CHAPTER 2

REVIEW OF LITERATURE

The very purpose of taking up a research problem is to achieve new findings. This kind of an approach would help the process of furtherance of knowledge. Also it provides continuity, in research so that identification of new problems and also probing into existing problems would contribute to the expansion of knowledge and specialization in that area. In doing so it is quite necessary to have a brief idea of the work done in the recent past by different authors. This process of listing out and giving a brief summary of the work done is called review of literature which provides continuity in the process of research and specialization. So in this chapter an account of the research done by different authors is provided. The studies which are discussed in the particular area of study can be given as groups. The main areas of study can be grouped as under

2.1 Historical background of activated carbon
2.2 Preparation of Activated Carbon using different raw materials
2.3 Preparation of Activated Carbon using different waste materials
2.4 Activated carbon preparation using different peels:
2.5 Activated carbon using different citrus fruit peels:
2.6 Synthesis of nanomaterial
2.7 Antibacterial activity of various metal nanoparticles
2.8 Applications of activated carbon in cancer therapy
2.1. Historical Background

Gottipati (2012) reviewed about the historical background of AC and presented in this manner. During 1500 B.C., AC was mainly used for medicinal purposes. The adsorptive powers of AC was discovered in 1773 by Scheele (Dietz 1994), when he conducted experiments with gases. The industrial production of AC was well developed in 19\textsuperscript{th} century and it replaced bone char in sugar refining processor (Bansal \textit{et al.}, 1988).

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Significance</th>
</tr>
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<tbody>
<tr>
<td>18\textsuperscript{th} Century</td>
<td></td>
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<tr>
<td>1773</td>
<td>Scheele</td>
<td>Identified the adsorptive power of the carbons (Charcoal) while measuring the volumes of various gases adsorbed by carbons which derived from different source materials.</td>
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<tr>
<td>1785</td>
<td>Lowitz</td>
<td>Studied the effectiveness of charcoal in decolorizing various aqueous solutions and it considered as the first systematic account for application of charcoal in liquid phase.</td>
</tr>
<tr>
<td>1793</td>
<td>Kehl</td>
<td>Carbon which prepared from animal tissues can be used for colour removal from solutions was discovered.</td>
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<tr>
<td>1794</td>
<td>-</td>
<td>Wood charcoal was used for decolorizing sugar syrup by an English sugar company but the method of preparing a carbon was kept as secret.</td>
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### 19th Century

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Description</th>
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<tbody>
<tr>
<td>1805</td>
<td>Delessert</td>
<td>The decolorizing power of charcoal for sugar-beet liquor was demonstrated.</td>
</tr>
<tr>
<td>1822</td>
<td>Bussy</td>
<td>AC was prepared by healing blood with potash which has 20-50 times the decolorizing power of bone char. It considered being the first recorded example of producing an AC with a combination of thermal and chemical processes.</td>
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<tr>
<td>1856</td>
<td>Stenhouse</td>
<td>By heating a mixture of flour, tar, and magnesium carbonate, the decolorizing chars can be prepared.</td>
</tr>
<tr>
<td>1862</td>
<td>Lipscombe</td>
<td>Carbon is used to purify potable water.</td>
</tr>
<tr>
<td>1865</td>
<td>Hunter</td>
<td>The gas adsorption properties of AC which prepared from coconut shells were identified.</td>
</tr>
<tr>
<td>1868</td>
<td>Winser</td>
<td>Heating of paper mill waste with phosphates AC was produced.</td>
</tr>
</tbody>
</table>

### 20th Century

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1900</td>
<td>Ostrejko</td>
<td>Processes involved in the development of commercial ACs are (a) incorporation of metal chlorides before carbonization (b) selective oxidation with carbon dioxide at high temperatures.</td>
</tr>
<tr>
<td>1911</td>
<td>-</td>
<td>Fanto works, Austria with the trade name ‘Eporit’, prepared AC by using the approach of ostrejko’s gasification.</td>
</tr>
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</table>
Review of literature

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1913</td>
<td>Wunch</td>
<td>AC with zinc chloride, rising of decolorizing capacity of Eponit was recognized.</td>
</tr>
<tr>
<td>1914-1918</td>
<td>-</td>
<td>The preparation of AC with high adsorption capacity was increased after the introduction of poisonous gasses in the first world war by activating world chips with zinc chloride, granular AC with reliably controlled adsorptive and physical properties was developed. Carbon which prepared from coconut shell has the combination of required characteristics was determined by a group which studied under Chaney (USA)</td>
</tr>
<tr>
<td>1931</td>
<td>Kubelka</td>
<td>Interpreted sorption phenomena on active carbon by the mechanism of capillary condensation.</td>
</tr>
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</table>

2.2. Preparation of Activated Carbon using different raw materials

AC can be prepared from a wide variety of raw materials (Da browski 2001), which should be abundant and cheap, with high carbon content and low inorganic content; raw materials should be easily activated and should have low degradation by aging (Moreno-Castilla and Rivera-Utrilla, 2001). Coal is the most commonly used precursor, mainly due to its low cost and large supply (Ahmadpour and Do, 1996). Many researchers used various precursors for the preparation of AC. Few of their studies were reviewed in this chapter.

Hedi Ben Amor et al., (2015) have conducted a study with the date stones. In that study, the date stones were first washed with water to remove impurities, dried at 105°C for 24h, crushed and sieved. Fraction with average particle size of about 300µm was selected for this study. The dried stones were soaked in ZnCl₂.
solution with a different impregnation ratios (0.25- 2.00) for 24 hours at 110°C. The dried mixture were put into a furnace and heated for different activation times (30-120 min) at different temperatures (400-700°C) under a constant N₂ (99.99%) flow of 120 cm³/min. Then, the produced AC was repeatedly washed with 0.1 mol/L HCl followed by hot distilled water until the pH of washed solution reached 6.7-7. Finally, the product was dried at 110°C for 24 h, ground and sieved to a particle size of 125 µm for further studies.

Giraldoa et al., (2007) have made a study on the preparation of AC by physical and chemical activation as below. Physical Activation: The starting material was Kevlar. Pyrolysis was carried out in a vertical quartz reactor, in which 3 - 4 g of the precursor were introduced. Temperature was programmed low increase at a rate of 4°C up to 800, 900 and 1000°C, under a N₂ flow (80 cm³ min⁻¹). After pyrolysis, the activation was carried out. First CO₂ was used (50cm³ min⁻¹), at temperatures 50°C below the pyrolysis one. The activation was carried out at different time intervals (3 and 6 hours) to achieve different degrees of burn off (BO). Then, the agent was changed by steam of water (flows of 3 and 8 drops per minute) at 750°C and times of 1 and 2 hours.

Chemical activation: The fibers have impregnated using 3 - 4 g of Kevlar and 100 ml of an aqueous solution of H₃PO₄ of different concentration in order to vary the impregnation ratio. Besides, different conditions of impregnation were used: Room temperature for 24 hours; 90°C for 7 hours and finally a rotary evaporator guaranteeing la homogeneous impregnation of the material. After that, the impregnated samples were died overnight at 110°C in a vacuum furnace. All
the activations were done in a quartz reactor using 3 – 4 g of impregnated Kevlar, a flow of N\textsubscript{2} (80\text{cm}^3\text{min}^{-1}) and a heating rate of 10°C\text{min}^{-1} until 700°C; once this temperature was attained, the samples were rapidly cooled down to room temperature. The resulting carbons were washed in a soxhlet extractor to remove the activating agent and/or its decomposition products.

Sivakumar \textit{et al.}, (2012) have studied various carbonizing process for the carbonization and activation of Balsamodendron caudatum wood waste. In this study the various processes were discussed as below. Acid Process: The dried material was soaked well with H\textsubscript{2}SO\textsubscript{4} solution for a period of 24 hours. At the end of 24 hrs the excess of H\textsubscript{2}SO\textsubscript{4} solution were decanted off and air-dried. Then the materials were placed in the muffle furnace carbonized at 120-130°C. The dried materials were powdered and activated in a muffle furnace kept at 800 °C for a period of 60 minutes. After activation, the carbon of obtained were washed sufficiently with large volume of water to remove free acid, Then the obtained material was washed with plenty of water to remove excess of acid, dried then to desired particle size. Another portion of the material was activated with activating agents H\textsubscript{3}PO\textsubscript{4} as per the H\textsubscript{2}SO\textsubscript{4} activation process described above and they sieved to desired particle size. Final products obtained in each case were stored separately in vacuum desiccators until used.

Carbonization with Carbonate Salts: The Balsamodendron caudatum wood waste has to be carbonized was soaked with 10% Sodium carbonate solution for a period of 24 hours. After impregnation, the liquid portion was decanted off and the material dried. The dried mass was subjected to carbonization process at 400°C,
then powdered well and finally activated at a temperature of 800°C for a period of 20 minutes.

Dolomite Process: A sufficient quantity of dried Balsamodendron caudatum wood waste was taken over a calcium carbonate bed and the upper layer of the waste was also covered with a layer of Calcium Carbonate. The whole material was carbonized at 400°C, powdered well and followed by the thermal activation at 800°C. After the activation, the material was repeatedly washed with plenty of water to remove calcium carbonate and dried at 110°C.

Carbonization with Sulphate salts: In this method the Balsamodendron caudatum wood waste to be carbonized were soaked in 10% solutions of sodium sulphate for a period of 24 hours. After impregnation, the liquid portion was decanted off and then dried. The dried mass was subjected to carbonization process at 400°C, powdered well and finally thermally activated at 800°C for a period of 10 minutes.

Kwaghger and Adejoh, (2012) have studied the preparation of AC using mango nuts. In that study, the mango nuts were cracked to remove the seeds which were cut into pieces (3cm in size approximately), dried in sunlight for about two weeks to ensure that reasonable moisture was removed. The dried mango seeds were crushed with laboratory mortar and pestle. The resulting particles were sieved and the particle sizes of 2.36mm were again dried in sunlight again for one day to ensure that the moisture in the products was reasonably removed. The activation method used for this work was chemical activation using zinc chloride salt (Zncl2)
as activating agent. To study the effect on concentration, 30g, 65g and 100g of the salt was diluted each in 100ml of distilled water to obtain concentrations of 30%, 65% and 100%. Also 30ml, 65ml and 100ml each from the obtained concentrations of 30%, 65% and 100% were respectively mixed with 100g of the prepared raw material respectively to obtain impregnation ratios of 1:3, 1:2 and 1:1 g/ml. The raw material was activated with ZnCl$_2$ for a period of 2, 4, and 6 hours. Furthermore, in obtaining the products, carbonization temperature of 500°C was employed to heat the obtained product for 1 hour.

Abdullah et al., (2001) have used Gelam wood bark (Melaleuca cajuputi) as precursor to prepare the AC. The preparation process consisted of ZnCl$_2$ impregnation followed by carbonization in nitrogen at 500°C for 3 hours and carbon dioxide for 1 hour. The optimum surface area was obtained at 25 % of ZnCl$_2$, which is 1213 and 1443 m$^2$/g for BET and Langmuir, respectively. The AC shows acidic properties and low ash content.

AlOthman et al., (2011) have prepared AC by the co-pyrolysis of mixed solid wastes (biomass, cartons and polystyrene) at low carbonization temperatures. The effects of carbonization temperature (200°C, 300°C and 400°C) and chemical activation using different concentrations of a ZnCl$_2$ solution (0.0, 0.5, 1.0 and 2 M) on the yield and adsorption capacity of AC were investigated. The results show that the AC yield is significantly dependent on both the carbonization temperature and the ZnCl$_2$ concentration. The yield increased as the ZnCl$_2$ concentration
increased from 0.0 to 2 M and decreased as the carbonization temperature increased from 200°C to 400°C.

Chiung-Fen Chang et al., (2000) have selected corn cob as a suitable precursor for production of good AC by chemical activation. However, respond to the need for cleaner production, this study focuses on the physical activation by gasifying agents such as CO₂ and steam. The activation temperatures under investigation are 1073 and 1173 K. Within the limit of 50 wt% burn-off, experimental results revealed that the BET surface area, pore volume, and average pore diameter of the resulting AC generally increased with the extent of burn-off in both gasifying agents and at both temperatures. It was found that the higher activation temperature can overcome the drawbacks of a longer period of activation required attaining larger surface area and can offer higher potential to produce AC of greater adsorption capacity from agriculture wastes such as corn cobs. Additionally, the BET surface areas of properly prepared ACs were satisfied commercial requirements, when compared with commercial AC. The BET surface areas of the ACs after about 71 and 59 wt% burn-off of CO₂ and steam activations at 1173 K are 1705 and 1315 m²/g, respectively, indicating high adsorption capacities. Thus, it is feasible to produce high-quality microporous AC from corn cob agrowaste using N₂ carbonization followed by physical activation with CO₂ or steam.

