature (Khan 2020). The main benefit of this method is that the nanoparticles formed are of high and stable surface area at the end of the process, which is a great advantage of this technique (51).

**4.6. Calcination:** This method generally uses a temperature between 400-600°C to synthesize nanoparticles. This process typically decides the end product of the sample. The final product may be a metal or mixed oxide, focusing mainly on calcination. Standard metal oxides are formed when the temperature is less than 400°C, but spinel oxides are formed when the temperature exceeds 600°C. The prominent phenomenon used in this method is temperature; we can change the type of material obtained and its function by controlling the temperature conditions only. We can accept different nanomaterials by controlling the temperature. When the calcination temperature is lower, the precursor is transferred to double-layered hydroxide, and it gets reconstructed when the material is placed in water or moist gas. The process of reconstruction of particles is known as the "memory effect". The main disadvantage of this process is that the spinel will become unrecoverable when the calcination temperature is very high (52).

**4.7. Application for Pollutant Remediation:** Various catalysts like photocatalysts, electrocatalysts, and Fenton-based catalysts are employed to promote the chemical oxidation of organic pollutants and antimicrobial effects (53). Different Nanocatalysts, such as semiconductors and metal oxides, are utilized for wastewater treatment. Recent studies have focused on using nanoparticles produced by processing industrial waste to remove organic and inorganic pollutants. This section discusses using nanomaterial generated from industrial waste for pollution remediation. Table 2 lists the application of removing impurities and their potential for removal when employing nanomaterial made from industrial waste. Techniques for removing contaminants from industrial waste include calcination, Co-precipitation, Acid leaching, Ball milling, Urea hydrolysis, Ferrite, Pulverization, Microwave irradiation etc. These techniques remove and recycle industrial waste pollutants to synthesize nanoparticles (Table 2).

**Table 2: Application of waste nanoparticles**

Nanoparticles	Source	Applications
Iron oxide	Mill scale	Dye removal
Magnetite	Iron ore	Dye removal
Graphene	Polyethylene terephthalate	Dye removal
CaCO <sub>3</sub>	Eggshell	Lead adsorption
Porous aerogels	Paper, cotton textile, plastic	Oil adsorption
Carbon nanoparticles	Pomelo peels	Mercury detection
Nano-cuprous oxide	Electrical waste	Dopamine and mercury detection
Porous silica	Rice husks	To capture CO <sub>2</sub>
Iron nanoparticles	Pickling line of a steel plant	Nitrobenzene removal

Source: Adopted from available review and literature

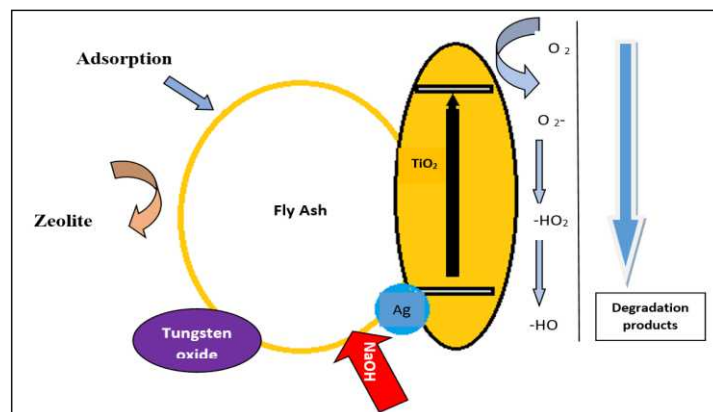
#### 4.7.1. Heterogeneous Photocatalytic

Organic pollutants can be removed from water using heterogeneous photocatalysis (54). The pre-adsorption of contaminants on the catalyst surface is crucial to the degradation of pollutants through heterogeneous photocatalysis. Wide surface area adsorption supports with high adsorption capacities are utilized to achieve this. The substrate's adsorption capacity should allow for TiO<sub>2</sub> diffusion into the substrate. Activated carbon, stainless steel, silica, zeolites, or clay compounds were used to create hybrid photocatalysts (55). Recently, there has been increasing in using waste material as surface support for a TiO<sub>2</sub> photocatalyst.

#### 4.7.2. Photocatalytic activity of Fly ash/TiO<sub>2</sub> nanocomposites

Fly ash is an adsorption substrate when combined with a TiO<sub>2</sub> photocatalyst, making it an effective and environmentally friendly method. By removing heavy metals, dyes, and surfactants simultaneously, nanocomposites treat wastewater with heavy metals, paints, and surfactants (56). There are unburned carbon and metal oxides in fly ash, with TiO<sub>2</sub> probably being active in photocatalysis and Fe<sub>2</sub>O<sub>3</sub> and MnO likely acting as Fenton systems in situ. Waste fly ash makes a promising support material due to its surface chemistry, charge, and shape (57) (fig.3).

