

Review

The Processing of Calcium Rich Agricultural and Industrial Waste for Recovery of Calcium Carbonate and Calcium Oxide and Their Application for Environmental Cleanup: A Review

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Abstract: Every year a million tonnes of calcium rich agro and industrial waste are generated around the whole globe. These calcium rich waste like finger citron, shells of cockle, mussel, oysters etc., and egg shell are biological sources which have various organic compounds. The inorganic calcium rich waste includes gypsum, dolomite, sludge etc., which are produced in surplus amount globally. Most of these by-products are mainly dumped, while few are used for land-filling purposes which leads to the pollution. These agro and industrial by-products could be processed for the recovery of calcium carbonate and calcium oxide particles by physical and chemical method. The recovery of calcium carbonate and calcium oxide particles from such by products make them biocompatible. Moreover, the products are economical due to their synthesis from waste materials. Here, in this current review work we have emphasized on the all the calcium rich agro industries and industrial by products, especially their processing by various approaches. Further, we have also focused on the properties and application of such calcium carbonate and oxide particles for the remediation of organic and inorganic pollutants from the environments. The recovery of such particles from these byproducts is considered not only economical and eco-friendly but it also minimizes the pollution present in the form of solid waste.

Keywords: calcium carbonate nanoparticles; calcium oxide nanoparticles; incense sticks ash; fly ash; sludge; eggshell

1. Introduction

Every day we encounter various agricultural and industrial products for our easiness and requirements. Out of these products, various products have different origin and chemical values. Agricultural industries is the backbone of any country, due to its importance in any countries GDP [1,2]. In addition, there are several other industries like steel, mineral processing, paper, and pulp industries etc., which also play a major role in a human's life. Both these types of industries fulfills our daily requirements. The progress of any country is measured by the growth of their industries. However, one major drawback with such industries is that they produces million tonnes of by-products every day throughout the whole world [3]. The accumulation of byproducts from such industries leads to the various forms of pollution due to the presence of toxic constituents [4]. The agricultural industry waste like citrus peel waste, paper and pulp waste contain moisture and attracts the flies and bugs leading to the health related issues [5]. While, the industrial waste like fly ash by-products of thermal power plants [6], gypsum waste from medical and hospitals leads [7] to the accumulation of hazardous by products due to the presence of heavy metals, etc. Here, we have focused on the recycling of calcium rich agricultural and industrial waste for the synthesis of value added minerals like calcium carbonate and calcium oxide. Both of these minerals are biocompatible, non-toxic, and used every day in oils, plastic, imaging purposes, alloys and catalyst [8], environment-friendly items [9], calcium-enriched food [10,11], drug delivery [12,13], cosmetics and pharmaceuticals [10], templates for microcapsules [14,15], and bone filling material [12]. Currently the commercial production of CaCO_3 , calcium oxide and other derivatives of calcium is mainly carried out by using quick lime as a precursor material. Most of these quick limes are obtained by the mining which is laborious, and energy intensive process hence the final product is comparatively expensive [16]. So, there is an immediate need of a sustainable, economical, and an alternative source of calcium rich materials. There are several materials in our environment which are rich source of CaCO_3 like limestone, marbles, gypsum waste, cockle shell, eggshell, incense sticks, and high calcium fly ash (class C) and hard shell of shellfish, i.e., marine organisms (snails, oysters, shrimps, and pearls) [17–19].

Calcium carbonate (CaCO_3) is a white color powder and water insoluble-inorganic biomaterials [18]. In nature, CaCO_3 is present in three different forms, i.e., calcite, aragonite, and vaterite [20]. Due to its biocompatible nature, aragonite receives extensive research attention worldwide. Among all these three polymorphs, calcite is thermodynamically most stable [21]. Calcite is the most stable polymorph of CaCO_3 [22], but aragonite has higher density and hardness from the other two polymorphs of calcium carbonate, which makes them very suitable material in plastic, paper, glass, fiber, and other industry [23]. A study reported the needle-shaped aragonite synthesis under a controlled injection of CO_2 in $\text{Ca}(\text{OH})_2$ slurry suspended MgCl_2 aqueous solution. These investigators also reported that the residual MgCl_2 solution from the previous step, could be reused for the synthesis of aragonite synthesis as both Mg^{2+} and Ca^{2+} ions are not incorporated into the aragonite crystals. At the time of formation of aragonite, Mg^{2+} ions acts as an impurity, which promotes the formation of aragonite crystals along with simultaneous impeding the nucleation and growth of calcite crystal. While another study carried by a group of investigators reported that the more the concentration of Ca^{2+} ions in the solution, the higher the possibility of formation of aragonite crystals will be [24–26]. To rationalize this cognition, numerous theories and empirical relationships have been provided such as alteration of surface charge, inhibition of calcite nucleation, and calcite poisoning model [21].

As an adsorbent calcium carbonate and calcium oxide particles have several advantages over the conventional adsorbents due to their low cost, biocompatibility, biodegradability, easy availability, non-toxic nature, and diverse polymorphs [27]. Due to all these properties calcium carbonate and calcium oxide particles have gained a huge attention in the field of environmental remediation especially for wastewater treatment. These calcium based minerals remediate the inorganic and organic pollutants from the environment by

the adsorption process. The low cost and eco-friendly nature of calcium based minerals reduce the expenditure of the whole adsorption process.

2. Types and Properties of Calcium Carbonate Particles

In general, there are two sources of CaCO_3 , one is ground calcium carbonate (GCC) and another one is precipitated calcium carbonate (PCC) [8], chalk, or marble. While the PCC is present as crystals and exists in three polymorphs, i.e., calcite, aragonite, and vaterite. Though they have several identical properties still they vary in the following manner as shown in Table 1. While all the PCC types of polymorphs are differentiated above in the Table 2.

Table 1. Differences between ground and precipitated calcium carbonate particles.

S. No.	Ground Calcium Carbonate	Precipitated Calcium Carbonate	References
1. Source	Extracted from earth	Present as crystals in calcite (rhombohedral), aragonite (orthorhombic), and vaterite (hexagonal) forms	[28]
2. Examples	Examples: chalks, marble	-	
3. Processing	Grinding is required either in wet or dry conditions.	-	
4. Available in market	-	Commercial PCC was produced in 1841.	
5. Methods for synthesis	Thermolysis	Three common processes for the production of synthetic PCC(1) lime soda process(2) calcium chloride process(3) the carbonation process	[29]

Table 2. Differences between different types of calcium carbonate nanoparticles polymorphs.

S. No.	Calcite	Aragonite	Vaterite	References
1. Thermal Stability	Thermodynamically most stable	Moderately stable	Least stable polymorph	[21]
2. Solubility	-	More soluble and denser than calcite	-	
3. Structure	Exists as a trigonal crystalline form in nature	Forms needle-like orthorhombic crystals and formed at higher temperature and pressure	Hexagonal structure and rarely seen in the natural mineral	
4. Stability	-	Metastable and slowly gets converted to calcite		[23]
5. Interaction with water and reorganization	-	-	Vaterite when exposed to H_2O , slowly dissolves and recrystallizes to a stable form	
6. Porosity, surface area	-	-	Large porosity and large surface area	
7. Disintegrability	-	-	Rapid disintegration under relatively mild conditions	
8. Biocompatibility	-	Biocompatible properties		[21]

Calcium based particles has drawn their attention towards different scientific filed in the last decade due to their diversity in morphology, biocompatible in nature, economical, and non-toxic effect on the environment [27]. Since the calcium is already present in our body, microbes, plants, etc., it does not have a detrimental effect on any of these species, so it is considered as superior particles, in comparison to other metal oxide particles. Such as, ZnO , TiO_2 , etc., are photo catalytic in nature, whereas CuO , CoNPs , etc., are toxic due to their heavy metal nature. These metals oxide particles persists in nature for much longer

time and may show, bio magnification in the higher animals in the food chain. Whereas calcium is already present in almost most of the organisms, so there is already degradation mechanism present in the organism for calcium based particles. The types of calcium carbonate particles are based on their morphology. Calcium carbonate particles (CCPs) are white color powder, insoluble in water but soluble in HCl, biocompatible, pH sensitive, biodegradable, abundant in nature, economically viable, and exhibit polymorphism [27]. CCPs aggregate easily during the process of preparation and disposal [30].

3. Different Sources of Calcium Carbonate Particles (CCPs)

In nature, there are numerous calcium-rich particles which can be used as a source of CCPs synthesis. For instance, there are biological materials like cockle and shellfish. All these sea animals have a hard covering on their surface, which is meant for protection, safety from the wear and tear, and prey. These animals have very soft internal organs, so a hard-calcareous covering is required. So, their shells can be used for the extraction of CCPs by various means of processing. Most of these sea animals lose their hard covering after their death and there is the mineralization of calcium into the seawater. In addition, there are several domestic and industrial waste which have also higher content of calcium. For instance, eggshell and incense sticks ash from the domestic waste. While high Ca fly ash, gypsum waste [30], calcium sulfide waste [31], sludge is industrial waste which is also rich sources of calcium. All these materials are discussed below in detail by emphasizing the steps for the recovery of CaO NPs. Most of these calcium-rich materials are waste so the recovery of CCPs and calcium derivatives from these materials are considered economical and environment-friendly.

3.1. Domestic Waste

The waste which is generated in the houses especially in the kitchen is called household waste, domestic waste, or kitchen waste [32]. Among all the high calcium-containing waste, incense sticks ashes are considered as most orphan and least considered; though it did produce about 1–2 MTs in India, and this figure would rise drastically if the major incense sticks consuming countries like China, USA, and South Asian countries were also considered. South Asian countries alone generates tonnes of ISA at religious places [33]. Though it is also produced in a small amount at various houses of South Asian counties [34]. Several investigators have classified the eggshell in household waste. However, the utilization of eggs at home is lesser than the industries so few investigators have categorized them into industrial waste. Therefore, here we will consider only incense sticks ash waste as a source of CCNPs.