Satonaka et al., (1983) have conducted a study on the preparation of AC using pulp waste. In this study, the pulping waste used for these ACs are KP waste liquor from a white birch (Betula platyphylla var. japonica), KP and SP waste
liquor from a spruce (*Picea glehnii*), pulp waste sludge and waste of deinking from H Paper Co. in K city located in the eastern Hokkaido and pulp waste sludge from J Paper Co. in the same city. Water in the above-mentioned waste liquors, waste sludges and waste from deinking was evaporated on the water bath and various solids were prepared. Every solid of O. D. 2.0 g equivalent was placed in a ZOO-tall beaker, and 10 g of 78% conc. phosphoric acid were added and heated on a horizontal rotary disc in an electric oven under four conditions. Carbonized substance was transferred in a mortar, ground well, washed with distilled water until pH 5 using a Buchner funnel.

Sodeinde (2012) was obtained the coconut shell samples, dirt was removed from samples after which they were washed and sun dried for 24hrs. The samples were crushed in order to be processed further in the furnace. Carbonization of the precursor was carried out at a temperature of 650°C, the carbonization was achieved in a muffle furnace for 2hrs. The coconut shell was cleaned from other materials such as coconut fiber or soil. It was then sun dried. The dried shell was burned in the furnace at 650°C for 2hours. The carbonized coconut shell was then crushed and separated into different mesh sizes. The charcoal was soaked in chemical solution of ZnCl₂ for 8 hours, to become AC. The AC was further treated by HCl (0.1M) and NaOH (1M) and Ammonia solution. Then the moist AC was kept in the furnace at 700°C (activated temperature) to increase the porosity of the AC. The resulting AC was washed with distilled water and dried in the furnace at 110°C for 2hours.
Arunrat and Sukjit, (2014) were made a value-added ACs from rice husk and studied the optimum conditions for gasoline adsorption using these ACs as adsorbents. All samples were analyzed for gasoline adsorption by gas chromatograph-mass spectrometry (GC-MS). The AC of rice husk, which was activated by H$_3$PO$_4$ at temperature of 450 °C, had the highest adsorption capacity. According to gasoline adsorption study, the optimum conditions were 0.1 g of AC, 70°C of adsorption temperature and 30 minutes of adsorption time. Physical characterization of the AC obtained was performed by scanning electron microscopy (SEM). From this analysis, they thus encourage the use of AC of rice husk as an adsorbent for the qualitative analysis of gasoline in order to apply for gasoline sampling in arson case and to reduce the analysis cost from commercial adsorbent.

Mourão et al., (2011) have stated that the raw materials more used in the preparation of carbons are of lignocellulosic origin. Wood and coconut shells are the major precursors and responsible for the world production of more than 300,000 tons/year of ACs. Yavuz et al., (2010) were stated that the precursor selection depends of their availability, cost and purity, but the manufacturing process and the application of the product are also important considerations.

Yahya et al., (2016) have studied the effect of temperature and impregnation ratio on the physicochemical properties of AC prepared from agricultural waste; desiccated coconut residue (DCR) by chemical activation using sodium hydroxide (NaOH). DCR sample was first carbonized at three different temperatures for 1 hour at 400°C, 500°C, and 600°C respectively. The resulting
chars were impregnated with NaOH at three different impregnation ratio; 1:1, 1:2, and 1:3 respectively and activated under nitrogen atmosphere for 1 hour at three different temperatures based on its carbonization temperature.

Wang et al., (2010) in the study have soaked dried pruning mulberry shoots with the mass of 6 g into a 50 mL 50% H$_3$PO$_4$ solution for 14 h at impregnation temperature (20, 60, 80, 90 or 100°C), the investigated impregnation ratio (1:1, 1.5:1, 2:1, 2.5:1 or 3:1) and concentration of H$_3$PO$_4$ solutions (40, 50, 60, 70 or 80%) were proposed by single-factor method, respectively. The soaked pruning mulberry shoot was first filtered, washed using double distilled water to remove residues acid, dried in an oven at 105°C, and then it was placed in a stainless steel horizontal tubular furnace and the inert stream of nitrogen gas made to flow through the furnace for 30 min with the flow rate of 100 cm$^3$ min$^{-1}$. After that, the furnace was heated at pyrolysis temperature (300, 400, 500 or 600°C) and kept at this temperature for 0.5, 1, 2 or 3 h, both were proposed using single-factor method. Finally, the produced AC was cooled in the inert atmosphere and washed with 1.5 M HCl solution and then with double distilled water until the pH of washing effluent reached 7.

Mopoung et al., (2015) have mixed the tamarind seed charcoal with KOH (CARLO ERBA Reagent) using KOH to tamarind seed charcoal ratios of 0.5 : 1, 1.0 : 1, and 1.5 : 1 (wt/wt). The mixtures were activated at 500°C, 600°C, and 700°C in furnace. Fourier transform infrared spectrometer (Spectrum GX, PerkinElmer) in the range of 4000–400 cm$^{-1}$ was used for characterization of functional groups on surface of the all samples. The samples were prepared as
pellets using KBr (IR grade). An X-ray powder diffractometer with a Cu tube anode (PW 3040/60, X’Pert Pro MPD) was used to record the X-ray patterns of samples. Scanning electron microscopy (PHILIPS LEO 1455 VP) was used to visualize the surface morphology of the carbonized and activated products. The samples were coated with gold by a gold sputtering device for a clear vision of the surface morphology. Elemental composition of these samples was also determined using scanning electron microscopy equipped with energy dispersive spectrometer (EDS). The EDS spectra showing elemental composition were obtained by scanning through the surfaces of the samples. The surface distributions were collected from SEM pictures using different magnifications. Textural characteristics of only AC prepared using the (1: 1) KOH: charcoal ratio with 500ºC activation was determined by N2 adsorption at –196ºC on Brunauer-Emmett-Teller surface area analyzer (Micromeritics TriStar II). The samples were degassed at 250ºC for 12h under vacuum before the measurements. The specific surface areas were estimated by the multipoint Brunauer-Emmett-Teller (BET) equation. The iodine (0.1 N, CARLO ERBA Reagent) and methylene blue (100 ppm, AR UNILAB) numbers were also determined for all ACs.

Baseri et al., (2012) have prepared AC (TPAC) with high adsorption capacities and highly active surface properties from Thevetia peruviana by physical and chemical processes such as direct pyrolysis, dolomite process, Chemical activation with H2SO4 + H2O2, impregnation of raw material with Conc. H2SO4, KOH, ZnCl2 and H3PO4 solution respectively followed by activation at 800ºC. Adsorption capacity of AC is due to porous structure, chemical nature of
the surface and pH of the aqueous solution. The physico chemical characteristics such as moisture content, volatile matter, pH, conductivity, bulk density, specific gravity, porosity, methylene blue number, iodine number and SEM were investigated to understand the adsorptive capacity of AC prepared from TPAC. Based on the results of the characterization studies, the AC prepared by impregnation of TPAC with H3PO4 (30%) solution followed by activation at 800°C was selected as a best quality adsorbent due to highest surface area with large number of pores and low ash content for the removal of dyes from textile industry effluent.

Tan et al., (2008) have prepared AC from coconut husk using physicochemical activation method which consisted of potassium hydroxide (KOH) treatment and carbon dioxide (CO₂) gasification. The effects of three preparation variables (CO₂ activation temperature, CO₂ activation time and KOH: char impregnation ratio) on the 2,4,6-trichlorophenol (2,4,6-TCP) uptake and AC yield were investigated. Based on the central composite design, two quadratic models were developed to correlate the preparation variables to the two responses. From the analysis of variance (ANOVA), the most influential factor on each experimental design response was identified. The AC preparation conditions were optimized by maximizing both the 2, 4, 6-TCP uptake and AC yield. The predicted 2, 4, 6-TCP uptake and carbon yield from the models agreed satisfactorily with the experimental values. The optimum conditions for preparing AC from coconut husk for adsorption of 2,4,6-TCP were found as follow: CO₂ activation temperature of
750\textsuperscript{0} C, CO\textsubscript{2} activation time of 2.29 h and KOH: char impregnation ratio of 2.91, which resulted in 191.73 mg/g of 2,4,6-TCP uptake and 20.16 % of AC yield.

Hussaro (2014) has investigated the production of cheap and efficient AC using waste from palm oil mill industries, which is palm oil shell. Palm oil shell is a by-product of the palm oil industry and was used as a raw material in this study due to its high carbon content, high density and low ash content. Normally, H\textsubscript{2}S in biogas, which is found the range between as low as about 50-10,000 ppm depending on the feed material composition to production, can cause corrosion to engine and metal substance via of SO\textsubscript{2} from combustion. H\textsubscript{2}S must be removed from biogas product prior to further utilization. Therefore, in this research the usage of palm oil shell is especially important due to its high value added for produced AC adsorbent for H2S adsorption in biogas product. In this study, fixed bed reactor (stainless steel with 54.1 mm internal diameter and 320 mm length) was studied to observe the effect of char product: Chemical agent ratio (Na\textsubscript{2}CO\textsubscript{3} and ZnCl\textsubscript{2}, 1:1 to 1:3), which there are activated at 700\textdegree C activation temperature for 2 hours on the chemical and physical properties, BET surface area, the pore volume, micropore volume and hydrogen sulfide adsorption. The result showed that the BET surface area, BET surface area, the pore volume and micropore volume increased progressively with increasing the char product: Chemical agent ratio. The value of mean total pore volume of AC increased with an increased char product: Chemical impregnation agent ratio (Na\textsubscript{2}CO\textsubscript{3} and ZnCl\textsubscript{2}) as is a 1:1 to 1:3. It was found that the efficiency of AC using Na\textsubscript{2}CO\textsubscript{3} agent is higher than AC using ZnCl\textsubscript{2} agent.
Verla et al., (2012) have successfully prepared AC by carbonization and activation of fluted pumpkin seed shell. Thermal activation was achieved at 300°C, 400°C, 500°C, 600°C and 700°C, while chemical activation was achieved by first impregnating the prepared raw material with activating reagents, and then carbonization at 500°C. Characteristics of the ACs were determined using standard methods. Increasing the activation temperature from 300°C to 700°C showed improved characteristics and optimum temperature for production of AC was obtained at 500°C after 2 hours.

Jianzhong et al., (2014) have carried out the study to prepare AC. In that study, Reedy grass leaves were washed with distilled water to remove the impurities (dust and water soluble substances) and dried at 110°C for 24 h, and sieved to obtain particles size lower than 80mesh prior to their activations. We adopted a two-step activation procedure (first pre carbonizing the reedy grass then impregnating the chemical activator-alkali with the pre-carbonized char .The char that was prepared from pre-carbonizing reedy grass leaves was prepared by the following procedures: the dried reedy grass leaves was carbonized at 450°C for 2 hours in a nitrogen gas environment. In a typical two-step activation process, pre-carbonized char was soaked with KOH solutions at a concentration of 3mol/l for 6, 8, 10, 12h at room temperature. These char containing solutions were then treated at room temperature. Afterwards, the chars were separated by filtration and activated at different temperatures for 1, 2, 3, 4hours respectively. After the activation, all the samples were washed with hot distilled water. This was
continued until the pH value of the washing effluent reached approximately 7. The wet samples were filtered, then dried at 105°C overnight.

Sugumaran et al., (2012) have produced AC from banana empty fruit bunch (BEFB) and Delonix regia fruit pod (DRFP) through single step chemical activation process. As both the lignocellulosic wastes showed maximum weight loss at temperatures lower than 500°C, they were carbonized at 450°C (BEFP) and 400°C (DRFP) respectively after impregnating with H₃PO₄ and KOH. Highest yield of 41.09% was recorded in DRFP treated with H₃PO₄ followed by other treatments. The KOH treated DRFP recorded maximum bulk density of 0.46 g/ml followed by H₃PO₄ treated DRFP.