**Fig. 3. Schematic diagram of the Fly ash/ TiO<sub>2</sub> nanocomposites and the mechanism of photo-degradation and adsorption**



A comprehensive study on the photo-degradation and adsorption of Methylene blue, Bemacid Blau, and Bemacid Rot, surfactant SDBS, Cd, and Cu by Fly ash/TiO<sub>2</sub> nanocomposites (57, 58). The alkali activation can create new active sites (SiO- and AlO-) on the FA surface, allowing metals to form surface complexes. The difference in surface affinities for Cd<sup>2+</sup> and Cu<sup>2+</sup> before and after treatment with 2N NaOH is caused by a change in chemical and structural properties (59). The degradation efficiency of benzene by Ag@TiO<sub>2</sub>/ZFAB and Rhodamine B by Zeolites fly ash bead (ZFAB)/TiO<sub>2</sub> composite (60) The composite was made by combining TiO<sub>2</sub> nanomaterial with an alkali that had been activated using NaOH. After five cycles, the RhB dye's degradation efficiency reaches 83.8%. This shows that the produced material well tolerates RhB degradation. After three rotations, the elimination rate of benzene gas came to 96.3 per cent, showing consistency in the Ag@TiO<sub>2</sub>/ZFAB-modified photocatalytic cementitious material.



#### 4.7.3. Photocatalytic activity of other nanocomposites

When semiconductor surfaces are exposed to light, electron-hole pairs are created, which produce oxidizing and reducing agents. Photons promote the breakdown of organic contaminants by these oxidizing and reducing agents. Several semiconductor metal oxide photocatalysts have been developed to improve photocatalytic efficiency, including CdO-SnO<sub>2</sub>, ZnO-Cu<sub>2</sub>O, SnO<sub>2</sub>-TiO<sub>2</sub>, SnO<sub>2</sub>-Graphene, TiO<sub>2</sub>/CuS, and NaNbO<sub>3</sub>/CdS (61). A magnetic iron oxide nanomaterial made from industrial waste has a positive zeta potential value between pH 2 and 3 and a negative zeta potential value between pH 5 and 10. Since the catalyst surface contains an OH ion, it absorbs H<sup>+</sup> ions in acidic and basic media, degrading dye molecules. Regarding photocatalytic degradation, magnetic iron oxide nanopowder showed 78 per cent recycling capacity up to 10 cycles (62).

## 5. Wastewater Treatment and Water Remediation

**5.1. Adsorption:** Industrial effluent contains contaminants specific to the industries that produce them. In the textile industry, waste streams are tainted with different colours. Polluted water must be remedied to protect public and environmental health (63). Several research teams are developing recycled nanoparticle-based solutions for industrial wastewater to achieve circularity and sustainability objectives. Iron oxide nanoparticles were produced from a mill scale and used to remove colour (64). During this procedure, magnetic separation techniques are used to separate the iron oxide particles from the undesirable elements in the mill scale. To prevent aggregation, hexadecyl trimethylammonium bromide was added after conventional and high-energy ball milling. Modified iron nanoparticles could adsorb dye wastewater by more than 99 per cent, with the best adsorption achieved with 53.76 nm particles (65). A technique for producing magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles from iron ore tailings was developed (66). These particles were produced using powder X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis), and Fourier-transform infrared spectroscopy (FT-IR). These particles effectively removed Methylene blue and Congo red dyes. For Methylene blue and Congo red, the monolayer adsorption capabilities under ideal circumstances were 70.4 mg g<sup>-1</sup> and 172.4 mg g<sup>-1</sup>. These nanoparticles performed favourably compared to particles made from reagent-grade materials, and as a result, they may be a value-added product with potential uses in wide-scale wastewater treatment (60). Using recycled Polyethylene terephthalate (PET) as a starting material for NP manufacture is a different method of colour removal from water (70). PET produces graphene by thermal dissociation. SEM, TEM, Raman, BET, TGA, and FT IR were used to analyze and describe the graphene. High surface area and micropore volume were visible in the generated graphene. The potential for adsorption was evaluated using the dyes methylene blue and acid blue 25. This graphene demonstrated effective methylene blue adsorption, with pH 12 providing the best conditions. Within 30 minutes, the methylene blue dye achieved equilibrium. Acidic solutions provided the best conditions for the acid blue 25 dye to bind, and it took the colour around 50 minutes to achieve equilibrium after adsorption. The PET-based graphene successfully eliminated both dyes from solutions (El Essawy et al. 2017). Engineered biochar containing discarded eggshell particles was created by Wang et al. The biochar is made of three different types of biomass that have been slowly pyrolyzed and processed