3.2. Incense Sticks Ash

Incense sticks ash (ISA) is one of the major household wastes in South-east Asian countries like China, Taiwan, Thailand, and India. Incense sticks are majorly used in the temples, churches, mosques, houses, and other religious places. In Taiwan alone, a total of 3580 tons of incense sticks are consumed yearly in temples alone and if household burning is also considered then this value may reach to double or triple and may indicate an environment hazardous situation [33,35]. The size and composition of an incense sticks varies from one country and one religion to another. Currently, most of the countries, including India, do not have exact data on the incense sticks ash production. The only information we have regarding this is that: Brazil, China, U.S.A and India, are the leading manufacturer of incense sticks. India is the third largest manufacturers of incense sticks and fourth largest consumer of incense sticks. Along with USA, India also exports most of the incense sticks to Gulf countries, and Mexico. In India, the average size of an incense sticks is 8–9 inches and width is about 1–3 mm. Generally, Indian markets have two types of incense sticks: one is charcoal, or coal based (black in color), whereas the other one is non charcoal based whose color could be grey, or any other color. The black color incense sticks ashes have ferrous, silica, alumina, carbon, and calcium oxides. Indian incense sticks

manufactures uses calcium phthalate in order to minimize the smoke released during burning of sticks. So, this is the one of the source of high amount of calcium oxides in the ISA. The ISA have nearly 50–56% calcium oxides [36]. The composition of incense are herbal and wood powder 21%, fragrant materials 35%, adhesive powder 11%, bamboo stick 33% by weight [37,38]. The complete combustion of a 9 inch and 1–2 mm incense stick, produces one-third ash by weight while the remaining 60–70% weight of incense sticks is made up of volatile matters like essential oil, fragrance, and combustible matter. Hazarika et al., 2018 and Yadav et al., 2020, reported that India alone consumes approximately 3–4 million tonnes of incense sticks, while USA was one of the largest importer of incense sticks from India. Based on the above information, we can predict that India alone generates 0.3–0.4 million tonnes of ISA from the various religious places and homes. The same information from other countries would be impossible to estimate as there is hardly any information available from the government or in the literature [36].

The chemical composition of incense sticks ash is given below in Table 3. The X-ray fluorescence analysis reveals that the incense ash has CaO 50–55%, Ferrous oxide ($\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$) 4–5%, Aluminum oxide (Al_2O_3) 4–5%, Silica oxide 15–20%, magnesium oxide 4–5%. In addition, it also has a high amount of alkali oxides, i.e., Na_2O , K_2O , traces of TiO_2 , CuO , and other heavy metals. Figure 1 shows the flowchart of the synthesis of CaCO_3 from ISA, while Figure 2 shows field emission scanning electron micrograph (FESEM) of calcium carbonate microparticles from incense sticks ash. Oral and Ercan (2018), also reported the calcium carbonate particles of various sizes synthesized by chemical routes. Out of these cuboidal shaped particles were also observed, by varying the temperature of synthesis [39]. In Figure 1, initially ISA was mixed with distilled water (1:5) to form a slurry. Further with the help of an external magnet, the ferrous particles were separated as ferrous will add impurity in the final calcium carbonate particles. Further, it was dried in an oven at 50 °C, followed by treatment with sulphuric acid at 90 °C for 90 min to extract alumina along with stirring at 400 rpm. Further, after completion of the reaction, mixture was cooled to room temperature (RT), followed by the centrifugation. The obtained residue was washed several times with distilled water, followed by drying in an oven at 60 °C. About 8 g of residue was treated with 4 M NaOH at 90 °C for 90 min along with stirring at 400 rpm. Further, the residue was calcinated at 600–700 °C for 6 h, followed by dilute HCl treatment in a round bottom (RB) flask, along with stirring at RT. Around 10 mL aqueous leachate obtained with HCl treatment was mixed with dropwise methanol in a RB flask at RT. The mixture was centrifuged at 7000 rpm for 10 min, where the residue was discarded while the supernatant was collected. Further, about 10 mL of supernatant was taken up, to which 2% solution of sodium bicarbonate was added drop wise along with stirring at RT in a RB flask. The mixture was centrifuged at 7000 rpm for 10 min, supernatant discarded while the precipitate was collected. Finally, it was washed twice each with distilled water and ethanol followed by drying at 60 °C for overnight.

Table 3. The elemental composition of incense sticks ash by X-ray fluorescence.

S. No.	Chemical Elements	Weight (%)
1.	CaO	50–55
2.	MgO	4–5
3.	SiO_2	15–20
4.	Al_2O_3	4–5
5.	$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$	4–5
6.	TiO_2	2–3
7.	Others ($\text{CuO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$)	5–10

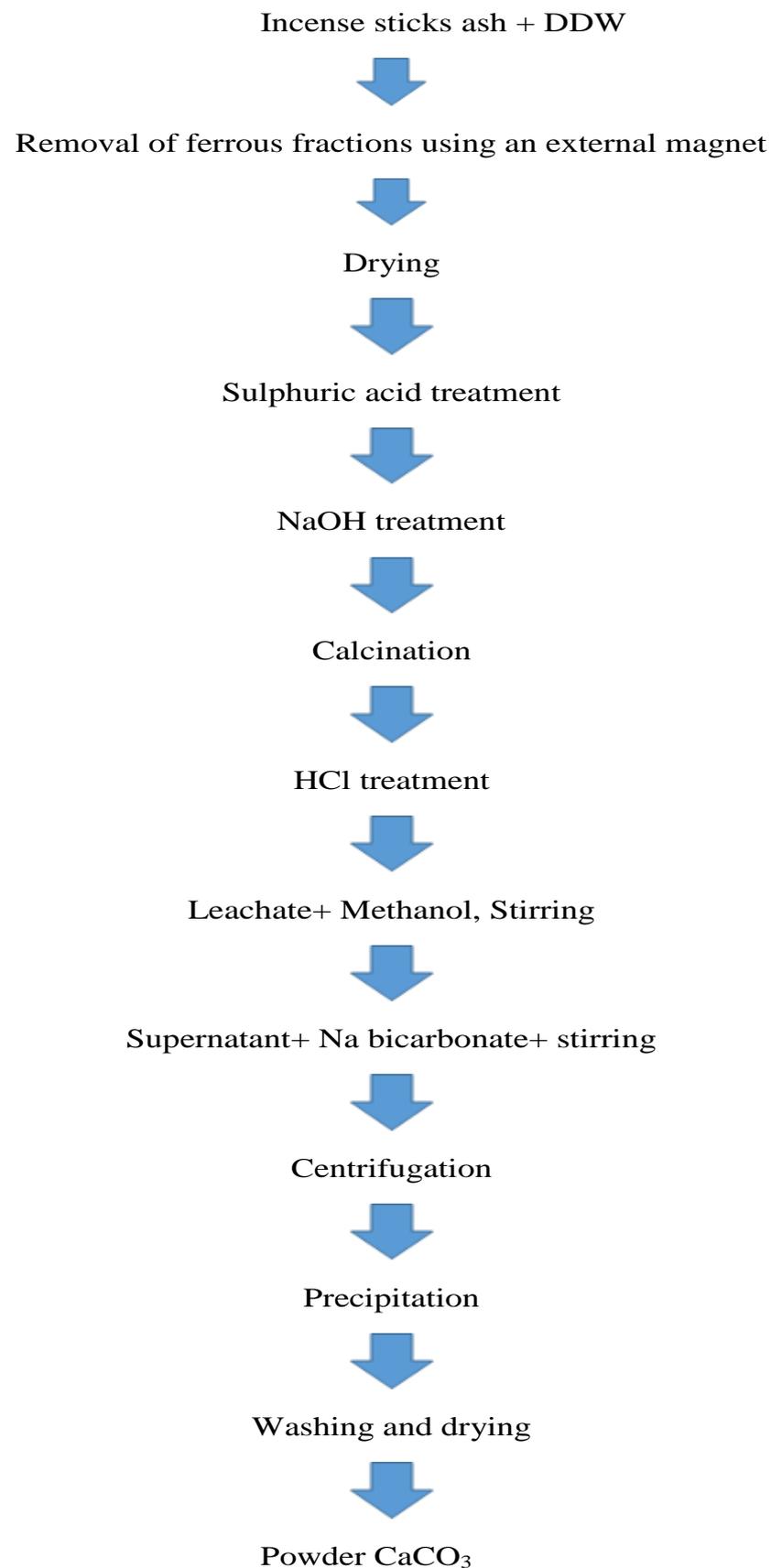


Figure 1. Flow chart for the separation of calcium carbonate from incense stick ash.

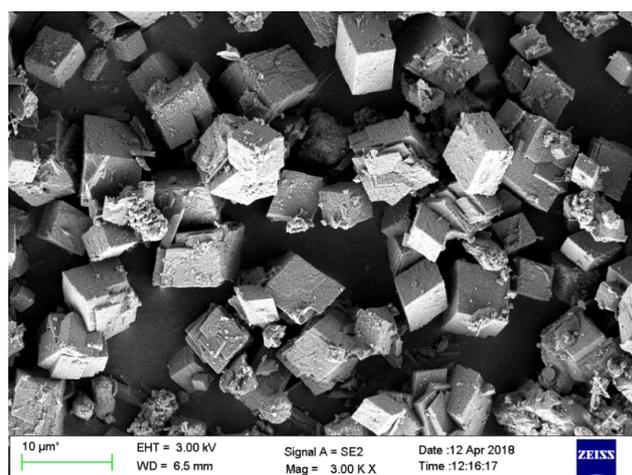


Figure 2. Field emission scanning electron micrograph (FESEM) of the calcite phase of calcium carbonate microparticles from incense sticks ash.