2.3. Preparation of Activated Carbon using Different Waste Materials

The preparation of AC from waste materials has several advantages, mainly of economic and environmental nature. A wide variety of AC has been prepared from different waste materials; conventional wastes (from agriculture and wood industry) as well as non-conventional wastes (from municipal and industrial activities) have been used. The preparation of AC from these waste materials was studied by different researchers, were reviewed by Joana M. Dias (2008). That review will be helpful to know the wastes used for the production of AC, process involved in the production, uses and advantages of prepared AC and thus it was presented below.

2.3.1. Conventional Wastes (from agriculture and wood industry)

Due to their abundance, agricultural wastes have low economic value; additionally, their current deposition creates significant environmental degradation.
Agricultural waste is a rich source for AC production due to its low ash content and reasonable hardness (Ahmedna et al., 2000); therefore, conversion of agricultural wastes into AC is a promising alternative to solve environmental problems and also to reduce the costs of AC preparation. There are currently a large number of studies regarding the use of several agricultural wastes to produce AC. Most of them focus on the use of waste materials of considerable rigidity, such as the shells and/or stones of fruits like nuts, peanuts, olives, dates, almonds, apricots and cherries; however, wastes resulting from the production of cereals such as rice, coffee, soybean, maize and corn as well as olive cakes, sugar cane and sugar beat bagasse, coirpith, oil-palm shell (from oil-palm processing mills) and various seed wastes were already used. The preparation of AC from these materials has been made using both PhA and ChA. In a study by Ioannidou and Zabaniotou (2007) an extensive revision regarding AC preparation from agricultural residues is made and the effects of different parameters regarding activation procedures are presented. The structure of the raw material tends to strongly influence the best parameters needed to obtain a specific AC. It is possible to obtain AC with different pore texture by varying the activation conditions, therefore optimizing their production for a specific purpose. High surface areas might be obtained, with values over 2500m2 g⁻¹. Among the revised studies, ChA was the most studied method, namely by using H3PO4, KOH, and ZnCl as activating agents. From the revision made considering recent studies on the preparation of AC from agricultural wastes, some relevant issues were summarized and are presented in Table 2.1.
Table 2.1.

Preparation of ACs using agricultural wastes as raw material

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Activation Agent</th>
<th>Relevant Issues</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Vineyard shoot</td>
<td>H$_3$PO$_4$</td>
<td>Well-developed pore structure. In general, AC were better when raw material was impregnated and heated at intermediate temperatures.</td>
<td>Corcho-Corral et al., (2006)</td>
</tr>
<tr>
<td>Cassavapeel</td>
<td>KOH</td>
<td>Activation time showed no significant effect on the porestructure Maximum surface area and pore volume were obtained using: impregnation ratio of 5:2 and carbonization temperature of 750°C.</td>
<td>Sudaryanto et al., (2006)</td>
</tr>
<tr>
<td>Olive pit</td>
<td>KOH</td>
<td>PAC adsorption capacity was the highest at 75% (w/w) KOH.</td>
<td>Martinez et al., (2006)</td>
</tr>
<tr>
<td>Olive cake</td>
<td>Steam</td>
<td>The best AC was obtained activating for 68 min at 1095 K.</td>
<td>Baccouzi et al., (2001)</td>
</tr>
<tr>
<td>Date pit</td>
<td>H$_3$PO$_4$</td>
<td>Iodine number increased with increasing activation temperature. Impregnation ratio increase caused an oscillation in the iodine number. Iodine number varied in average 7-10% for all particle sizes used.</td>
<td>Haimour and Emeish, (2006)</td>
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<tr>
<td></td>
<td>ZnCl$_2$</td>
<td>Raw material showed potential to prepare AC also used as catalytic supports. AC modifications must be performed when procedure and starting material is well known.</td>
<td>Boucherif-Sab et al., (2005)</td>
</tr>
<tr>
<td></td>
<td>H$_3$PO$_4$</td>
<td>Porosity and cellular structure of raw material influenced acid concentrations and/or temperatures. Best AC were obtained using 50 and 60% (w/w) H$_3$PO$_4$. Excess acid reduced raw materials activation. The important effect H$_3$PO$_4$ in porosity generation was demonstrated.</td>
<td>Girgis and El-Hendawy, (2002)</td>
</tr>
<tr>
<td>Walnut shell</td>
<td>KOH</td>
<td>Macroporous texture with more homogeneous pore size distribution than the ones prepared from olive pits.</td>
<td>Martinez et al., (2006)</td>
</tr>
<tr>
<td></td>
<td>CO$_2$</td>
<td>The best activation was at 800°C, 2.5h, and CO$_2$ flow rate of 100 cm$^3$ min$^{-1}$. Surface area: 1064.2m$^2$g$^{-1}$.</td>
<td>Yang and Lua, (2003a)</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td>High-surface area (2259.4m$^2$g$^{-1}$) and pore volume (1.10 cm$^3$ g$^{-1}$) where obtained using the following activation conditions:  0.5% (w/w) KOH, 3h at 8001°C.</td>
<td>Yang and Lua, (2003b)</td>
</tr>
<tr>
<td>Walnut shell</td>
<td>H$_3$PO$_4$,  ZnCl$_2$</td>
<td>Most important activation parameters: impregnation ratio and carbonization temperature. High surface area were obtained.</td>
<td>Ahmadpour and Do, (1997)</td>
</tr>
<tr>
<td>Coffee bean husk</td>
<td>H$_3$PO$_4$</td>
<td>Characteristics could be easily controlled by varying H$_3$PO$_4$ impregnation ratio. High impregnation ratios yielded essentially mesoporous carbons with high surface areas and pore volumes</td>
<td>Baquero et al., (2003)</td>
</tr>
</tbody>
</table>
AC prepared from different agricultural wastes have been used for several treatment purposes. There is a considerable amount of studies regarding the use of these materials, (many of them considering ChA) to remove contaminants from aqueous phase, namely different types of dyes, herbicides, heavy metals and volatile organic compounds (VOC). Kadirvelu et al., (2003) showed that AC prepared from agricultural solid wastes removed very significant amounts of different types of dyes, Hg (II) and Ni (II), in shorter time and with better adsorption rates and removal capacities than when applying other methods. Most of the revised studies show that these materials can compete with the commercial AC, and some of them have even better behaviour than the commercial ones. Some relevant issues concerning different recent studies on the application of these materials in aqueous phase were summarized and are presented in Table 2.2.
Due to their particular porous characteristics, woody materials are very relevant and challenging raw materials to prepare AC, namely for the adsorption of solutes in the liquid phase (Wu and Tseng, 2006). The wood industry is responsible to produce great amounts of woody waste materials that might be recycled to produce AC. Also, several forest residues can be used, additionally
contributing to a better forest management and conservation. Many studies were made concerning the recycling of these materials for the production of AC. Woody materials of different types such as cedar, fir, oak, as well as from tropical trees have already been used. Activation by using either PhA or ChA has been recently studied, namely the use of PhA preceded by chemical treatment using for instance H2O2 or H2SO4 as chemical agents. The use of such pre-treatments mainly influences the surface chemistry of the AC, and lead to the preparation of enhanced adsorbents. Also, compression treatment of sapwood followed by carbonization was studied as a possible way of producing AC, essentially microporous (Abe et al., 2001). It was concluded that preparation procedures using woody materials should be carefully optimized to produce AC with very good porous texture and that can also be used as catalyst supports.

2.3.2. Non-conventional wastes (from municipal and industrial activities)

The economical activities in the modern society gradually created a pattern of mass production, mass consumption as well as mass deposition (Gao et al., 2005). As a consequence, there is an accumulation of several industrial and post-consumer waste products, which by their nature are difficult or poorly effective to be regenerated into other materials and that more currently end up in incineration plants or landfills. Due to the more restricted environmental standards, limitations on the application of such alternatives are remarkably increasing. The discharge of plastic wastes, such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC), industrial wastes, such as oil combustion residues and fabrics, as well as the discharge of tires, sewage sludges, and fertilizers, represents a serious
challenge for waste management strategies. It is therefore of main relevance to find alternatives by which such materials can be reused or recycled according to environmentally acceptable procedures (Hayashi et al., 2005). The use of such non-conventional wastes as carbon source for the production of AC might be an efficient alternative for both, adoption of effective waste management practices, and production of low-cost AC. A revision of the literature showed that there are a considerable amount of studies dedicated to the valorization of such wastes, namely for the production of AC. Plastic wastes, various industrial wastes like fly ashes, pitch, and polymeric residues from factories as well as other wastes such as tires and sewage sludge have been used as raw material for AC production. For instances, a waste commercial ion-exchange resin might be used to prepare AC with values of specific surface area and pore volume suggesting its application in different purposes, that might include aqueous-phase treatments (Gunko et al., 2005). Also, AC can be successfully prepared from both old newspaper and paper prepared from simulated paper sludge by PhA and ChA (Okada et al., 2003a, b). A great amount of the revised studies focus on the use of physical treatment, sometimes preceded by a chemical treatment; however, ChA was also made, and AC with high specific surface areas could also be obtained. Due to the nature of most of the raw materials, such as plastics and polymeric materials, ACF are the physical form of AC more commonly prepared. Naturally, studies show that raw materials with higher carbon content lead to the achievement of a better AC. Generally, AC show good texture and potential to compete with commercial ones. From the revision made considering recent studies on the preparation of AC from
such non-conventional wastes, some relevant issues were summarized and are presented in Table 2.3.

**Table 2.3.**

Preparation of AC using non conventional wastes as raw material

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Activation Agent</th>
<th>Relevant issues</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PLASTICS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td>Steam (H₂SO₄, PT)</td>
<td>Combined treatment might replace physical activation AC were mainly micro and mesoporous with surface areas up to 1030 m² g⁻¹. Nitrogen-enriched absorbents could be obtained by carbonization of PET waste and N-compounds.</td>
<td>Sych et al., (2006)</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td></td>
<td>Arenillas et al., (2005)</td>
</tr>
<tr>
<td>PVC</td>
<td>Steam</td>
<td>PVC based ACF were mainly composed of micropores with surface areas between 1000 and 2000 m² g⁻¹.</td>
<td>Qiao et al., (2004)</td>
</tr>
<tr>
<td><strong>INDUSTRIAL WASTES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer</td>
<td>K₂CO₃</td>
<td>High specific surface areas (2800 m² g⁻¹) were obtained mainly due to the activating agent action. Optimal conditions were: Carbonization temperature of 773 K, impregnation ratio of 1.0.</td>
<td>Hayashi et al., (2005)</td>
</tr>
<tr>
<td>Fly ash</td>
<td>CO₂</td>
<td>AC showed low surface area. The mesoporous texture suggests their possible use in adsorption of large molecules.</td>
<td>Caramusco et al., (2003)</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>AC with high surface area, high content of oxygen, and surface sites with prevalent basic characteristics were obtained.</td>
<td>Davini (2003)</td>
</tr>
<tr>
<td>Acrylic fabric</td>
<td>Steam</td>
<td>Activation at 900°C for 5 min significantly increased surface area (to 240 m² g⁻¹) and total pore volume (1.15 cm³ g⁻¹). ACF performance was superior to those of conventional carbons.</td>
<td>You et al., (2000)</td>
</tr>
<tr>
<td>waste</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pitch</td>
<td>Steam (addition of ferrocene)</td>
<td>Pitch-based spherical AC with high mesopore texture was obtained. Catalytic activation reaction took place at the vicinity of iron particles.</td>
<td>Liu et al., (1999)</td>
</tr>
<tr>
<td><strong>OTHERS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tire</td>
<td>Steam, CO₂</td>
<td>AC with a surface area of 1150 m² g⁻¹ and pore volume of 0.43 cm³ g⁻¹ was obtained.</td>
<td>Ismadji et al., (2005)</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>ZnCl₂</td>
<td>Surface areas were comparable with those of commercial carbons.</td>
<td>Zabanistiotou and Stavropoulos, (2003)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AC presented remarkable micropore and mesopore surface area and distinct physical and chemical properties from commercial carbons.</td>
<td>Chen et al., (2002)</td>
</tr>
<tr>
<td></td>
<td>ZnCl₂</td>
<td>The anaerobically undigested sludge had higher carbon content and lower ash content than the digested one, therefore yielding a better C.</td>
<td>Tay et al., (2001)</td>
</tr>
</tbody>
</table>


Review of literature
2.4. Activated carbon preparation using different peels:

Fayza S.Hashem et al., (2016) have collected fresh Pomegranate, kiwi, mandarin and banana peels from local store/area and used for the AC preparation. The collected peels were first washed by distilled water, and then dried in sun light for 7 days then in oven at 100° C for 24 hrs. After drying, the peels were crushed and sieved to 125 mm sieve. The AC was prepared by chemical activation. This was done by boiling 40 g of the fruit peel powder with 120 mL of concentrated H$_3$PO$_4$ (1:3 weight ratios) for 6 h in an air condenser system. After cooling, the final products were filtrated and washed several times with NaHCO$_3$ solution and distilled water till neutral pH was reached. After that, the resultant AC was dried at 110° C for 24 h.