with eggshell waste. A technique for creating colloidal and Nano-sized eggshell particles is used to create the eggshell particles (58). On the surface and within the pore networks of the biochar, eggshell particles were discovered using characterization technologies, including scanning electron microscopy. Due to the presence of CaCO<sub>3</sub> in the eggshells, the biochar treated with eggshells was shown to be more effective in adsorbing lead (Pb<sup>2+</sup>) than pure biochar (59). The synthesis of extremely porous aero gels from recycled materials such as paper, cotton textiles, and plastic bottles was reviewed (60). A straightforward procedure was used to create paper-derived aero gels, which involved sonicating a recycled cellulose solution with polyamide-epichlorohydrin, followed by freeze-drying at 98°C. Similarly, textile-derived aero gels were made by combining cotton fabric scraps with deionized water and sonication in a polyamide epichlorohydrin solution. At 98°C, the resultant dispersion was freeze-dried, and at 120°C, it was cured. PET fibres from recycled PET bottles were used to create aerogels by soaking them in a NaOH solution heated to 80°C, rinsing them with DI water, and combining them with a mixture of polyvinyl alcohol, glutaraldehyde, and HCl. The mixture was then freeze-dried, heated to 80°C, and sonicated. A covering of methyltrimethoxysilane was applied after the production to give these aero gels superhydrophobicity. These waste-derived aero gels are particularly appealing for remediation applications, such as the cleanup of oil spills in water bodies, due to their ultra-low density and high absorption capacity. For instance, cotton-based aero gels may absorb more than 100 grams of motor oil per gram of aerogel, outperforming the majority of conventional sorbents (61). Another approach to treating waste dyewater was presented and tested, utilizing iron obtained from the production of saccharin (62). In this procedure, the difficult-to-treat saccharin wastewater is first processed to remove the NiFe<sub>2</sub>O<sub>4</sub> nanoparticles, which are utilized as a catalyst. Then, a mesoporous magnet NiFe<sub>2</sub>O<sub>4</sub>/ZnCuCr-LDH composite is produced via a hydrothermal process. Congo red could be removed by the developed NiFe<sub>2</sub>O<sub>4</sub>/ZnCuCr-LDH composites with an efficiency of about 97 per cent when the dye's starting concentration was between 100 and 450 mg. The method cleans up any iron pollution in the saccharin wastewater and then utilizes the excess iron to make a magnetic composite to treat dye water (63). The ability of the nanoparticles to remove acid orange 8 (AO8) dye as an absorbent material was investigated. The silicon nanoparticles could be recycled up to five times and had an absorption capacity of 230 mg/g (64). Peres et al. 2018, produced silica nanoparticles from leftover maize husks using both a conventional synthesis method and a microwave synthesis technique. These silicon nanoparticles were used to enhance methyl blue dye absorbency. Compared to conventionally synthesized silica nanoparticles, microwave-produced ones exhibit greater values for surface area, pore volume, pore diameter, porosity, and purity. The microwave silica nanoparticles showed an 80% clearance rate and a 679.9 mg/g absorption capacity. The thermodynamic analysis of the absorbent showed that both nano-silica particles had a favourable spontaneous exothermic reaction (65).

**5.2 Sustainable Approach:** Different options for employing waste materials as inputs for the creation of NPs have been illustrated and addressed throughout this review in the context of research. The knowledge gaps are particularly concerning energy use, the production of secondary wastes, fate and transport behaviour, exposure routes in various environments, and toxicity levels (66).

Careful cost-benefit calculations must be done when feasible procedures pass the proof-of-concept stage. This is so we can account for ageing transformations and the potential release of nanomaterials and by-products in the environment. Hence, reducing the possibility of future waste damage being revealed (67, 68, 69). However, doing the necessary risk studies and life cycle assessments requires access to a good collection of data on designed NP emissions and environmental concentrations. A limiting factor is the lack of empirical data on release coefficients at all stages of the life cycle, including production, usage, and disposal, as the majority of data in the literature have been obtained through modelling and simulation of the release of NPs from containing products during consumer manipulation (69, 70). The twelve green chemistry principles offer an appropriate framework for producing NPs and NP-enabled technologies during production. These guidelines are meant to serve as a design manual for chemical pathways that result in improved sustainability results (71). However, just because synthetic NPs can be made using environmentally friendly methods does not indicate that their usage and release in the environment are entirely safe. Studies conducted in the past ten years have revealed that engineered nanoparticles (engineered NPs) used in various settings, such as food production and packaging, can potentially disrupt epigenetic mechanisms significantly and raise several concerns about their potential to cause disease (72). One of the more well-known classes of engineered NPs may be fullerenes. Studies on the interactions and toxicity of carbon nanomaterials with diverse biological systems have been conducted both *in vitro* and *in vivo* (73). The characteristics that make CNTs appealing for technological applications are also linked to inflammatory responses and fibrogenic processes that decrease lung function in mice, rendering their respiratory systems more vulnerable to infections (74). CNTs have been likened to asbestos fibres, known to be cytotoxic and carcinogenic particles, in terms of how they affect the body after inhaling (75).

## 6. Conclusion

Applying waste-derived NPs requires recognizing a complex web of influencing factors, and judgments should be based on prudence and ethics. Even though there is no easy way to overcome the adverse effects of the current "end-of-life" waste management systems, many experts emphasize the importance of performing life cycle assessments and risk analyses early on while developing new technologies and processes. It may appear appealing at first glance to recycle waste into cutting-edge technologies for environmental applications, but many engineered nanomaterials knowledge gaps need to be filled before these concepts can be applied in the field. The scale and breadth of uses of engineered nanomaterials should be determined regionally, and management policies should be based on health and environmental considerations.

## Author Contributions

The author contributes to the outline and leads the drafting and editing of the manuscript. MS and DC performed an extensive literature search and contributed to writing sections and constructing figures and tables. PK provided professional advice and participated in the revision of the final document. All authors read and approved the final manuscript.

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