4. Extraction of Calcium Oxide Particles from Eggshell Waste

The bioconversion of waste material like eggshell from poultry industries into a valuable material is highly significant for economic development and waste management [40]. The eggshell waste is classified in both industrial wastes as well as in agricultural waste. The utilization of these wastes for the production of valuable materials like fertilizers, feed supplements, adsorbents, and CCNPs not only provides a solution to the disposal of eggshell but also minimizes the pollution in the environment [41,42]. Among all the countries, China, USA, and India is the leading producer of eggs which contributes near about 80 million metric tonnes, where China's share is 458, USA's share is 109, and India's share is 95 billion eggs per shell as per the 2017 literature. While in 2018, the global egg production was approximately, 78 million metric tonnes. These 78 million metric tonnes produced about 8.58 million metric tonnes of eggshells which are mainly dumped as waste, while some parts of the world, it is used as landfills, and for fillers, etc. [43]. The eggshell consists of about 10–11% weight of the total weight of an egg. Annually around, 250,000 tons of eggshell waste is generated during processing [44]. There are 150,000 tons of chicken eggshell disposed of in landfills every year in the U.S alone. The eggshell comprises about 95% CaCO_3 as calcite and 5% organic materials such as type X collagen, sulfated polysaccharides, and other proteins which is provided below in Table 4 [45]. The disposal methods for waste eggshells are 26.6% as fertilizer, 21.1% as animal feed ingredients, 26.3% discarded in municipal dumps, and 15.8% used in other ways [41]. Habte et al., 2020 reported the synthesis of microsized (10–30 μm) aragonite calcium carbonate particles from eggshell waste by carbonation method along with calcination at high temperature.

Table 4. The chemical composition of chicken eggshell.

S. No.	Chemical Elements	Concentration (mg/L)
1.	Ca	2296–2304
2.	Mg	849–852
3.	Na	33–35
4.	K	16–19
5.	Fe	1.01–1.43
6.	Zn	0.95–1.03
7.	Cu	0.062–0.064

India is also one of the major poultry industry countries which have a poultry population of 489 million, producing 47 billion eggs per year. India ranks third among the highest egg producing countries in the world [46]. The outermost cover of the egg is called

eggshell whose weight is 10–11% to that of the total weight of the egg and made up of mainly CaCO_3 (96%) and trace elements. The chemical composition of eggshell waste is given below in the table. Currently, it is mainly dumped as landfills in most of the developed or developing countries. Disposal of eggshell and the underlying membrane further contributes to environmental pollution [47].

Hassan et al. (2013) reported the synthesis of CCPs from the chicken eggshell waste, which encompasses the following steps cleaning and size reduction of eggshell, followed by surface modification by the sonochemical method for enhanced dispersion [48,49]. Hariharan et al. (2014) reported the successful synthesis of calcite NPs from eggshell waste using gelatin [50,51]. The calcite polymorph of CaCO_3 was synthesized using from chicken eggshells employing gelatin via precipitation method and the confirmation of the nano calcite was done by X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), UV-Visible (UV-Vis) spectroscopy and scanning electron microscopy (SEM). The identified particles were calcite polymorphs with a particle size of 25 nm. The analysis results confirmed the formation of calcite NPs and the obtained results were compared with CaCO_3 synthesis without using gelatin. Render et al. (2016) reported the synthesis of CCPs by using eggshell waste that has been used for enteric drug delivery. The sequential steps involved in the synthesis of CCPs from eggshell was initial cleaning, mechanochemical milling, and Sonochemical irradiation [52]. Pandita and Fulekar in 2017 and 2019 reported the synthesis of CCPs from eggshell waste [53]. The investigators, have reported the synthesis of micron and nano sized CaCO_3 and further transformed them into the CaO NPs by calcination at 900 °C for 4 h. They used these CaO NPs for increasing the efficiency of biodiesel by as micronutrient for the algae the microalgae. Further, Ahmad et al. (2020) has synthesized nano calcium oxide from the eggshell waste and utilized them for the direct transesterification of *Chlorella pyrenoidosa*. The eggshell was washed properly, crushed by mortar pestle, dried at 105 °C, and calcined at 870 °C for three hours. The final powder was analyzed by the sophisticated instruments, for their morphological properties. The size of CCPs was varying from 25 to 100 nm. Further they have used these nano CaO successfully up to six cycles for the transesterification [54]. Figure 3 demonstrates the flowchart of synthesis of CaCO_3 from egg shells.

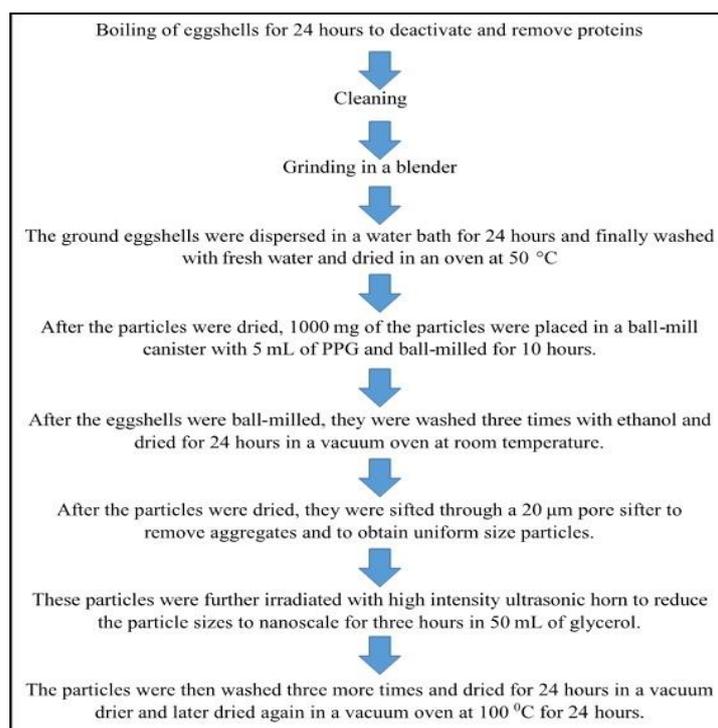


Figure 3. Steps involved in the synthesis of calcium carbonate nanoparticles from eggshell waste.

5. Biogenic Waste of Marine Organisms

5.1. Shells of Shellfish

Shellfish are sea animals that belong to the class invertebrates, having mainly two types of animals: crustaceans and mollusks. They mainly include lobsters, shrimps, crayfish, crab, and krill. They have a very hard covering on their external surface which consists of chitin. The shells of such marine organisms have a high content of CaCO_3 which is meant for protection from the external environment and predator. After the death of such marine organisms, there is biomineralization of CaCO_3 and ultimately calcium ion is added into the seawater [55]. Every year a million tonnes of sea foods are generated in the whole world and major contributors are countries with larger coastal area in the form of their boundary which favors the aquaculture. As far as India is concerned, till 2018, it occupies second rank in aquaculture and third rank in fisheries contributing 1.07% to the nations GDP. Major, waste of sea foods are heads, trimming residue, tails, shells, and scales. Out of these shell fish soft flesh part is consumed as food while the hard calcareous covering is considered as waste which is mainly dumped of as landfills. Numerous investigators have also reported the synthesis of CCPs from the shells of shellfish. Jaannah et al., 2018, reported the synthesis, characterization, and application of shellfish-derived CCPs for the antibacterial assay [17]. Initially, they synthesized the CCPs and formed a nanocomposite with MgO which was further assessed for their antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus* bacteria. They have also reported the synthesis of CaCO_3/MgO nanocomposite material by the optimum clear zone and able to utilize shell waste as an antibacterial ingredient of natural materials [17]. The schematic step involved in the synthesis of CCNPs from shellfish is given below in Figure 4.

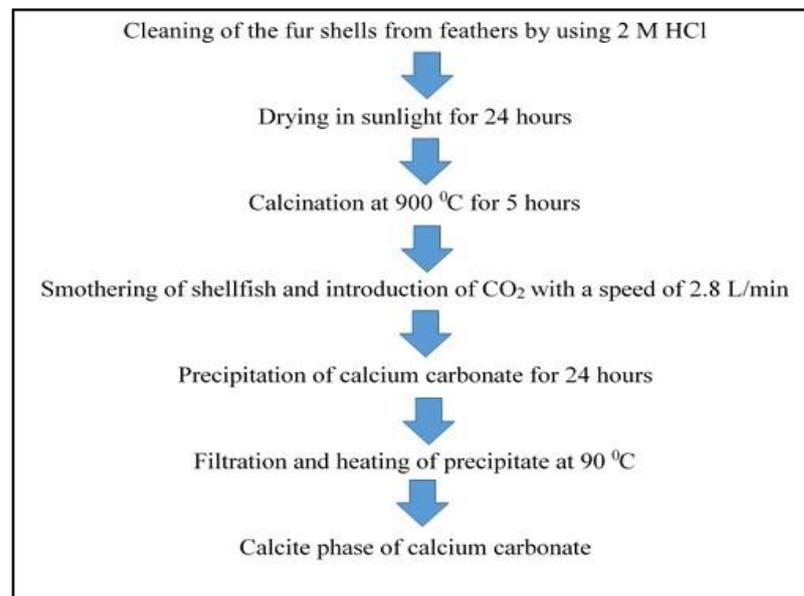


Figure 4. Schematic diagram of extraction of calcite phase from the shellfish.