Ilaboya et al., (2013) have carried out the study for preparing AC, in that study, Peels of cassava were thoroughly washed with distilled water, dried and pulverized. A predetermined weight of the pulverized sample was placed in a muffle furnace which allows limited supply of air at a temperature of 350°C for 30 - 60 minutes. The carbonized samples were then activated using the method 25g of the charred sample was soaked in 250 ml of 5.5M ZnCl solution. The mixture was thoroughly mixed until it formed a paste. The paste was then transferred to an evaporating dish which was placed in a furnace and heated at 200°C for 30 minutes. This was allowed to cool and washed with distilled water to remove the residual salt, oven dried at 105°C for one hour, grind using mortar and pestle.
Olayiwola (2013) has prepared AC from waste cassava (*Manihot esculenta* Crantz) peels. In the process the waste cassava peels were collected; cassava peels were then inspected, washed and sundried to a moisture content of between 8-10% wet basis. The dried cassava peels were then carbonized using a muffle furnace at a temperature of 420°C for a period of 90 minutes. Then the cassava peel carbon (CPC) was allowed to cool overnight under inert conditions thereby yielding the base carbon material for activation.

Arenst Andreas Arie *et al.*, (2016) have studied the preparation of AC. In that study, the carbonaceous precursor selected was salacca peel. The peels were crushed and sieved to particle sizes of 2.0-2.8 mm. The powders were initially subjected to the pre-carbonization process at temperature of 500 °C for 1 h. After this process, the salacca peel powders were impregnated with solution of KOH with different mass concentration (10 %, 15 % and 20 %-w) by varying impregnation ratios (weight of KOH to weight of salacca peel) from 1:1, 2:1 and 4:1. The salacca peel powders were impregnated for 20 hours. The slurries were then heated at 80 °C for 24 hours to dryness. Next, samples were pyrolyzed under $N_2$ flow at 800 °C for 1 hour. Prepared ACs was washed with 0.1 M HCl and then with distilled water until the pH of the washing water was neutral.

Akpor *et al.*, (2013) have investigated into the preparation of AC. In that the plantain peels were cleaned in deionised water to remove sand and other debris. The cleaned peels were oven-dried at 50°C for 5 days, after which they were pulverized into fine powder using a sterilized food mill. The pulverized powder was stored in air-tight plastic containers at room temperature until use or further
treatment. The raw pulverized peel, which did not undergo any form of further treatment after drying, a raw pulverized peels which were treated with 20 % sulphuric acid, carbonated peels that was not subjected to any form of treatment, and carbonated peels that were treated with 20 % sulphuric acid. For carbonation, approximately 250 g of the pulverized peel was placed in a crucible and placed in an oven at a temperature of 300°C for 1 hour.

Shamala Devi et al., (2010) have conducted the study with mangosteen peel. In the study, researchers were soaked 10g of dried mangosteen peel with 100ml of acid with different concentration. Then, impregnated material was dried in oven for 12 hours at 100 °C. After that, the dried material were activated by using nitrogen gas which was provided for the whole of activation process with heating rate 5°C/min and flow rate of 150cc/min. After activation, samples were cooled down to room temperature in order to obtain AC. The obtained AC was thoroughly washed with distilled water until the wash liquor pH reading is at 6–7. On the average, 7–8 washings were able to neutralize the sample. The AC will be washed with 0.1 M sodium hydroxide solution and finally with distilled water. Then the samples were dried in oven for 24 hours at 70°C and store in dessicator.

Mahakalkar et al., (2014) were weighed the carbonized waste coconut shell, Orange peel, Saw dust, and Calotropis leaves separately and poured in different beakers containing known quantity of dilute hydrochloric acid, Nitric acid and Sulphuric acid ( HCL, HNO₃ and H₂SO₄). The content of the beakers was thoroughly mixed until a paste of each was formed. The pastes of the samples were then transferred to crucibles and the crucibles were placed in a Muffle furnace and
were heated at 500°C for two hours. The activated samples were then cooled at room temperature, washed with distilled water to a pH of 6-7, and dried in an oven at 105°C for three hours. Finally the AC carbon was obtained.

Hazzaa and Hussien, (2015) have collected banana peels from a local market, washed thoroughly with distilled water to remove surface dirt and adhering impurities, cut into small pieces, crushed, and sieved in a mesh size 150 μm size by standard sieves (Model Φ200) . The banana peels dried in an air oven at 105°C for 2 hours until a constant weight was reached. The dried banana peels was then divided into two portions. The first portion of dried banana peels was used as adsorbent termed BP, while the second portion was thermally activated by carbonization in a muffle furnace for an hour at 900°C in the absence of air by placing the sample in a well-sealed stainless steel tube and termed as Banana peel AC.

Pradeep singh et al., (2013) have prepared Guava peels AC (GPAC) from Guava peels unactivated carbon (GUPC). GUPC powder was soaked in KOH (0.1N) solution during 10 minutes with an impregnation ratio (GUPC: KOH) of 1: 1.5 to obtain thick syrupy solution. The solution was placed in microwave oven with an input powder of 600 W and 6 minutes of irradiation time. The activated samples were treated with 0.5 N HCL to remove any remaining KOH and then filtered and dried at 800°C for 3 hours. Finally GPAC was obtained.

Prahas et al., (2008) have used using phosphoric acid and chemical activation method to prepare the AC from jackfruit peel. 20 grams of jackfruit peel
was impregnated by weighing and mixing certain amount of 85 wt % phosphoric acid with occasional stirring. The amount of phosphoric acid solution used was adjusted to give a certain impregnation ratio (weight of activating agent/weight of raw material) of 4:1. The resulting slurry was then kept in a desiccator for 24 hours. After 24 hours, the slurry was then ready to have two-stage activation process with semicarbonisation as first stage. In the first stage, the slurry was put in a horizontal tubular reactor and kept in a muffle furnace to experience semicarbonisation at a temperature 200°C for 30 minutes. After semi-carbonisation, the black and sticky dry powder was heated until certain heat treatment temperature (HTT) was reached. The carbonisation was performed under a nitrogen flow of 100 cm³ min⁻¹ STP for 45 minutes. After activation, the AC product was cooled in a desiccator. The AC product was then repeatedly washed with warm distilled water (70°C) until the pH of the solution close to the initial pH of rinsing water. Finally, the AC was dried in a vacuum oven at 110°C for 24 hours.

Gin et al., (2014) have studied the AC preparation. In that study, watermelon peel gathered were sun-dried for 5-7 days to drastically reduce their moisture contents before they were then crushed with a mortar and pestle into powder form and 15 g of the powdered samples was weighed into six different clean and pre-weighed crucibles, which were then introduced into the hot zone of a muffle furnace. The peels were carbon-ized at different temperatures (250, 300, 350 and 400°C). The samples were held at each of the temperatures for various times (15, 30, 45 and 60 min) in order to establish the optimum conditions for the
process. The content was then removed from the muffle furnace after the set period and cooled in an open air for one hour. The process was repeated until a substantial amount of AC sample was obtained.

Prachpreecha et al., (2016) have identified the effective process for the preparation of AC from peel and bunch of banana. In which the peel and bunch of banana wastes were cut into small pieces (1-2 cm), collected, dried, crushed and washed thoroughly tree times with deionized water to remove the adhering dirt. They then were air dried in an oven at 100–120 °C for 24 hours and then bring the peel and bunch of banana had dried in a ceramic packaging for burned in carbolite until the desired temperature (300, 400, 500 600 and 700°C) by increasing the temperature at a rate of 5°C/ minutes to the desired temperature at the freezing temperature about 1 hour. After cooling the resulted charcoal burnt carbonized at different temperature was tested iodine number. The selected charcoal of highest iodine number as tested by standard method ASTM D 4607-94 was ground and sieved to be use in the study (at 500 °C carbonization temperature was chosen for this study because iodine number were highest). After that the charcoal was carbonized with phosphoric acid (50 % H₃PO₄) and then was burnt to charcoal to be used as a raw material in the synthesis of AC. The charcoal was activated in the carbolite to 600, 700, 800 and 900°C by increase the temperature at a rate of 10°C/minutes. When the desired temperature is reached soaked at this temperature for about 2 hours and then left to cool down for 30 minutes at 200°C. The products were washed thoroughly with hydrochloric acid (5% HCl), followed by hot water many times until pH 6.5-7.0. The ACs from both produces were kept dried at a
temperature of 120°C and selected ACs of highest iodine number as tested by standard method ASTM D 4607-94 was etherification in order to study the adsorption efficiency after modification (at 800 °C carbonization temperature, the iodine number highest of ACs from both produces).

Mohammad et al., (2015) were first washed the waste peels of Banana fruits with double distilled water and dried in an oven at 80°C overnight. The dried adsorbent was thermally activated at 500°C in a muffle furnace for 1h in the presence of air. After activation, the ash contents were removed by washing with distilled water and dried in an oven at 110°C overnight in order to obtain banana peel AC.

2.5. Activated carbon using different citrus fruit peels:

Niraj and Pratik, (2015) have investigated orange peel AC and found that the orange (specifically, the sweet orange) is the fruit of the citrus species Citrus sinensis in the family rutaceae. Citrus sinensis (orange) fruit is one of the common traditional plants grown in many areas in India. The wastes of the Citrus sinensis (orange) fruit called orange peels were used to prepare AC through chemical activation method. Thus prepared AC will be an excellent adsorbent.

Dutta et al., (2011) have prepared a low-cost adsorbent by carbonizing citrus fruit peel with o-phosphoric acid and explored the possibility of this adsorbent for removal of methylene blue. Operating parameters for carbonization of citrus fruit peel viz., weight ratio of citrus fruit peel to activating agent, temperature and time have been optimized by statistical tool Response Surface
Methodology (RSM) considering decolorizing power of prepared sample as response. Maximum 99.08 % removal was achieved during kinetic study in a batch contactor In search of a low-cost and eco-friendly adsorbent.

Foo and Hameed, (2011) have carried out a study with pomelo skin obtained from fruit juice processing plants, to prepare AC via microwave-induced NaOH activation. The adsorptive property was tested using methylene blue and acid blue 15 dyes, where the monolayer adsorption capacity was observed to be 501.10 and 444.45 mg/g, respectively. The findings revealed the potential use of pomelo skin-derived AC for removal of both cationic and anionic dyes.

Ajmal Mohammad et al., (2000) have studied fruit peel of orange AC for removal and recovery of Ni (II) from electroplating waste water. He also studied the ability of fruit peel of orange to remove Zn, Ni, Cu, Pb and Cr from aqueous solution. The absorption was in the order Ni (II) > Cu(II) > Pb(II) > Zn(II) > Cr(II). The adsorption follows first order kinetics. The process is endothermic and follows Langumir and Freundlich isotherm. The absorbed Ni (II) can be recovered using 0.05 M HCl solution. However the recovery of Ni (II) by column operation is higher (95.8%) as compared to batch process (76%). The spent absorbent can be regenerated and reused making the absorption process more economical.

Yarbay Sahin et al., (2013) study the use of low cost, locally available and eco-friendly absorbent, tomato plant waste AC.

Zhigang Xie et al., (2014) were cleaned, cut, dried, and then crushed orange peel to study orange peel AC. In which 10 g samples were immersed into
100mL zinc chloride solution. After 36 hours, these samples were centrifuged from the solution and dried. And then, we added proper amount of coal tar and mixed with samples. The samples with partial size of 5-8mm were formed by extrusion. The heating process was under the protection of nitrogen. The flow of nitrogen was 0.2 mL/min. The reaction temperature increased to 150°C with 3°C/min, and the reaction time is 30 min when the temperature reached 150°C. Then, we increased the temperature to 300°C continuously to carbonize for 30min. Solid samples were taken out when the temperature decreased to 20°C and were cleaned by 10% HCl and deionized water successively. The as-prepared citrus peel granular AC was obtained after being dried at 105°C. The AC is as follows: reaction temperature of 550°C; impregnation ratio of 3:1; and reaction time of 1hour.

Kavita Kulkarni and Hadi Hamdi Mahdi, (2014) have selected Orange peel powdered AC as adsorbent for carbon dioxide. In the study, the orange peel were collected, peels were washed thoroughly to remove dirt, dried and powdered. The powder was analyzed for chemical composition, structure and surface area. Original powder used for the capture of carbon dioxide. Carbon was made from the powder with the help of 98% H₂SO₄. The yield of reaction was 66.3% with concentrated H₂SO₄ and orange peel powder to produce carbon.

2.6. Synthesis of Nanomaterial

Materials scientists and engineers have made significant developments in the improvement of methods of synthesis of nanomaterial solids (Pal et al., 2011) (Hasany et al., 2012) (Lue and Juh Tzeng, 2007). Namita Rajput (2015) made a
brief review in the article and listed out various methods of synthesising NPs as below in sections (2.6.1 to 2.6.7). It is classified as bottom-up manufacturing which involves building up of the atom or molecular constituents as against the top method which involves making smaller and smaller structures through etching from the bulk material as exemplified by the semiconductor industry.

2.6.1. Gas Condensation

Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys. In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as a Joule heated refractory crucibles, electron beam evaporation devices, in an atmosphere of 1-50 m bar. In gas evaporation, a high residual gas pressure causes the formation of ultra fine particles (100 nm) by gas phase collision. The ultrafine particles are formed by collision of evaporated atoms with residual gas molecules. Gas pressures greater than 3 mPa (10 torr) are required. Vaporization sources may be resistive heating, high energy electron beams, low energy electron beam and inducting heating. Clusters form in the vicinity of the source by homogenous nucleation in the gas phase grew by incorporation by atoms in the gas phase. It comprises of a ultra high vacuum (UHV) system fitted evaporation source, a cluster collection device of liquid nitrogen filled cold finger scraper assembly and compaction device. During heating, atoms condense in the supersaturation zone close to Joule heating device. The NPs are removed by scraper in the form of a metallic plate. Evaporation is to be done from W, Ta or Mo refractory metal crucibles (Tissue and Yuan, 2003). If the metals react with crucibles, electron beam evaporation technique is to be used.
The method is extremely slow. The method suffers from limitations such as a source-precursor incompatibility, temperature ranges and dissimilar evaporation rates in an alloy. Alternative sources have been developed over the years. For instance, Fe is evaporated into an inert gas atmosphere (He). Through collision with the atoms the evaporated Fe atoms loose kinetic energy and condense in the form of small crystallite crystals, which accumulate as a loose powder. Sputtering or laser evaporation may be used instead of thermal evaporation (Hasany et al., 2012). Sputtering is a non-thermal process in which surface atoms are physically ejected from the surface by momentum transfer from an energetic bombarding species of atomic/molecular size. Typical sputtering uses a glow discharge or ion beam. Interaction events which occur at and near the target surface during the sputtering process in magnetron sputtering has advantage over diode and triode sputtering. In magnetron sputtering, most of the plasma is confined to the near target region. Other alternate energy sources which have been successfully used to produce clusters or ultra fine particles are sputtering electron beam heating and plasma methods. Sputtering has been used in low pressure environment to produce a variety of clusters including Ag, Fe and Si.

2.6.2. Vacuum Deposition and Vaporization

Before proceeding to the other methods, it is important to understand the terms vacuum deposition and vaporization or vacuum evaporation. In vacuum deposition process, elements, alloys or compounds are vaporized and deposited in a vacuum. The vaporization source is the one that vaporizes materials by thermal processes. The process is carried out at pressure of less than 0.1 Pa (1 m Torr) and
in vacuum levels of 10 to 0.1 MPa. The substrate temperature ranges from ambient to 500°C. The saturation or equilibrium vapor pressure of a material is defined as the vapor pressure of the material in equilibrium with the solid or liquid surface. For vacuum deposition, a reasonable deposition rate can be obtained if the vaporization rate is fairly high. A useful deposition rate is obtained at a vapor pressure of 1.3 Pa (0.01 Torr). Vapor phase nucleation can occur in dense vapor cloud by multibody collisions. The atoms are passed through a gas to provide necessary collision and cooling for nucleation. These particles are in the range of 1 to 100 nm and are called ultra fine particles or clusters (Tissue and Yuan, 2003) (Gohil et al., 2007) (Chang et al., 1994). The advantages associated with vacuum deposition process are high deposition rates and economy. However, the deposition of many compounds is difficult. NPs produced from a supersaturated vapor are usually longer than the cluster.

2.6.3. Chemical Vapor Deposition (CVD) and Chemical Vapor Condensation (CVC)

CVD is a well known process in which a solid is deposited on a heated surface via a chemical reaction from the vapor or gas phase. CVC reaction requires activation energy to proceed. This energy can be provided by several methods. In thermal CVD the reaction is activated by a high temperature above 900°C. A typical apparatus comprises of gas supply system, deposition chamber and an exhaust system. In plasma CVD, the reaction is activated by plasma at temperatures between 300 and 700°C. In laser CVD, pyrolysis occurs when laser thermal energy heats an absorbing substrate. In photo-laser CVD, the chemical
reaction is induced by ultra violet radiation which has sufficient photon energy, to break the chemical bond in the reactant molecules. In this process, the reaction is photon activated and deposition occurs at room temperature. Nano composite powders have been prepared by CVD. SiC/Si3N composite powder was prepared using SiH4, CH4, WF6 and H2 as a source of gas at 1400°C. Another process called chemical vapor condensation (CVC) was developed in Germany in 1994. It involves pyrolysis of vapors of metal organic precursors in a reduced pressure atmosphere. Particles of ZrO2, Y2O3 and nanowhiskers have been produced by CVC method [5-8]. A metalorganic precursor is introduced in the hot zone of the reactor using mass flow controller. For instance, hexamethyldisilazane (CH3)3 Si NHSi (CH3)3 was used to produce SiCxNyOz powder by CVC technique. The reactor allows synthesis of mixtures of NPs of two phases or doped NPs by supplying two precursors at the front end of reactor and coated NPs, n-ZrO2, coated with n-Al2O3 by supplying a second precursor in a second stage of reactor. The process yields quantities in excess of 20 g/hr. The yield can be further improved by enlarging the diameter of hot wall reactor and mass of fluid through the reactor. Typical nanocrystalline materials which have been synthesized are shown in Table 2.4.
Table 2.4.

Typical nanocrystalline materials synthesized by the CVC method

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Product Powder</th>
<th>Phase as prepared</th>
<th>Average Particle size (nm)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3)_3\text{SiNHSi(CH}_3)_3)</td>
<td>SiC,\text{NyOz}</td>
<td>Amorphous</td>
<td>4</td>
<td>377</td>
</tr>
<tr>
<td>Si(CH3)4</td>
<td>SiC</td>
<td>β-phase</td>
<td>9</td>
<td>201</td>
</tr>
<tr>
<td>\text{Al}[\text{2-OC4H9}]\text{3}</td>
<td>\text{Al}_2\text{O}_3</td>
<td>Amorphous</td>
<td>3.5</td>
<td>449</td>
</tr>
<tr>
<td>\text{Ti}[\text{I-OC3H7}]\text{4}</td>
<td>TiO2</td>
<td>Anatase</td>
<td>8</td>
<td>193</td>
</tr>
<tr>
<td>\text{Si}[\text{OC2H5}]\text{4}</td>
<td>SiO2</td>
<td>Amorphous</td>
<td>6</td>
<td>432</td>
</tr>
<tr>
<td>\text{Zr}[\text{3-OC4H9}]\text{4}</td>
<td>ZrO2</td>
<td>Monoclinic</td>
<td>7</td>
<td>134</td>
</tr>
</tbody>
</table>

Source: Namita Rajput, Methods of Preparation of Nanoparticles – A Review, Journal of Advances in Engineering & Technology, 2015, 1806-1811

2.6.4. Mechanical Attrition

Unlike many of the methods mentioned above, mechanical attrition produced its nanostructures not by cluster assembly but by the structural decomposition of coarser grained structures as a result of plastic deformation. Elemental powders of Al and β-SiC were prepared in a high energy ball mill. More recently, ceramic/ceramic nanocomposite WC-14% MgO material has been fabricated. The ball milling and rod milling techniques belong to the mechanical alloying process which has received much attention as a powerful tool for the fabrication of several advanced materials. Mechanical alloying is a unique process, which can be carried out at room temperature. The process can be performed on both high energy mills, centrifugal type mill and vibratory type mill, and low...
energy tumbling mill (Konrad et al., 2001) (Rostislav and Andrievskii, 1994) (Sharma et al., 2009).

High energy mills include:

- Attrition Ball Mill
- Planetary Ball Mill
- Vibrating Ball Mill
- Low Energy Tumbling Mill
- High Energy Ball Mill

2.6.4.1 Attrition Ball Mill

The milling procedure took place by a stirring action of a agitator which has a vertical rotator central shaft with horizontal arms (impellers). The rotation speed was later increased to 500 rpm. Also, the milling temperature was in greater control.

2.6.4.2 Planetary Ball Mill

Centrifugal forces are caused by rotation of the supporting disc and autonomous turning of the vial. The milling media and charge powder alternatively roll on the inner wall of the vial and are thrown off across the bowl at high speed (360 rpm).
2.6.4.3 Vibrating Ball Mill

It is used mainly for production of amorphous alloys. The changes of powder and milling tools are agitated in the perpendicular direction at very high speed (1200 rpm).

2.6.4.4 Low Energy Tumbling Mill

They have been used for successful preparation of mechanically alloyed powder. They are simple to operate with low operation costs. A laboratory scale rod mill was used to prepare homogenous amorphous Al30Ta70 powder by using S.S. cylinder rods. Single-phase amorphous powder of AlxTm100-x with low iron concentration can be formed by this technique.

2.6.4.5 High Energy Ball Mill

High-energy ball milling is an already established technology, however, it has been considered dirty because of contamination problems with iron. However, the use of tungsten carbide component and inert atmosphere and /or high vacuum processes has reduced impurity levels to within acceptable limits. Common drawbacks include low surface, highly poly disperse size distribution, and partially amorphous state of the powder. These powders are highly reactive with oxygen, hydrogen and nitrogen. Mechanical alloying leads to the fabrication of alloys, which cannot be produced by conventional techniques. It would not be possible to produce an alloy of Al-Ta, because of the difference in melting points of Al (933 K) and Ta (3293 K) by any conventional process. However, it can be fabricated by mechanical alloying using ball milling process.
2.6.5. Chemical Precipitation

In this strategy the size is control by arrested precipitation technique. The basic trick has been to synthesis and studies the nanomaterial in situ i.e. in the same liquid medium avoiding the physical changes and aggregation of tiny crystallites. Thermal coagulation and Oswald ripening were controlled by double layer repulsion of crystallites using non-aqueous solvents at lower temperatures for synthesis. The synthesis involved reaction between constituent materials in suitable solvent. The dopent is added to the parent solution before precipitation reaction. Surfactant is used to maintain separation between the particles formed. Thus formed nanocrystal are separated by centrifugation, washed and vacuum dried. The dried material was further subjected to UV curing for possible polymerization of surfactant capping film on the surface of nano cluster for imparting true quantum confinement (Konrad et al., 2001) (Rostislav and Andrievskii, 1994) (Sharma et al., 2009).