5.2. Cockle Shells

As per the World Fisheries and Aquaculture, USA, 2020, report, about 17,510.9 thousand tonnes of mollusks produced in the 2018, out of which cockle were 433.4 thousand million tonnes, i.e., 2.5% share of mollusks. Which need to draw the attention towards the cockle shell management otherwise it will lead to the loss of economy in the form of disposal of these cockle shells. So, the recycling of such cockle shells, will not only provide an alternate source of calcium carbonate and their derivatives, but it will also minimize the solid waste. Numerous investigators have reported the recycling of cockle shells for value added materials like calcium oxides and calcium carbonates out of which most recent ones are cited below.

Majusha Hariharan et al. (2014) synthesized and characterized the nano calcite through the precipitation method from the cockle shells using chitosan as precursor materials. The schematic steps involved in the synthesis of CCNPs from cockle shell are given below in Figure 5. The nano calcite was characterized by SEM, XRD, UV-Vis, and FTIR for confirmation of the particles which was later on compared with the commercial nano calcite. It was found that cockle shells are a potential source of nano calcite, which was by-products of the seafood industry so the method was cheaper and environment-friendly [50].

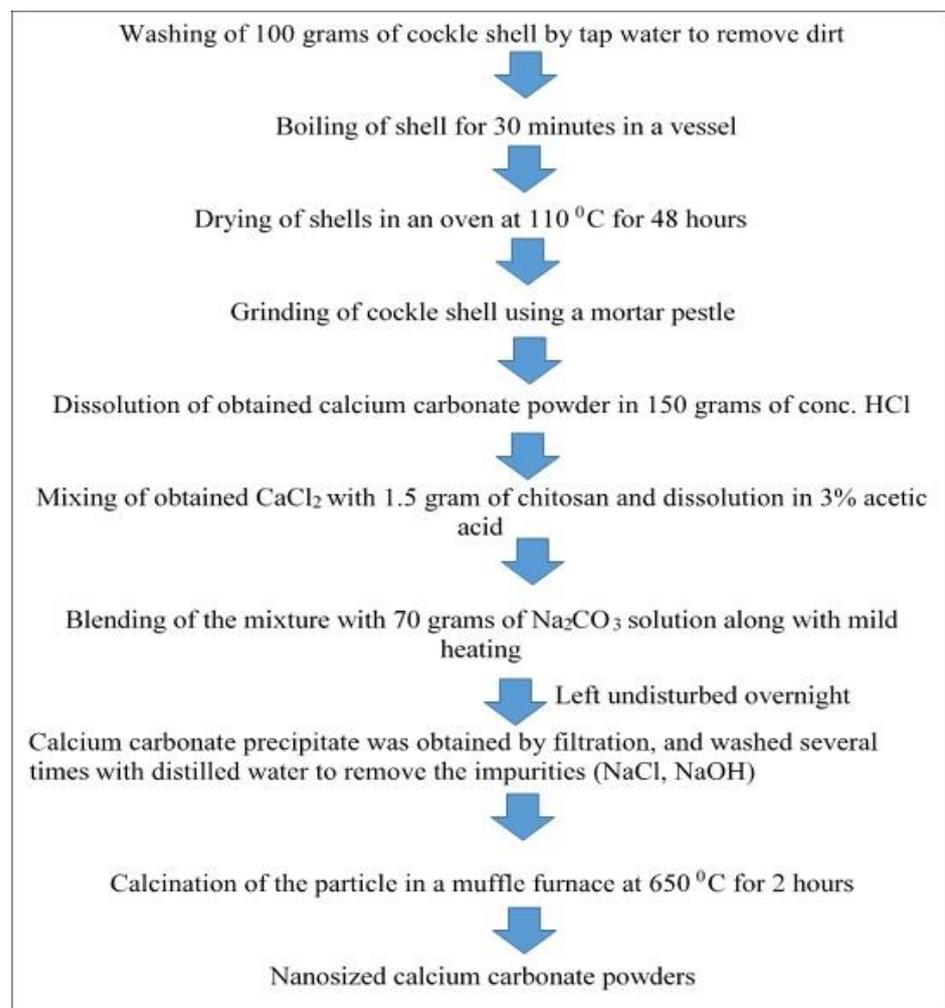


Figure 5. Steps involved in the synthesis of calcium carbonate nanoparticles from cockle shells.

Islam et al. (2012) reported an easy, cost-effective, and novel method for the synthesis of CCPs (aragonite) from the cockle shells whose schematic synthesis is given below in Figure 6. Aragonite is one of the least abundant biogenic polymorphs of CaCO₃ which is commonly used as a biomaterial for the repair of the fractured bone, development of advanced drug delivery systems, and tissue scaffolds. The size of obtained aragonite NPs size was 20 ± 5 nm with high purity which was confirmed by the variable pressure SEM, transmission electron microscopy (TEM), FTIR, thermogravimetric analyzer (TGA), XRD, and energy-dispersive X-ray spectroscopy [23].

5.3. From Oyster and Mussel Shells

Oysters and mussels are also one of the major sea foods consumed in most of the countries around the globe. Out of 17,510.9 thousand tonnes of mollusks produced in 2018, the mussels share was 1205.1 thousand tonnes, i.e., 6.9% which after processing generates tonnes of shells every day. So, the waste generated from such seafoods maybe requires

attention towards recycling, otherwise their disposal will lead to the loss of economy [50]. Numerous investigators reported the synthesis of calcium carbonate and oxide from the oyster and mussel shells by various chemical methods out of which most recent ones are cited below.

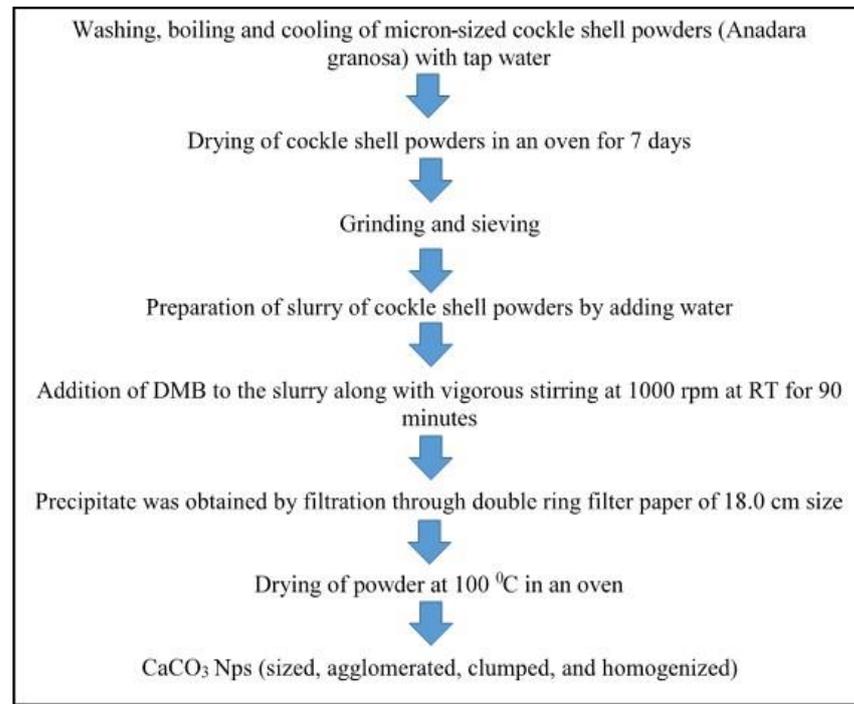


Figure 6. The schematic diagram for the synthesis of calcium carbonate nanoparticles from cockle shells.

Hamester et al. (2011) obtained calcium carbonate from mussel and oyster shells were further used as filler in polypropylene and compared their properties with polypropylene and commercial calcium carbonate composites [56]. For the synthesis of calcium carbonate, the mussel and oyster shells were heated in an oven at 200 °C for 1 h to make the shells more brittle and submitted to milling in a high-speed planetary mill with porcelain jar and alumina balls for 15 min with water. The obtained powders are again heated to 500 °C and maintained for 2 h. Further, to undo the clusters a new milling was performed without addition of water for 1 min. The resulted powders were characterized by a laser diffraction analyzer and X-ray fluorescence for chemical composition [57].

6. Recovery from Industrial Waste

Every year a million tons of industrial waste in the form of gypsum, calcium sulfide, sewage sludge, high calcium fly ash, wollastonite, etc., are produced around the whole world. Most of these are the byproducts of the industries which are generally dumped in the near vicinity of the industries or as landfill [58–60]. The dumping of these waste materials may invite mosquitos and other insects and may lead to various diseases. Moreover, most of these materials are processed materials that have a higher amount of toxic metals that may leach into the land or water bodies and may contaminate them. The aquatic animals may accumulate these toxic metals, i.e., bioaccumulation and lead to bio magnification. So, there is an urgent need to utilize these waste materials for the recovery of value-added materials like calcium. The recovery of calcium-based products from such waste will reduce pollution and provide an alternate source for the CaCO₃ particles via a cost-effective and eco-friendly method [61]. Some of the materials that have been used earlier for the synthesis of CCNPs are described below in detail.

6.1. Recovery of Calcium Oxide/Carbonate from Sludge

Sludge is one of the major wastes from houses and industries. Though it has numerous mixtures in it has a high amount of calcium. In a highly populous country like India, about 61,754 million liters per day sewage is generated, and 38,791 MLD is untreated sludge. Every year India produces 277 MTs of solid municipal waste according to estimate of 2016. Whereas this figure is projected to reach to 378.8 MTs in 2030 and 543.3 MTs by 2050. This figure is really need to focus the government and other bodies for recycling and recovery of value added materials from such waste [62,63]. The sludges are reported to have higher percentage of calcium makes it a suitable material for the extraction of CCNPs. Moreover, the raw material is again a waste that needs special treatment for disposal. So, the recovery of CaCO_3 from sludge not only reduces solid waste or pollution but also helps in producing valuable minerals from it [64]. The synthesis of CaCO_3 from sludge is a low-cost technique, eco-friendly. Till yet an only a countable number of works is done in this filed.