2.6.6 Sol-Gel Techniques

In addition to techniques mentioned above, the sol-gel processing techniques have also been extensively used. Colloidal particles are much larger than normal molecules or NPs. However, upon mixing with a liquid colloids appear bulky whereas the nanosized molecules always look clear. It involves the evolution of networks through the formation of colloidal suspension (sol) and gelatin to form a network in continuous liquid phase (gel). The precursor for synthesizing these colloids consists of ions of metal alkoxides and aloxysilanes. The most widely used are tetramethoxysilane (TMOS), and tetraethoxysilanes.
(TEOS) which form silica gels. Alkoxides are immiscible in water. They are organo metallic precursors for silica, aluminum, titanium, zirconium and many others. Mutual solvent alcohol is used. The sol gel process involves initially a homogeneous solution of one or more selected alkoxides. These are organic precursors for silica, alumina, titania, zirconia, among others (Bhargava et al., 1994) (Yu et al., 2001) (Lu and Jagannathan, 2002) (Morita et al., 2004). A catalyst is used to start reaction and control pH. Sol-gel formation occurs in four stages.

1) Hydrolysis
2) Condensation
3) Growth of particles
4) Agglomeration of particles

2.6.6.1 Hydrolysis

During hydrolysis, addition of water results in the replacement of [OR] group with [OH-] group. Hydrolysis occurs by attack of oxygen on silicon atoms in silica gel. Hydrolysis can be accelerated by adding a catalyst such as HCl and NH₃. Hydrolysis continues until all alkoxy groups are replaced by hydroxyl groups. Subsequent condensation involving silanol group (Si-OH) produced siloxane bonds (Si-O-Si) and alcohol and water. Hydrolysis occurred by attack of oxygen contained in the water on the silicon atom.
2.6.6.2 Condensation

Polymerization to form siloxane bond occurred by either a water producing or alcohol producing condensation reaction. The end result of condensation products is the formation of monomer, dimer, cyclic tetramer, and high order rings. The rate of hydrolysis is affected by pH, reagent concentration and H₂O/Si molar ratio (in case of silica gels). Also ageing and drying are important. By control of these factors, it is possible to vary the structure and properties of sol-gel derived inorganic networks.

2.6.6.3 Growth and Agglomeration

As the number of siloxane bonds increase, the molecules aggregate in the solution, where they form a network, a gel is formed upon drying. The water and alcohol are driven off and the network shrinks. At values of pH of greater then 7, and H₂O/Si value ranging from 7 to 5. Spherical nano-particles are formed. Polymerization to form siloxane bonds by either an alcohol producing or water producing

\[ 2 \text{HOSi (OR)₃} \rightarrow (\text{OR})₃ \text{Si O Si (OR)₃} + \text{H₂O} \]

or

\[ 2 \text{HOSi (OR)₃} \rightarrow (\text{OR})₂\text{OH Si O Si (OR)₃} + \text{H₂O} \]
Above pH of 7, Silica is more soluble and silica particles grow in size. Growth stops when the difference in solubility between the smallest and largest particles becomes indistinguishable. Larger particles are formed at higher temperatures. Zirconium and Yttrium gels can be similarly produced.

Despite improvements in both chemical and physical methods of synthesis, there remain some problems and limitations. Laser vaporization technique has offered several advantages over other heating techniques. A high energy pulsed laser with an intensity flux of 106 - 107 W/cm² is forced on target material. The plasma causes high vaporization and high temperature (10,000°C). Typical yields are 1014-1015 atoms from the surface area of 0.01 cm² in a 10-8 s pulse. Thus a high density of vapor is produced in a very short time (10-8 s), which is useful for direct deposition of particles.

2.6.7 Electro deposition

Nanostructured materials can also be produced by electrodeposition. These films are mechanically strong, uniform and strong. Substantial progress has been made in nanostructured coatings applied either by DVD or CVD. Many other non-conventional processes such as hypersonic plasma particle deposition (HPPD) have been used to synthesize and deposit NPs. The significant potential of nanomaterial synthesis and their applications is virtually unexplored. They offer numerous challenges to overcome. Understanding more of synthesis would help in designing better materials. It has been shown that certain properties of nanostructured deposits such as hardness, wear resistance and electrical resistivity are strongly
affected by grain size. A combination of increased hardness and wear resistance resulted in a superior coating performance. (Dikusar et al., 2009) (Silkin et al., 2010).

2.7. Antibacterial activity of various metal nanoparticles

In this part, the focus on the role of various metallic NPs as potential antimicrobials and the possible mechanism of their inhibitory actions was studied by different researchers, were reviewed by Ravishankar Rai and Jamuna Bai, (2011) were presented below. This review focused on the properties of different types of metallic NPs such as copper, aluminium, gold, silver, magnesium, zinc and titanium NPs will be helpful to provide a detailed idea about the same and thus it was presented below.

2.7.1 Silver nanoparticles

Silver compounds had been used to treat burns, wounds and infections [12] (Dunn et al., 2004). Various salts of silver and their derivatives were used as antimicrobial agents (Russell et al., 1994) (Ip et al., 2006). Recent studies have reported that nanosized silver particles exhibit antimicrobial properties (Petica et al., 2008) (Rai et al., 2009). NPs of silver have been studied as a medium for antibiotic delivery, and to synthesize composites for use as disinfecting filters and coating materials (Kim et al., 2007) (Li et al., 2005) (Ruparelia et al., 2006). Several mechanisms have been proposed to explain the inhibitory effect of silver NPs on bacteria. It is assumed that the high affinity of silver towards sulfur and phosphorus is the key element of the antimicrobial effect. Due to the abundance of

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sulfur-containing proteins on the bacterial cell membrane, silver NPs can react with sulfur-containing amino acids inside or outside the cell membrane, which in turn affects bacterial cell viability. It was also suggested that silver ions (particularly Ag+) released from silver NPs can interact with phosphorus moieties in DNA, resulting in inactivation of DNA replication, or can react with sulfur-containing proteins, leading to the inhibition of enzyme functions (Gupta et al., 1998) (Matsumura et al., 2003). The general understanding is that Ag NP of typically less than 20 nm diameters get attached to sulfur-containing proteins of bacterial cell membranes leading to greater permeability of the membrane, which causes the death of the bacteria (Morones et al., 2005). The dose dependent effect of silver NPs (in the size range of 10-15 nm) on the Gram-negative and Gram-positive microorganisms has been studied (Shrivastava et al., 2007). At micromolar levels of Ag+ ions have been reported to uncouple respiratory electron transport from oxidative phosphorylation, inhibit respiratory chain enzymes, or interfere with the membrane permeability to protons and phosphate (Bragg et al., 1974) (Schreurs et al., 1982) (Bard et al., 2005). In addition, higher concentrations of Ag+ ions have been shown to interact with cytoplasmic components and nucleic acids (Semeykina et al., 1990) (Dibrov et al., 2002). The effect of silver NPs on the cell morphology of Escherichia coli and Staphylococcus aureus has been studied using TEM, SEM and X-ray microanalyses (Feng et al., 2000) (Jung et al., 2008)]. It was revealed that treatment with the silver ions results in similar morphological changes in both the Gram positive and Gram negative bacteria. The cytoplasmic membrane detaches from cell walls and an electron-light region
containing condensed deoxyribonucleic acid molecules appears in the centre of the cell. The inhibitory activity of silver ions is higher in case of Gram negative bacteria. This might be due to the thickness of the peptidoglycan layer in Gram-positive bacteria cell wall which may prevent to some extent, the action of the silver ions (Feng et al., 2000). The formation of electron-dense granules containing silver ions and sulphur ions in the cytoplasm of the bacterial cell suggests that the possible mechanism of action of silver NPs may be due to the interaction of silver ions with nucleic acids and impairment of DNA replication which results in loss of cell viability and eventually resulting in cell death (Gogoi et al., 2006). The bactericidal effect of silver NPs typically ranging from 2 to 5 nm has been investigated using green fluorescent protein (GFP)-expressing recombinant *Escherichia coli* (Alexander et al., 2008). Apart from the conventional viability tests, the morphological changes of the fluorescent bacteria and electrophoretic analysis of cellular DNA and protein migration profiles were performed to establish the effect of silver NPs on GFP bacteria. The silver NPs of less than 10 nm diameters attached to the bacterial cell wall causes perforation of the cell wall, which leads to the cell death. This study suggests that the mode of action of silver NPs is that the NPs get attached to the sulfur-containing proteins on the bacterial cell wall, leading to increased permeability of the membrane, finally causing cell death (Alexander et al., 2008). There are also studies reporting that metal ions induce generation of intracellular reactive oxygen species in bacterial cells (Stohs and Bagchi, 1995). Ag ions released by active surfaces of silver NPs and silver oxide present on the surfaces of these NPs are reported to be the actual biocidal
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agents (Sondi and Salopek-Sondi, 2004). The silver ions enter the bacterial cells, where they are reduced as the cell attempts to remove them from the cell interior, eventually leading to cell destruction (Morones et al., 2005). It has been recently demonstrated that silver NPs of less than 10 nm diameter make pores on the bacterial cell walls. The cytoplasmic content is released to the medium, which leads to cell death without affecting the intracellular and extracellular proteins and nucleic acids of the bacterium (Sondi and Salopek-Sondi, 2004). It has been demonstrated that composites of silver NPs with polymer results in the improvement of antimicrobial activities of silver NPs at lower concentrations (Aymonier et al., 2002) (Melaiye et al., 2005) (Kumar et al., 2005). Among the polymers chitosan, a cationic polysaccharide composing randomly distributed (1,4)-linked 2-amino-2-deoxy-β-D-glucose units has been reported to be used as such or in the form of composite with silver NPs with high antimicrobial efficacies. It is generally accepted that polycationic chitosan can bind with negatively charged cell membranes, which will then lead to decrease in the osmotic stability of the cell, followed by subsequent leakage of intracellular constituents. The chitosan silver NPs have enhanced antimicrobial activity than its individual components i.e. chitosan and silver. In the composite, the essential function of the positively charged chitosan matrix was to capture negatively charged bacteria on its surface, while small sized Ag NPs created pores on bacterial wall, thereby causing rapid disintegration of the bacteria (Banerjee et al., 2010). A proteomic approach (two dimensional electrophoresis and proteins identification by mass spectrometry) was used to investigate the mode of antibacterial action of nano-Ag
against *E. coli* (Lok *et al.*, 2006). The proteomic studies revealed for the first time, several primary actions of nano-Ag in *E. coli* cells, namely in envelope protein processing, outer membrane permeability, plasma membrane potential and energization. The proteomic analyses revealed that just a short exposure of *E. coli* cells to nano-Ag resulted in alterations in the expressions of a number of envelope proteins and heat shock proteins which are usually induced in a variety of stress conditions. The envelope proteins (OmpA, OmpC, OmpF, OppA, and MetQ) are integral outer membrane or periplasmic components guarding against the entry of foreign substances. In particular, the expression of the heat shock proteins LbpA and LbpB is stimulated during the over expression of heterologous proteins that are associated inclusion bodies (Otani *et al.*, 2001) (Jakob U Gaestel *et al.*, 1993) (Kitagawa *et al.*, 2000) (Allen *et al.*, 1992). The treatment with nano-Ag destabilizes the outer membrane and disrupts the outer membrane barrier components such as lipopolysaccharide or porins, culminating in the perturbation of the cytoplasmic membrane. The proteomic signatures of nano-Ag treated *E.coli* cells are characterized by an accumulation of envelope protein precursors. This indicates that nano-Ag may target the bacterial membrane, leading to a dissipation of the proton motive force. Although the detailed mechanism by which NPs with a diameter of 10 nm can penetrate and disrupt the membranes remains to be elucidated, electron microscopy and optical imaging results suggest that nano-Ag penetrate the outer and inner membranes of the Gram negative bacteria, with some NPs found intracellularly (Jakob U Gaestel *et al.*, 1993). Nano-Ag and Ag+ ions share a similar membrane targeting mechanism of action. But the effective
concentrations of nano-Ag and Ag+ ions are at nanomolar and micromolar levels, respectively. Nano-Ag appears to be significantly more efficient than Ag+ ions in mediating their antimicrobial activities (Dibrov et al., 2002). Size-controlled silver colloid NPs generated using a one-step modified Tollens process was assessed for antimicrobial activity against drug resistant pathogens (Panacek et al., 2006). The pH and type of reducing saccharide of the reaction system were found to influence the size of particles. A wide range of particle size, particularly 25-100 nm with narrow size distributions were obtained using four different saccharides. NPs with size less than 25 nm have exhibited minimum inhibitory concentration of 6.75-54 μg/mL whereas 25 nm size particles showed MIC in the range of 1.69- 13.5 μg/mL against including highly multiresistant bacteria such as methicillin-resistant Staphylococcus aureus, methicillin-resistant coagulase-negative staphylococci (e.g., Staphylococcus epidermidis), vancomycin-resistant Enterococcus faecium, and ESBL-positive Klebsiella pneumoniae. This is an important result, particularly when antibiotic resistance among bacterial species is increasing at an alarming rate and very few alternative options are available to address the issue. Silver NPs have been evaluated for their antimicrobial activities against a wide range of pathogenic organisms (Yamanaka et al., 2005) (Lara et al., 2010) (Shahverdi et al., 2007) (Yoon et al., 2007) (Sarkar et al., 2007) (Shrivastava et al., 2007). The highest sensitivity was observed against Methicillin resistant Staphylococcus aureus (MRSA) followed by Methicillin resistant Staphylococcus epidermidis (MRSE) and Streptococcus pyogenes. A moderate antimicrobial activity was observed in case of the gram negative pathogens Salmonella typhi and Klebsiella pneumoniae.
(Nanda and Saravanan, 2009). The size of the particle plays a central role in antimicrobial activity (Morones et al., 2005). The colloidal silver particles, with variablesizes (44, 50, 35, and 25 nm), synthesized by the reduction of [Ag(NH$_3$)$_2$]$^+$ complexes with carbohydrates were tested for antimicrobial activity (Panacek et al., 2006). The antibacterial activity was particle size dependent. The silver NPs also exhibit a shape-dependent interaction with the bacterial cells. The truncated triangular silver nanoplates displayed the strongest biocidal action against *E. coli*, when than the spherical and rod-shaped NPs (Pal et al., 2007). Small particles exhibited higher antimicrobial activity than big particles. This result can be due to high particle penetration when these particles have smaller sizes. The antibacterial properties are related to the total surface area of the NPs. Smaller particles with larger surface to volume ratios have greater antibacterial activity (Cho et al., 2005) (Baker et al., 2005) (Martínez-Castañón et al., 2008).

2.7.2 Gold nanoparticles

The therapeutic use of gold can be traced back to the Chinese medical history in 2500 BC. Red colloidal gold is still used in the Indian Ayurvedic medicine for rejuvenation and revitalization during old age under the name of Swarna Bhasma (“Swarna” meaning gold, “Bhasma” meaning ash) (Mahdihassan 1985) (Higby 1982) (Shaw 1999). Gold also has a long history of use in the western world as nervine, a substance that could revitalize people suffering from nervous conditions. In the 16th century gold was recommended for the treatment of epilepsy. In the beginning of the 19th century gold was used in the treatment of syphilis. Following the discovery of the bacteriostatic effect of gold cyanide
towards the tubercle bacillus by Robert Koch, gold based therapy for tuberculosis was introduced in 1920s (Shaw 1999). The major clinical uses of gold compounds are in the treatment of rheumatic diseases including psoriasis, juvenile arthritis, planindromic rheutamitism and discoid lupus erythematosus (Felson et al., 1990). Au particles are particularly and extensively exploited in organisms because of their biocompatibility (Bhattacharya and Mukherjee, 2008) (Daniel and Astruc, 2004). Gold NPs (Au) generally are considered to be biologically inert but can be engineered to possess chemical or photothermal functionality. On near infrared (NIR) irradiation the Au-based nanomaterials, Au nanospheres, Au nanocages, and Au nanorods with characteristic NIR absorption can destroy cancer cells and bacteria via photothermal heating. Au-based NPs can be combined with photosensitizers for photodynamic antimicrobial chemotherapy. Au nanorods conjugated with photosensitizers can kill MRSA by photodynamic antimicrobial chemotherapy and NIR photothermal radiation (Kuo 2009) (Pissuwan et al., 2009). A hydrophilic photosensitizer, toluidine blue O was conjugated on the surface of Au nanorods for photodynamic antimicrobial chemotherapy. The Au nanorods served as both photodynamic and photothermal agents and inactivated MRSA. The combined effect of PACT and hyperthermia has enhanced antimicrobial effect of gold NP. The study clearly showed that gold nanorods conjugated with a hydrophilic photosensitizer such as toluidine blue O act as dual-function agents in photodynamic inactivation and hyperthermia against methicillin-resistant Staphylococcus aureus (Gil-Tomas J. Lethal 2007) (Perni 2009). Light absorbing gold NPs conjugated with specific antibodies have also been exploited to
photothermally kill *Staphylococcus aureus* by using laser (Zharov 2006). Recent studies have focussed on functionalising the gold NPs as phothermal agents for hyperthermically killing pathogens (Norman 2008) (Simon-Deckers 2008) (Huang 2007). The efficacy of the antibacterial activity of gold NPs can be increased by adding antibiotics (Burygin 2009). The antimicrobial activity of the antibiotic vancomycin was enhanced on coating with gold NP against vancomycin resistant enterococci (VRE) (Gu *et al.*, 2003). The coating of aminoglycosidic antibiotics with gold NPs has an antibacterial effect on a range of Gram-positive and Gram-negative bacteria (Grace and Pandian, 2007) (Saha 2007). Cefaclor (a second-generation β-lactam antibiotic) reduced gold NPs have potent antimicrobial activity on both Gram-positive (*S. aureus*) and Gram-negative bacteria (*E. coli*) compared to cefaclor and gold NPs alone. Cefaclor inhibits the synthesis of the peptidoglycan layer, making cell walls porous. Further, the gold NPs generate holes in the cell wall, resulting in the leakage of cell contents and cell death. It is also possible that gold NPs bind to the DNA of bacteria and inhibit the uncoiling and transcription of DNA (Rai 2010). The Au NPs can be used to coat a wide variety of surfaces for instance implants, fabrics for treatment of wounds and glass surfaces to maintain hygienic conditions in the home, in hospitals and other places (Das 2009).

### 2.7.3 Magnesium oxide nanoparticles

Highly ionic nanoparticulate metal oxides can be prepared with extremely high surface areas and unusual crystal morphologies having numerous edge/corner and reactive surface sites (Stoimenov 2002). Magnesium oxide (MgO) prepared
through an aerogel procedure (AP-MgO) yields square and polyhedral shaped NPs with diameters varying slightly around 4 nm, arranged in an extensive porous structure with considerable pore volume (Klabunde et al., 1996). An interesting property of AP-MgO NPs is their ability to absorb and retain for a long time (in the order of months) significant amounts of elemental chlorine and bromine (Huang 2005). The AP-MgO/X2 NPs exhibited biocidal activity against certain vegetative Gram-positive bacteria, Gram-negative bacteria and the spores (Richards et al., 2000). AP-MgO NPs are found to possess many properties that are desirable for a potent disinfectant (Koper O et al., 2002). Because of their high surface area and enhanced surface reactivity, the nanocrystals adsorb and carry a high load of active halogens. Their extremely small size allows many particles to cover the bacteria cells to a high extent and bring halogen in an active form in high concentration in proximity to the cell. Standard bacteriological tests have shown excellent activity against *E.coli* and *Bacillus megaterium* and a good activity against spores of *Bacillus subtilis* (Koper O et al., 2002). The bioactivity of AP-MgO/X2 NPs is due to the positive charge they have in water suspension, opposite to those of the bacteria and spore cells, which enhances the total bactericidal effect. Confocal microscopy studies have shown that in water suspension the opposite charge brings the bacteria and NPs together in aggregates composed of both AP-MgO NPs and bacteria. Atomic force microscopy and electron microscopy studies demonstrate that halogenated magnesium oxide has a very strong influence on microorganisms and their membranes in particular. Overall, the halogen such as chlorine and
bromine treated MgO NPs have a stronger and faster effect on the killing action of both bacteria and spores (Koper O et al., 2002).

2.7.4 Copper oxide nanoparticles

Copper oxide (CuO) is a semiconducting compound with a monoclinic structure. It is the simplest member of the family of copper compounds and exhibits a range of potentially useful physical properties such as high temperature, superconductivity, electron correlation effects and spin dynamics. Therefore, it finds a wide application (Cava 1990) (Tranquada et al., 1995). CuO crystal also has photocatalytic or photovoltaic properties and photoconductive functionalities (Kwak and Kim, 2005). There is limited information available about the antimicrobial activity of nano CuO. As CuO is cheaper than silver, easily mixes with polymers and relatively stable in terms of both chemical and physical properties, it finds a wide application (Xu et al., 1999). It is suggested that highly ionic nanoparticulate metal oxides, such as CuO, may find potential application as antimicrobial agents as they can be prepared with extremely high surface areas and unusual crystal morphologies (Stoimenov 2002). CuO NPs were effective in killing a range of bacterial pathogens involved in hospital-acquired infections. But a high concentration of nano CuO is required to achieve a bactericidal effect (Ren et al., 2009). It has been suggested that the reduced amount of negatively charged peptidoglycans makes Gram-negative bacteria such as Pseudomonas aeruginosa and Proteus spp. less susceptible to such positively charged antimicrobials. However, in the time–kill experiments the Gram-negative strains showed a greater susceptibility to nano CuO combined nano Ag. Studies have been conducted to
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assess the potential of nano CuO embedded in a range of polymer materials. A lower contact-killing ability was observed in comparison with release killing ability against MRSA strains. This suggests that a release of ions into the local environment is required for optimal antimicrobial activity (Ren et al., 2009) (Cioffi et al., 2005). Copper NPs have a high antimicrobial activity against B. subtilis. This may be attributed to greater abundance of amines and carboxyl groups on cell surface of B. subtilis and greater affinity of copper towards these groups. Copper ions released may also interact with DNA molecules and intercalate with nucleic acid strands. Copper ions inside bacterial cells also disrupt biochemical processes (Rupareli et al., 2008). The exact mechanism behind bactericidal effect of copper NPs is not clear.

2.7.5 Aluminium nanoparticles

Aluminum oxide NPs have wide-range applications in industrial and personal care products. The growth-inhibitory effect of alumina NPs over a wide concentration range (10–1000 μg/mL) on Escherichia coli have been studied (Sadiq M, et.al, 2009). Fourier transform–infrared studies have shown differences in structure between NPs treated and untreated cells. Alumina NPs have exhibited a mild growth-inhibitory effect, only at very high concentrations. This is attributed to surface charge interactions between the particles and cells. It is possible that the free-radical scavenging properties of the particles might have prevented cell wall disruption and drastic antimicrobial action (Sadiq et al., 2009). Alumina is thermodynamically stable over a wide temperature range and has a corundum-like structure, with oxygen atoms adopting hexagonal close packing and Al3+ ions
filling two thirds of the octahedral sites in the lattice (Martínez Flores et al., 2003). The alumina NPs carry a positive charge on its surface at near-neutral pH. The electrostatic interaction between the negatively charged *E. coli* cells and the particles resulted in the adhesion of NPs on the bacterial surfaces (Li and Logan, 2004). The adhesion increased with increase in concentration of the particles in the suspension, a negative effect on growth was observed with respect to concentration. This electrostatic interaction between bacteria and particle surface, along with hydrophobic interactions and polymer bridging, may be responsible for the phenomenon of bacterial adhesion onto the particles. The antimicrobial property of these metal oxides is attributed to the generation of reactive oxygen species (ROS) which causes disruption of cell wall and subsequently cell death. But alumina NPs may act as free radical scavengers. These NPs are able to rescue cells from oxidative stress-induced cell death in a manner that appears to be dependent upon the structure of the particle but independent of its size within the range of 6–1000 nm (Mohammad et al., 2008).