The recovery of CCNPs from the waste sludge by the flotation technique [65]. They investigated the effective dosage of floating agents such as sodium oleate and sunlight dish liquid) and the percent solids of the slurry. They have used floating sieved and un-sieved materials and CaCO_3 was estimated for both conditions as well as from tailings. Initial CaCO_3 analysis for the bulk material indicated that sieved and un-sieved materials had 63.4% and 32.9% CaCO_3 content by weight, respectively. Therefore, it was concluded that for un-sieved material sunlight dishwashing liquid was a better collector compared to the latter. The results proved that there is a great potential for recovering commercial-grade limestone from wastewater sludge.

6.2. Recovery of Calcium Carbonate/Oxide from Dolomite

Dolomites [$\text{CaMg}(\text{CO}_3)_2$] are anhydrous carbonate minerals of calcium and magnesium carbonate [66]. It is widely used in the steel and industries. Such iron or steel based industries produces 40–70% byproducts including dolomite as waste. In general, dolomite is used for the preparation of precipitated CaCO_3 by separating Ca and Mg fractions. The major problem in their separation from dolomite is that both the elements have a lower solubility in the water [67]. Some investigators have successfully used sucrose for the extraction of Ca and Mg from dolomite. When the calcinated dolomite is dissolved in a sucrose solution, then there is the conversion of CaO into calcium sucrate leaving unreacted Mg in the mixture as a precipitate [68]. When calcined dolomite (CaO.MgO) is dissolved in a sucrose solution, CaO will be converted into soluble calcium sucrate, while MgO remains unreacted and presents in the precipitated form [69]. Figure 7 illustrates the stepwise synthesis of CCPs from dolomite.

6.3. Synthesis of Calcium Oxide/Carbonate Particles from Gypsum Waste

Gypsum waste is a waste product of the reverse osmosis (RO) desalination process [70]. Gypsum is widely used for dental applications [71] which on disposal into the environment may challenge as a hazardous material. When such gypsum are landfilled into the environment, there is a reaction with biodegradable waste which may produce poisonous and odorous hydrogen sulfide gas [72,73]. Gypsum alone is widely used in the dentistry in hospitals and medical colleges. Every year one medical college produces 100–500 kg of gypsum waste which could vary based on the patient footfall per year. As per the literature, there are about 345 dental colleges in India, so approximately these colleges generates about 173 tonnes of gypsum waste. In addition, gypsum waste is also generated from various construction site, industries, and mineral processing industries. Gypsum waste can be thermally reduced into CaS, which is then subjected to a direct aqueous carbonation step for the generation of H_2S and CaCO_3 . CaS can be successfully converted into CaCO_3 ; however, the reaction may yield low-grade carbonate products (99% as CaCO_3) or precipitated CaCO_3 can be developed and optimized [70].

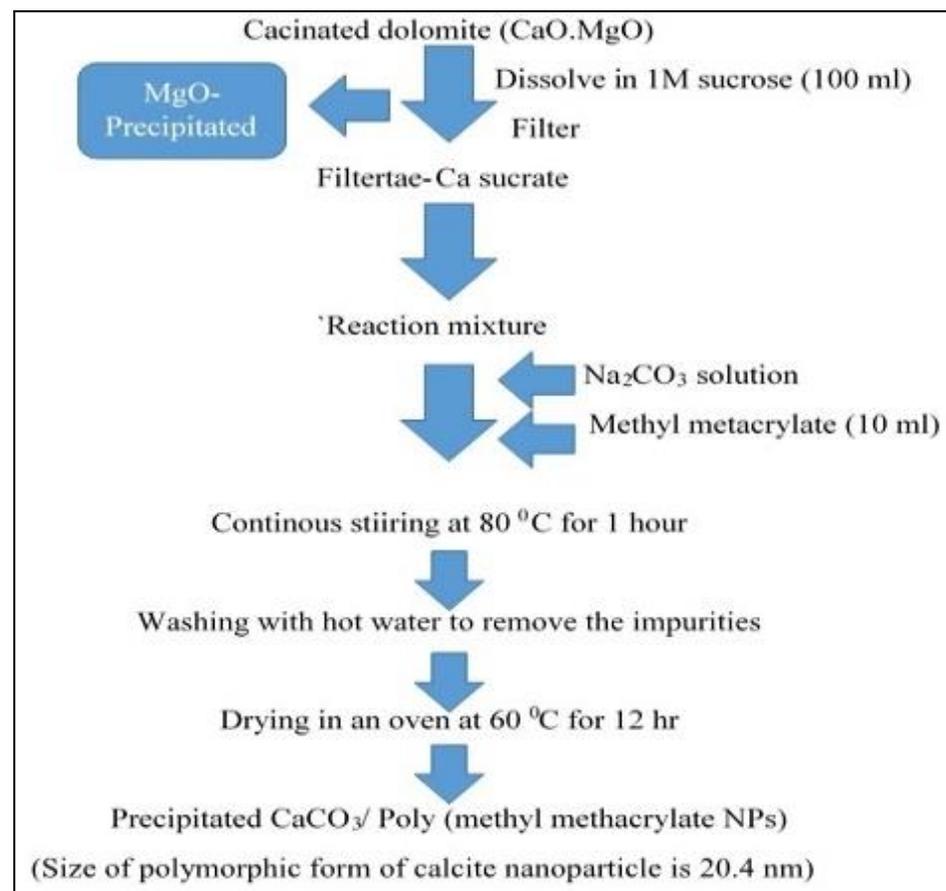


Figure 7. Steps involved in the synthesis of calcium carbonate nanoparticles from dolomite.

Beer et al. (2014) reported the synthesis of CCPs from the gypsum waste, where elemental sulfur was the by-product. Here the first step was the thermal reduction of gypsum waste into calcium sulfide (CaS) followed by its direct aqueous carbonation yielded low-grade carbonate products or precipitated CaCO_3 . The process used an acid gas (H_2S) to improve the aqueous dissolution of CaS, which is otherwise poorly soluble. The carbonate product was primarily calcite (99.5%) with traces of quartz (0.5%). Calcite was the only CaCO_3 polymorph obtained; no vaterite or aragonite was perceived. The schematic steps involved in the synthesis of CCNPs from gypsum waste are shown below in Figure 8. The product was made up of micron-size particles, which were further characterized by XRD, TGA, SEM, Bruner–Emmett–Teller (BET), and true density. The batch recovery of CaCO_3 from waste gypsum slurry using sodium carbonate under ambient conditions that were further utilized for pre-treatment of acid mine drainage from coal mines [70]. US patent no 2013/0288887 A1 reported a simple, cost-effective, and novel method for the recovery of nano CaCO_3 from the gypsum waste slurry [74]. There is a lower decomposition temperature of CaCO_3 . The synthesized nano CaCO_3 was used as a nano adsorbent for the adsorption of carbon dioxide, and as a complex catalyst for reactive sorption enhanced the reforming process for hydrogen production from methane. The CaO-based carbon dioxide adsorbent shows good cycle stability and fast sorption rate, and complex catalyst used for reactive sorption enhanced methane steam reforming can obtain the hydrogen with a purity of more than 90%.

The CCPs can be synthesized by a simple thermal decomposition method [75], where the dolomite is calcined at $800\text{ }^\circ\text{C}$, and it is decomposed into CaCO_3 and CaO in the presence of air. The major disadvantage with this method is that there are adsorption and precipitation of AsCO_3 and AsO [76]. Chilakala et al. (2016) reported an innovative convenient, and cost-effective carbonation method for the synthesis of pure aragonite

needle phase of CCPs from dolomite [77]. The characterization of PCC was done by XRD and SEM for the morphological and mineralogical and aspect ratio (ratio of length to the diameter of the particles). The synthesis of PCC was carried out in two steps, at first, after calcinated, dolomite fine powder was dissolved in water for hydration, the hydrated solution was then mixed with an aqueous solution of magnesium chloride at 80 °C, and then CO₂ was bubbled into the suspension for three hours to produce aragonite PCC. Finally, aragonite type precipitated CaCO₃ can be synthesized from natural dolomite via a simple carbonation process, yielding a product with an average particle size of 30–40 μm [78].

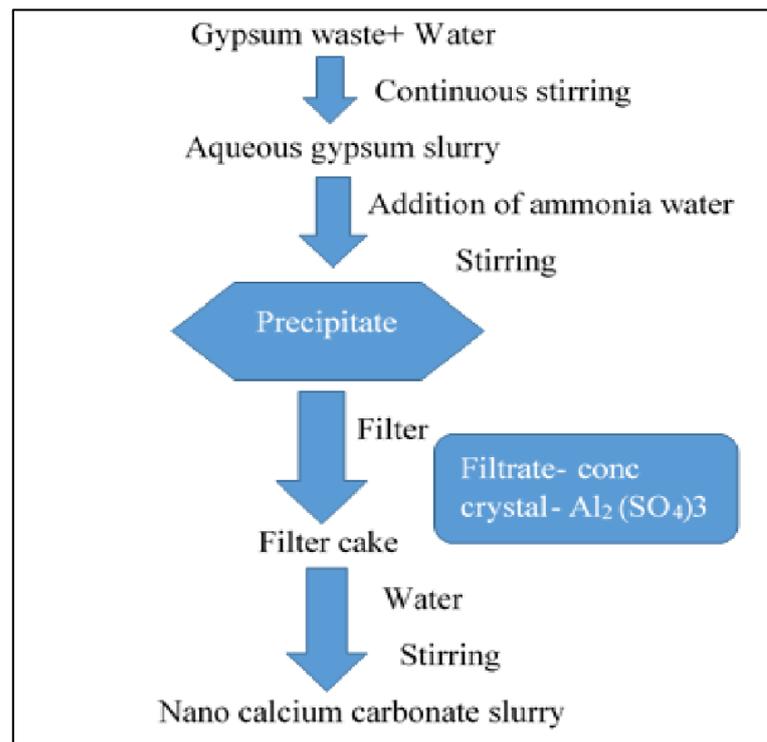


Figure 8. Steps involved in the synthesis of calcium carbonate nanoparticles from gypsum waste.