2.7.6 Titanium dioxide nanoparticles

The inhibitory activity of TiO$_2$ is due to the photocatalytic generation of strong oxidizing power when illuminated with UV light at wavelength of less than 385 nm (Chorianopoulos et al., 2011) (Fujishima and Honda, 1972) (Fujishima et al., 1992). TiO$_2$ particles catalyze the killing of bacteria on illumination by near-UV light. The generation of active free hydroxyl radicals (_OH) by photoexcited TiO$_2$ particles is probably responsible for the antibacterial activity (Wei C, et.al, 1994) (Pham et al., 1995) (Ireland et al., 1993). The antimicrobial effect of TiO$_2$
photocatalyst on *Escherichia coli* in water and its photocatalytic activity against fungi and bacteria has been demonstrated (Matsunaga *et al*., 1998) (Matsunga *et al*., 1988) (Kim *et al*., 2003) (Chawengkijwanich and Hayata, 2008). There are also studies on bactericidal activity of nitrogen-doped metal oxide nanocatalysts on *E. coli* biofilms and on the photocatalytic oxidation of biofilm components on TiO$_2$-coated surfaces (Matsunga *et al*., 1988). In conclusion, the use of TiO$_2$ photocatalysts as alternative means of self-disinfecting contaminated surfaces by further development may provide potent disinfecting solutions for prevention of biofilm formation. TiO$_2$ photocatalysts can be used as effective biofilm disinfectant in food processing industries (Liu *et al*., 2007) (Wolfrum *et al*., 2002). Suspensions containing TiO$_2$ are effective at killing *Escherichia coli*. This has led to the development of photocatalytic methods for the killing of bacteria and viruses using TiO$_2$ in aqueous media (Saito *et al*., 1992) (Duffy *et al*., 2002). It has been suggested that nanostructured TiO$_2$ on UV irradiation can be used as an effective way to reduce the disinfection time, eliminating pathogenic microorganisms in food contact surfaces and enhance food safety (Chorianopoulos *et al*., 2011). The major disadvantage of using TiO$_2$ is that UV light is required to activate the photocatalyst and initiate the killing of the bacteria and viruses. In recent years, visible light absorbing photocatalysts with Ag/AgBr/TiO$_2$ has proved to be successful at killing *S. aureus* and *E. coli* (Sunada K, et.al, 1998) (Hu *et al*., 2006).

**2.7.7 Zinc oxide nanoparticles**

Among the various metal oxides studied for their antibacterial activity, zinc oxide NPs have been found to be highly toxic. Moreover, their stability under
harsh processing conditions and relatively low toxicity combined with the potent antimicrobial properties favours their application as antimicrobials (Stoimenov 2002). Many studies have shown that some NPs made of metal oxides, such as ZnO NP, have selective toxicity to bacteria and only exhibit minimal effect on human cells, which recommend their prospective uses in agricultural and food industries (Brayner et al., 2006) (Thill et al., 2006) (Reddy et al., 2007) (Zhang et al., 2007). The antimicrobial activity of zinc oxide NPs have been studied against the food related bacteria Bacillus subtilis, Escherichia coli and Pseudomonas fluorescens (Jiang et al., 2009). ZnO NP could potentially be used as an effective antibacterial agent to protect agricultural and food safety from foodborne pathogens, especially E. coli O157:H7 (Zhang et al., 2007). ZnO NPs possess antimicrobial activities against Listeria monocytogenes, Salmonella enteritidis and E. coli O157:H7 in culture media (Jiang et al., 2009). There are also other studies confirming the strong antimicrobial activity of ZnO NPs wherein the NPs could completely lyse the food-borne bacteria Salmonella typhimurium and Staphylococcus aureus (Liu et al., 2009). In another study, ZnO NPs (12 nm) inhibited the growth of E. coli by disintegrating the cell membrane and increasing the membrane permeability (Jin et al., 2009). The above findings suggest that ZnO NPs can find applications in food systems and can be used to inhibit growth of pathogenic bacteria. There are several mechanisms which have been proposed to explain the antibacterial activity of ZnO NPs. The generation of hydrogen peroxide from the surface of ZnO is considered as an effective mean for the inhibition of bacterial growth (Yamamoto 2001). It is presumed that with decreasing particle
size, the number of ZnO powder particles per unit volume of powder slurry increases resulting in increased surface area and increased generation of hydrogen peroxide. Another possible mechanism for ZnO antibacterial activity is the release of Zn2+ ions which can damage cell membrane and interact with intracellular contents (Brayner et al., 2006).

2.8 Applications of activated carbon in cancer therapy

In recent days the AC is being used as drug carrier for the treatment of cancer. Niranjan and co-workers (2014) reported that the various ways of carbon being used for the treatment of cancer. One among these the AC in the form of nano-tubes could be successful method to deliver drugs. The carbon nanotubes (CNTs) are allotropes of carbon and have a cylindrical framework and are formed rolling graphine sheets into a cylindrical form that can be open ended or capped. They have a high aspect ratio with lengths extending to several micrometers with small diameters of the magnitude of 1 nm. There are different naon tubes namely single-walled nanotubes (SWNT), made of single graphine sheets or multiwalled carbon nanotubes (MWNTs) are made up with several graphine sheets. CNTs are a promising novel carrier system for both small and large therapeutic molecules including drugs, genes and proteins and unique need like shape of the carbon particles enable the drug molecules to attach either covalently or non covalently (Niranjan and Ashwatha, 2014). Interestingly the non-spherical NPs (like CNTs) are reported to retain in lymph nodes for prolonged periods of time. Hence, CNTs could be used for targeting lymph node cancer (Niranjan and Ashwatha, 2014). Recent days the scientists are evaluating the anticancer potential of the anticancer
drugs by labelling them with CNTs and their biological effect was evaluated by co-culturing them with cancer cell line and this method is very easy to carry out rather than other methods (Niranjan and Ashwatha, 2014).

Brain cancer is a leading cause of cancer-related death in the US in patients under the age of 35. Among the various types of brain cancers the anaplastic astrocytoma’s also known as Grade III and glioblastoma, also called as Grade IV are the most aggressive brain cancers with survival period of 24 and 9 months, respectively. Children who survive with brain cancers often suffer substantial adverse effects related to the toxicities of therapy such as development of impairment of nervous system. Hence, the current conventional chemotherapy is less effective due to presence of the blood-brain barrier (BBB) which restricts the penetration of most drugs into the brain. Interestingly, many of the CNT-based targeting approaches have been developed for the treatment of brain cancer and are very successful.

In addition to these MWCNTs are the biocompatible and it was observed from an in-vitro experiments revealed that the viability of the cell was less in the presence of Reactive Oxygen Species (ROS) detected when prolonged cultures of cells. Whereas, the cells cultured in the presence of pure MWCNTs and acid treated pure MWCNTs not affected cell viability even in the presence of ROS.

Acute lymphoblastic leukemia (ALL) is one of the main type of leukemia, is a slowly growing blood cancer that starts in bone marrow cells called lymphocytes or white blood cells. The researchers developed an enhanced targeted
delivery of daunorubicin (Dau) to acute lymphoblastic leukemia by developing a tertiary complex of Sgc8c aptamer, daunorubicin, and SWCNT termed as Dauaptamer SWCNTs. The studies with flow cytometric analysis exhibited that the tertiary complex of daunorubicin was internalized effectively into human T cell leukemia cell (MOLT-4 cells) but not to U266 myeloma cells. The result of the study will be more useful to treat blood cancer using the carbon nano tubes (CNT).

Breast cancer (BC) has become the most common malignancy and the leading cause of cancer-specific death in women as per GLOBOCAN 2008 (Ferlay et al., 2010). Blocking of the HER2/neu receptor could be one of the most recent and important treatment approaches to treat breast cancer (Qin et al., 2013). Recently Pan and co-workers (2009) investigated the efficiency of MWCNTs to deliver gene to the tumor cell for cancer therapy. In their study human breast cancer cell line MCF-7 cells and MDA-MB- 435 cells were incubated with modified MWCNTs (asODN-dMNTs) and the results of the study revealed that the composites inhibited the cell growth in time and dose dependent manner by down regulating the expression of c-myc gene and C-Myc protein (Pan et al., 2009).

Colorectal cancer is the leading cause of death amongst the men and women worldwide and afflicts more than 135,000 patients per year in America. This cancer has usually been viewed as a homogeneous entity rather than a complex heterogeneous disease developing through multiple genetic and epigenetic abnormalities, such as defective DNA mismatch repair (dMMR) and the CpG island methylator phenotype (CIMP). Abdolahad et al., (2012) utilized the vertical arrays of MWCNTs for entrapping the metastatic human colon...
adenocarcinoma SW-48 cells and HT-29 cancerous cells. Due to the dangerous deformability and softness of higher metastatic malignant cells, they show greater fraction of entrapment by the vertically aligned MWCNTs as compared to the less deformable and rigid lower grades of metastatic cancerous cells. This novel application of MWCNTs distinguishes the healthy and highly deformable cancerous cells more precisely than SWCNTs and also showed better delivery of anticancer drug like Doxorubicin or monoclonal antibody to these cancer cells (Abdolahad et al., 2012).

Hepatocellular carcinoma (HCC) is a highly predominant malignancy, especially in Asia. Liver cirrhosis is the strongest predisposing factor for HCC, accounting for approximately 80% of patients with this disease. In the United States, Japan and Europe, hepatitis C virus (HCV) infection is the major etiology of liver cirrhosis and HCC. Hepatitis virus B (HBV) infection, however, is the foremost cause of HCC development in most Asian countries other than Japan. In addition to HBV and HCV infection, metabolic disorders and alcoholic cirrhosis can also act as risk factors for HCC. c-myc is among the most frequently over expressed genes in human cancers. Overexpression of c-mycin hepatic cells leads to the development of hepatocellular carcinoma (Lin et al., 2010). Pan and co-workers made an attempt to suppress the appearance of cmyc gene and C-Myc protein in the tumor bearing cell by Polyamidoamine dendrimer modified CNTs (dMWCNTs) were fabricated for the efficient delivery of antisense c-myc oligonucleotide (asODN) into liver cancer cell line HepG2. These composites suppressed the cell growth in time and dose dependent means and down regulated
the expression of the c-myc gene and c-myc protein when cultured alone with the liver cancer cell line HepG2.

Lymph node metastasis is a powerful predictor of recurrence and death in patients with cutaneous melanoma. Metastasis to regional lymph nodes grows during the course of the disease in approximately 30% of patients with cutaneous melanoma. Yang et al. compared the in vitro and in vivo potential therapeutic effect of gemcitabine (GEM) loaded magnetic MWCNTs (mMWCNTs) this carbon nano tubes act as magnetic-carbon particles (mACs). From the study the researchers found that MWCNT were efficient method of delivering the drugs to treat lymphnode metastasis of cancer.

Oncogenic human papillomavirus (HPV) has a causal role in nearly all cervical cancers and in many vulvar, penile, vaginal, and or pharyngeal cancers. HPV types 16 and 18 are mostly responsible for 70% of cervical cancers. In HPV-associated cancers, oncogenic antigens E6 and E7 were overexpressed on the tumor cells and thus, they represent a best target for developing antigen-specific immunotherapy for the control of cervical cancer (Wu et al., 2011). Wu et al. developed a novel approach of utilizing natural biocompatible polymer chitosan for imaging the tumor cells. In this assay, SWCNTs were modified by using chitosan (CHIT) fluorescein isothyocyanate (FITC). In addition to these Zhang and co-workers developed five types of CNTs and tested against cancer cells. The results of the study indicated that both “dot like” and “dash like” focal adhesion kinases (FAKs) were mainly distributed at the periphery of the cells cultured on
SWCNTs and acid-treated SWCNTs and due to this they were found undergoing apoptosis with damaged cell membrane and condensed chromatin.

**Unaddressed areas in previous studies and uniqueness of the present study**

From this chapter it was noted that, even though many researchers were studied the preparation of AC using many different materials and different forms of waste materials as raw materials, few of them only used the municipal waste material as the raw material. Similary many researchers used different peels in the preparation of AC. Among them only few researchers were studied the AC preparation using citrus fruits peels and out of them studies used mosambi fruit peels were very very limited. But in the proposed study MPs one of the major municipal wastage were used as a precursor in order to reduce the environmental causes created by them. In literature of the past majority of the researcher were studied individually about the adsorption characteristics of AC and the anti bacterial activity of the metal NPs even though they possess adverse effect on human. But in the present study along with these two factors, the aspects like synthesis of 7 metal NPs, formation of 7 nanocomposites by impregnating metal NPs into MPAC to reduce adverse effect, and studies to test the anti bacterial activity of MPAC, 7 metal NPs, and the 7 nanocomposite were conducted against 7 bacterial strains and the results were revealed. The past researchers were used carbon nanotubes highly toxic material as the carriers of anti cancer drugs. But the current researcher has given due importance to study the toxicity of the MPAC, and to test its potentiality as drug carrier of anti cancer drug in this study. These could be elaborately seen in the following chapters.