6.4. Recovery of Calcium Oxide/Carbonate Particles from Finger Citron Residue

About two-thirds of the world's citrus fruits are produced by Brazil, China, India, Mexico, Spain, and the USA. In 2016, about 124 Million gallons of citrus fruits were produced out of which 50–60% used as fresh fruits while the remaining 40–50% was subjected to industrial processing for extraction of juices, etc. Based on the applied technology and type of cultivars, the citrus peel waste of such industries varies from 50 to 70% *w/w* of processed fruits [79,80]. This leads to the generation of 10 Mg of citrus peel waste, which has moisture whereby it attracts flies, insects, and mosquitoes and leads to the pollution. So, it is important to process the citrus peel waste for the recovery of value added materials. One such citrus fruit is finger citrons (FG) whose shape is unusual and the fruit is segmented into finger-like sections [81]. Finger citron, which is a subtropical plant, is grown in China's Sichuan, Fujian, Guangdong, and Zhejiang provinces [82]. In the time of finger citron beverage processing, a huge amount of Finger citron residues (FCRs) are produced which is disposed of as garbage. Such disposals sometimes may give rise to other environmental problems [83]. It has a porous texture and contains numerous organic compounds which makes them a preferable precursor material for the synthesis of porous materials that can also be potentially applied for environmental protection. They are almost similar to lemon and used as a substitute for lemon in China. FCR is the residual of the fruit after extraction of juices from it. The FCR is reported to have numerous valuable minerals and elements

but it has a high amount of Ca which makes them a suitable material for the extraction of CCPs. The synthesis mechanism of CC NPs from FCR is given below in Figure 9.

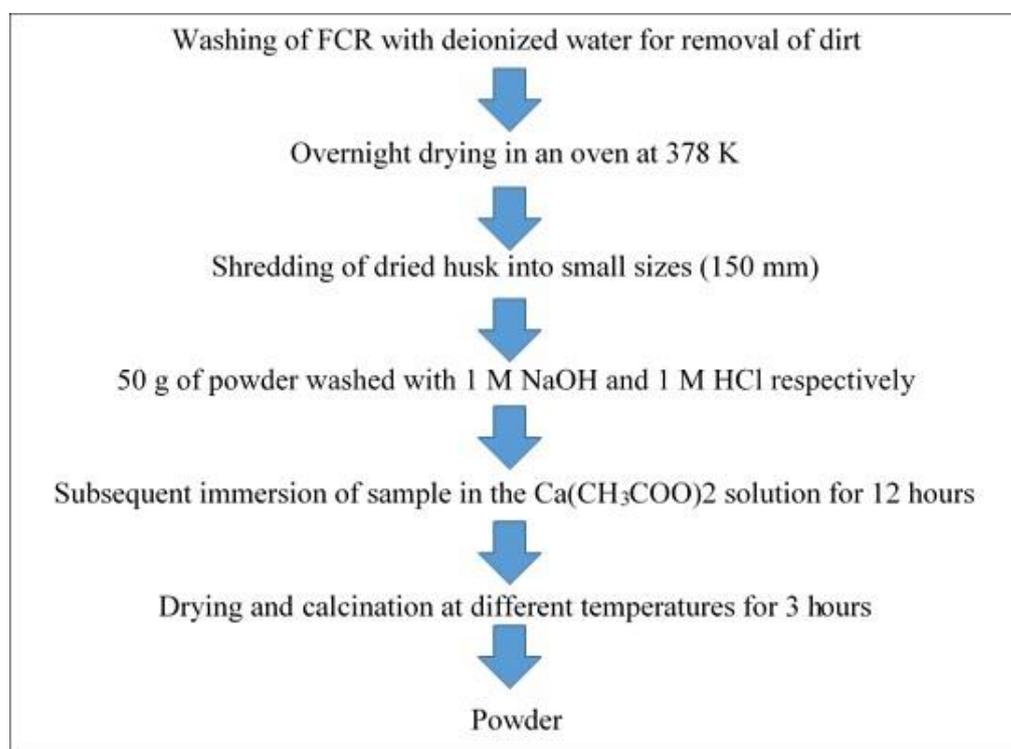


Figure 9. Steps involved in the synthesis of calcium carbonate nanoparticles from finger citron residue.

6.5. Recovery of Calcium Oxide/Carbonate from Waste Calcium Sulfide

Calcium sulfide (CaS) is one of the major waste of several industries which are based on coal [84]. This is a waste material that is produced in large amounts for example, gasification of 1000 tons/day of 3% sulfur coal produces 67 tons/day of CaS) during the desulfurization of hot coal gas by a limestone-based adsorbent. The main problem with such waste is that it is rich in sulfur so cannot be landfilled as there could be potential H₂S gas evolution and leaching of sulfur in the soil. Brooks and Lynn (1997) reported the synthesis of CaCO₃ and H₂S from the waste CaS where, the calcium sulfide is dissolved by reacting with H₂S forming a complexed either with aqueous methyl diethanolamine (MDEA) or other alkanolamines [85]. Further, in the very next stage, Ca(HS)₂, which is extremely soluble, reacts with CO₂ complexed with MDEA (aqueous). These precipitates the pure and uniformly sized crystalline CaCO₃ and to forms MDEA-complexed hydrogen sulfide.

6.6. Synthesis of Calcium Carbonate from Yellow Phosphorus Slag

Chen et al. (2020) used yellow phosphorus slag as a raw material to obtain high-purity calcium carbonate whiskers at low temperature and pressure. During the experiments, the effect of reaction conditions, i.e., temperature, time, concentration of Ca²⁺, ammonia dosage, and CO₂ flow rate was systematically discussed by researchers. The above mentioned parameters have an important effect on the crystal shape and microscopic morphology of the product. It was found that the content of calcium carbonate (aragonite) in the product was about 93.67% under optimal conditions. The whiteness of the product was 97.6%. The single particle diameter was found to be about 1.5–3 μm, and the length of a single particle was about 8–40 μm. SiO₂ was produced as by-products during the whole preparation process could also be reused [86]. Researches indicated that the production strategy had a good application prospect.

7. Characterization of Calcium Carbonate and Oxide Particles

The characterization of calcium carbonate NPs (CCNPs) can be done by all the sophisticated instruments but especially by FTIR, XRD, scanning electron microscopy-electron diffraction spectroscopy (SEM-EDS), TEM, and Raman spectroscopy. The characterization of CCNPs plays an important role in the confirmation of synthesis and identification of polymorphs. Fourier transform infrared spectroscopy plays an important role in the identification of functional groups in the synthesized CCNPs. A typical FTIR spectrum of a CCNPs is shown in Figure 10. The FTIR analysis of CaCO_3 reveals that there is a strong peak for carbonate ions due to vibration peaks ν_1 , symmetric stretching; ν_2 , out-of-plane bending; ν_3 , doubly degenerate planar asymmetric stretching; and ν_4 , doubly degenerate planar bending. The spectrum shows vibrational bands at 1456.3, 876.7, 712.7, and 409.8 cm^{-1} indicates plane bending vibration of carbonate [87]. The FTIR analysis confirmed that the CaCO_3 nanopowder had the characteristic peak of the carbonate group. A sharp peak at 876.7 cm^{-1} confirmed that the CaCO_3 nanopowder obtained from the cockleshell was calcite.

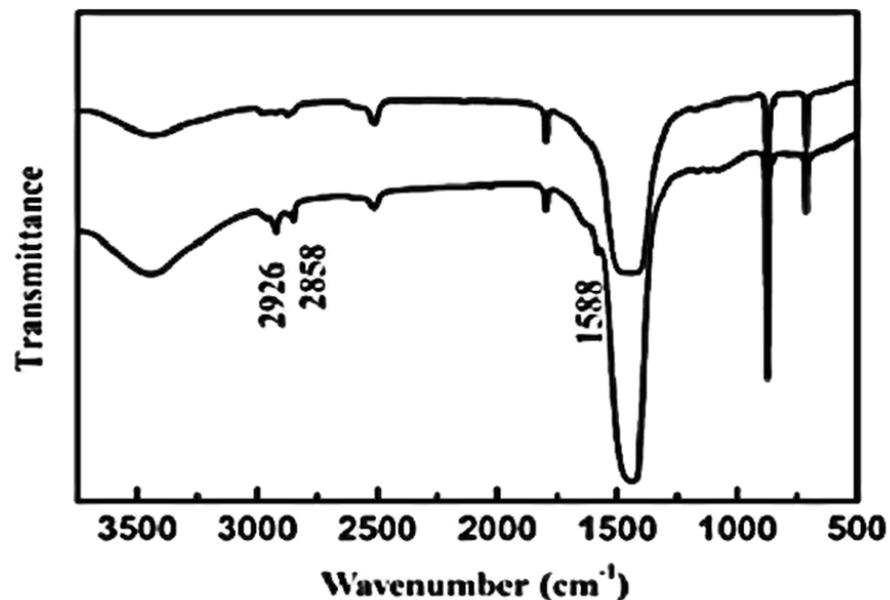


Figure 10. Fourier transform infrared spectra of calcium carbonate nanoparticles adapted from Chen et al., 2010.

Similarly, Raman spectroscopy also helps in the identification of molecules and functional group identification. The most important technique is the SEM which helps in the differentiation among the three polymorphs of CCNPs otherwise all these three polymorphs will look alike. The TEM also helps in the size determination of the particles. Based on the external morphology these polymorphs can be easily recognized as nano calcite. They are rhombohedral in shape, aragonite is needle-shaped and the vaterite is either spherical or flower shape. The typical field emission scanning electron microscope images of nano calcite, aragonite, and vaterite are shown in Figure 11a–d. The rhombohedral shaped particles confirm the calcite phases whose surface is smooth with sharp edges and corners [88].

Figure 11b is showing the aragonite phase, which is rod-shaped. The vaterite phase in Figure 11c,d is showing flower and spherical shape. The EDS attached with SEM helps in the confirmation of the formation of CaCO_3 along with its purity. The EDS also reveals the purity of the CCNPs by giving a molecular percentage of elements mainly C, O, and Ca in the elemental spectra. While the TEM image in Figure 12A reveals a rhombohedral shaped micron particle whose morphology is similar to the SEM images in Figure 12A [88].

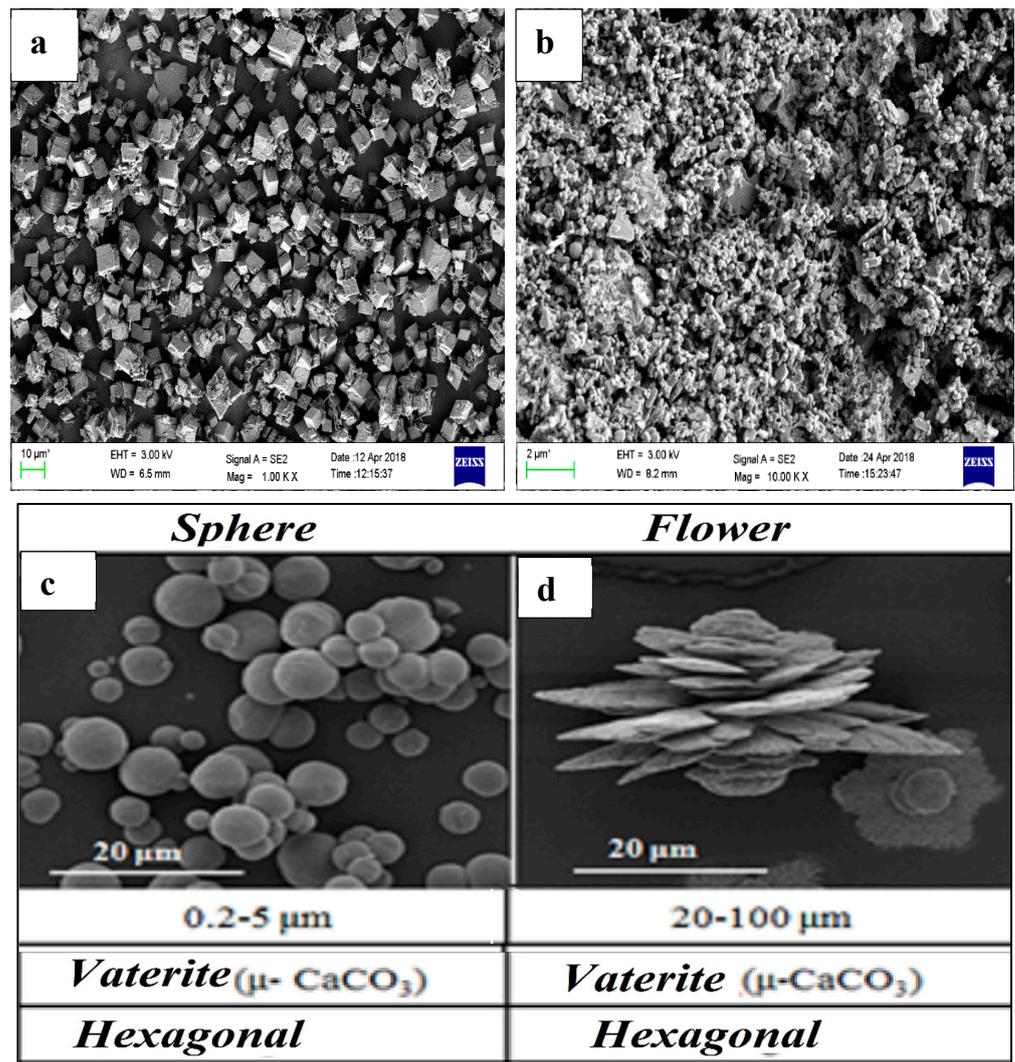


Figure 11. FESEM of (a) nano calcite; (b) aragonite; (c) spherical vaterite; (d) floral vaterite [89].

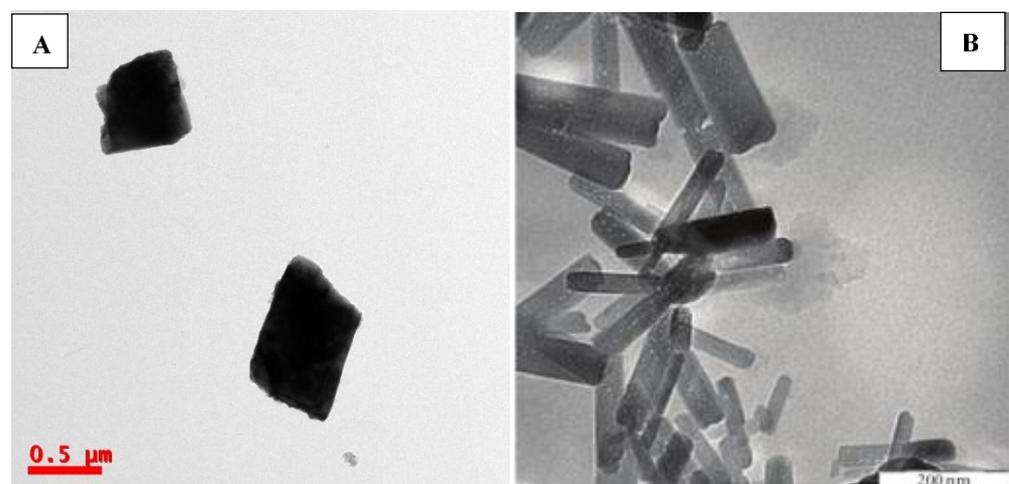


Figure 12. Transmission electron microscopic images of (A) calcium carbonate of microparticles and (B) aragonite nanorods adapted from (Islam et al., 2012).

While Figure 12B is showing nanorods whose diameter in width is below 50 nm and the length is above 200 nm. The rod-shaped particles indicate the aragonite phase of Ca NPs [88].

X-ray diffraction (XRD) analysis helps in the confirmation of mineralogy and phase determination of the CCNPs. A typical XRD pattern is shown in Figure 13, which exhibits characteristics peaks of aragonite at 2θ values of 26.34° , 33.24° , 45.98° , 33.24° , 45.98° , and 26.3° , which correlate with (hkl) indices of (111), (012), (221), and (021), (0.12), and (221), respectively [23].

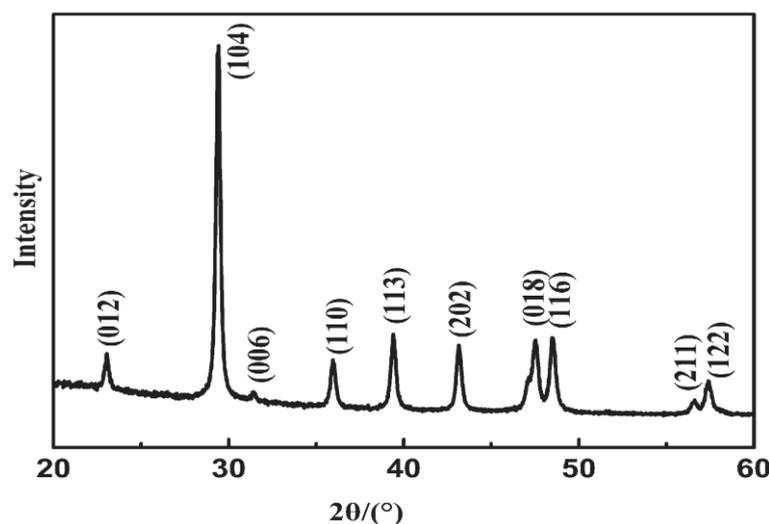


Figure 13. X-ray powder diffraction (XRD) spectrum of calcium carbonate nanoparticles adapted from Chen et al., 2010 (Chen et al., 2010).

8. Applications of Calcium Carbonate Nanoparticles

CaCO_3 is one of the materials which are used very frequently in the fields of ceramics [23], medicine, drug delivery, paints, fertilizers, food, cosmetics and drugs, papers, fillers, inks [9], catalysts, rubbers, plastics, and paints. In most of these industries, it is used as a viscosity modifier. It is also used as a nano adsorbent for the remediation of pollutants from the wastewater.

8.1. Applications of Calcium Carbonate Particles for Environmental Cleanup

The application of CCPs in the field of environmental cleanup is very significant due to the low cost of the nanoparticle, easy availability, and biocompatible nature [23]. It can be used for the removal of both organic as well as organic pollutants from the wastewater. Moreover, the insolubility of CaCO_3 in water makes them more suitable for application in aqueous solutions [90]. Among inorganic pollutants, it can be applied for the removal of heavy metals [91] from the wastewater [92], while the organic pollutants that can be removed by CCPs are phenols, pesticides, and dyes [93]. In addition, it can also be used as a nano biosensor for the detection and removal of pollutants (microbial, chemical). All these examples are given below where CCPs have been used for the remediation of inorganic and organic pollutants.

8.2. Heavy Metals Removal

Heavy metals contamination is one of the serious nuisances in the area of water and wastewater management. The elimination of heavy metals from the aqueous solutions is carried out by numerous methods that we have already seen above in the introduction section. We know that adsorption is a reliable, economical, and efficient technique [94]. Some of the most common adsorbents are zeolites, activated carbon, alumina, zinc oxide, etc. Here the size of adsorbents falls in the size of microns, so the process is less efficient.

When adsorption is done employing biological material like microbes then the process is called bioremediation [95]. When biological material and NPs are used together with either by surface modification or in the form of composite, the process is called nano bioremediation. When the adsorption process is carried out by NPs then the process is called nano remediation [96]. In the above section, we have already seen the advantages of CCPs as an adsorbent. So, here we have highlighted the examples where CCPs have been applied for the removal of heavy metals and other pollutants.

Hong et al., 2011, reported the removal of heavy metals (Cu^{2+} , Cr^{6+} , Cd^{2+} , and Pb^{2+}) by using calcium carbonate particles extracted from the starfish by using enzymes like alpha-amylase, beta-amylase, and protease. It was found that the obtained adsorbent were comparatively effective in the heavy metal removal than the calcium carbonate obtained from crabs, oyster, and cockle shells. Moreover, the calcium carbonate was highly porous in nature, which again made them suitable and effective candidate for the remediation of heavy metals [91].

The remediation of heavy metals from the aqueous solution by using CCPs synthesized through chemical method metals [97]. In this experiment, CaCO_3 was used to remove the Fe and Pb ions from the aqueous solutions and studied the adsorption mechanism including the kinetic and isotherm models at room temperature. From the above study following findings were obtained: (i) adsorption kinetics follows a pseudo-second-order equation; (ii) Langmuir isotherm revealed that the maximum monolayer adsorption capacity of CaCO_3 for Pb (II) was 1210 ± 30 mg/g and for Fe (II) ions, it was 845 ± 8 mg/g; (iii) optimal dose of CaCO_3 was 200 mg/L at 25 °C, and (iv) and the removal efficiency of Fe and Pb ions is enhanced by a precipitation transformation mechanism instead of adsorption.

Jacob et al. (2018) reported the use of CaCO_3 coated bacterial magnetosomes (biogenic magnetite obtained from the internal structures of magnetotactic bacteria) for remediation of Cr (III) and Ni (II) ions from tannery effluent. The following findings were observed from the experiment.

- (i) Equilibrium was attained within an hour for Cr (III) ions at pH-6.0 and Ni (II) ions at a pH-8.0.
- (ii) The adsorption process followed a pseudo-second-order reaction kinetics, along with Langmuir and Freundlich adsorption isotherms.
- (iii) Adsorption of metallic ions on calcite microcrystals was spontaneous and endothermic.
- (iv) Almost equal removal efficiency (Cr-94% and Ni-84%) was observed with both magnetic calcite and calcite crystals but it was higher than magnetosomes and activated carbon.
- (v) Removal of both the metal ions was facilitated by applying an external magnetic field.
- (vi) It is concluded that the magnetic calcite could act as a potential and alternative adsorbent for the elimination of heavy metals from tannery effluents [98].

Abeykoon et al. (2017) reported the elimination of the excess of fluoride ions from different water sources from Sri Lanka using porous CCNPs. The reported approach is quite simple, cost-effective, and innovative for the elimination of fluoride ions from the wastewater. The synthesized porous CCNPs removes the fluoride by simple adsorption mechanism and about 100% removal efficiency was achieved within one hour only [99].

8.3. As a Biosensor

CCPs can be used in developing a simple and economical biosensor due to their unique properties like high porosity, high surface area, and low mass transport barrier. Earlier investigators have reported the utilization of CCPs to detect phenols and glucose by immobilizing enzymes polyphenol oxidase (PPO) and glucose oxidase, respectively. The PPO/nano- CaCO_3 electrode possesses a wide detection range (i.e., 6×10^{-9} to 2×10^{-5} M), sub-nanomolar detection limit (0.44 nM at a signal to noise ratio of 3), good stability (70% remained after 56 days), the shorter response time (i.e., <12 s), large current density, and very high sensitivity (i.e., 474 mA/M). Similarly, the glucose biosensor also provided the same benefits and was very little influenced by other compounds (like ascorbic acid, glutathione, L-cysteine, and p-acetaminophen) at their normal levels. The development

of a highly sensitive amperometric phenol biosensor by using CCNPs of size around 80 nm. The sensor was developed by casting (nano-CaCO₃)-PPO bio composite on the surface of a glassy carbon electrode by glutaraldehyde cross-linking. The special three-dimensional structure, porous morphology, hydrophilicity, and biocompatibility of the nano-CaCO₃ matrix provided high enzyme loading, and the enzyme entrapped in this matrix retained its activity to a large extent. In addition, the effects of pH value applied potential, temperature, and electrode construction were also studied [100]. In one of the experiments, investigators have used the polyelectrolyte capsules (with or without CaCO₃ core) as a pH indicator that works even in the presence of salt in the solution. High removal capacities of heavy metals, i.e., Cd²⁺ 515, Pb²⁺ 1028, Cr³⁺ 259, Fe³⁺ 321, and Ni²⁺ 537 mg/g were achieved from aqueous solutions using precipitated amorphous calcium carbonate (ACC) NPs. The removal process was via precipitation, so the ACC became non-reusable. Few investigators have developed multi-structured CaCO₃/magnetite composite crystals by microwave radiation method which was used for the photocatalytic splitting of water to liberate oxygen. One special advantage with such photocatalyst is that it can be recycled after extraction from the solution.

8.4. Phenolic Compounds Removal

Phenolic compounds are a class of polluting chemicals, which are exploited extensively and discharged into the environment. These phenolic compounds have a high tendency to be absorbed by living beings from their skin and mucous membranes. Therefore, it is of utmost importance to determine the content of phenolic compounds due to their toxicity and persistent nature in the environment. a biosensor is one of the most important tools for the detection of such phenolic compounds, out of which amperometric biosensor based on PPO or tyrosinase is most widely used for the detection of phenols due to its effectiveness and simplicity [101]. PPO is a metalloenzyme that contains a binuclear copper active site and catalysis, in the presence of dioxygen, the hydroxylation of monophenols to catechols (monooxygenase activity), which in turn are oxidized to ortho-quinone (catecholase activity). The phenol biosensor transduction is thus based on the amperometric detection of the enzymatically generated o-quinone.

8.5. Dye Removal

Mosleh (2018) synthesized 15–50 nm, cobalt tungstate, and CaCO₃ nanocomposite for the removal of organic pollutants (dyes) from the wastewater. The morphological and chemical properties were analyzed by vibrating sample magnetometer, UV–Vis diffuse reflectance spectroscopy, XRD, and SEM where the latter two instruments helped in the confirmation of the average crystallite size of nanocomposites, whose size was in the range 15–50 nm. The high absorption with 3.2 eV bandgap of synthesized nanocomposite was identified with the DRS spectrum. The synthesized nanocomposite exhibits photocatalytic activity which was used for the degradation of methyl violet, methylene blue, phenol red, and eosin Y dyes. The developed nanocomposite degraded the MV dye up to 99%, within 200 min [102]. Ma et al. reported the synthesis of CCNPs from finger citron residue (FCR) that have already been discussed above in the synthesis section and utilized them for the removal of Congo red (CR) from the wastewater [82]. Here Nickel-doped porous CaCO₃ monoliths were developed from the FCR and applied for the removal of anionic dye CR by adsorption method in a batch experiment. The adsorption of CR by such NPs showed a pseudo-second-order kinetic model and Langmuir adsorption isotherm. It was found that due to the differences in positive and negative charge effects between CR and Nickel, a higher amount of CR dye was adsorbed on the Nickel-doped porous CaCO₃ monoliths which authenticate that later are a promising adsorbent for the removal of the anionic dyes from wastewater.

The removal of various organic and inorganic pollutants from different water and wastewater indicates that the main process for the removal of pollutants was adsorption. In some cases, CCPs were without surface functionalized while in some cases the CCPs

surface were modified by various capping agents. These capping agents were used in order to make the CCPs more specific for a specific pollutants. The adsorption is a simple technique which is practiced from a century to remediate the pollutants. In this process inorganic pollutants like heavy metals gets reduced on the surface of the CCPs. Due to this reduction, the toxic heavy metals gets converted into nontoxic form which is beneficial for the flora and fauna. Moreover, adsorption process do not involve any sophisticated instruments, and machinery so it is considered easy, and economical. The only problem faced is the disposal or recycling of the CCPs loaded with the toxic heavy metals.

9. Conclusions

The CCPs have enormous potential in the field of electronics, medicine, drug delivery, paints, feed supplements, and environmental cleanup due to their biocompatibility, biodegradability, and low cost. However, the recovery of CCPs makes all these properties more justified, which further lowers the cost of the product and minimizes the pollution on the environment. Undoubtedly, the recovery of CCPs from the waste by products like fly ash, incense sticks ash, egg shell, cockle shell, gypsum, and dolomite provides an alternative for the calcium-based industries. The CCPs exhibit three polymorphisms, viz., calcite, aragonite, and vaterite. These polymorphs vary in the stability of the particle. The CCPs have the potential for the remediation of heavy metals, pesticides, dyes, and other pollutants from the wastewater. Moreover, the biodegradable, biocompatible, and economical nature of CCPs make the process of adsorption much economical.

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