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Research Article

BIOGENIC CARBON NANOFIBER SYNTHESIZED FROM AGRO-WASTE FOR REMOVAL OF HEAVY-METAL FROM WASTEWATER

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ABSTRACT

The advent of inexorable human, and industrial activities as well as the input of nature has impacted the environment by releasing Heavy Metals into the aquatic system. Hence, the physical removal of hazardous HM remains a demand of the day. This review envisages the use of agro-waste with the incorporation of nanotechnology for the removal of HM from aquatic systems. The focus is on plant parts, plant metabolites, and plant-cellulose-derived Carbon Nanofibers (CNF) as materials used for the removal of Heavy Metals. Owing to their high surface area, high mechanical strength, greater chemical reactivity due to the presence of dangling bonds, non-toxicity, high porosity,channel-like morphology, and lower costas the precursor, energy-efficient production; makes CNF an effective adsorbent of Heavy Metals.CNF synthesized from agro-waste and plant-metabolite to adsorb Heavy Metals; as well as acts as a filtration base has been touched upon with the hope of bridging the gap between ever-increasing demand and available clean water. A brief introduction to the CNF, its structure, properties as well as common methods of synthesis of CNF is given. Moreover, Physico-Chemical and Biological methods that are being used is also touched upon. The article suggests the need for innovative, low-cost, and environmentally friendly surface modification techniques and the use of agro-waste-derived CNF for the removal of HM from water.

KEYWORDS

Adsorption, Agro-waste, Bioremediation, Carbon Nanofiber, Chemical Vapor Deposition, Desorption, Filtration, Heavy-Metal, Phytoremediation, Porosity.

INTRODUCTION

In this review removal of one of the gifts of mother nature i.e. Heavy Metals (HM); is called so because of theirhigh atomic weight, relatively high density (>5 gm cm-3), and atomic number >20.Those that form a part of concern because they are toxic even at trace levels are Antimony, Arsenic, Bismuth, Cadmium, Cerium, Chromium, Cobalt, Copper, Gallium, Iron, Lead, Mercury, Nickel, Tellurium, Thallium, Uranium, Vanadium, and Zinc (Mosby et.al.1996).Some of these HM(Co, Cu, Fe, Ni, and Zn)are required by the living system in trace amounts; but in larger amounts, they become toxic. All other HMis not metabolized by the body and accumulates in the soft tissuesleading to deleterious effects, and altered pharmacological activities in both plants and animal cells.Based on the impact of HMs on living beings, HM can be broadly classified into two categories: Essential and Nonessential HM. Essential HMs are required by living organisms.

Sources of HM polluting the aquatic environment are not only man-made (due to their multiple industrial, mining, domestic, agricultural, medical, and technological applications) but also caused by nature. Unlike organic pollutants, HM is non-biodegradable and tends to accumulate in living beings. Moreover, HM is not degraded by bacteria, hence remaining permanently in the marine environment and can potentially induce severe oxidative stress in aquatic organisms.HM released into aquatic systems are generally bound to particulate matter, which eventually settles down and becomes incorporated into sediments. Sediment-bound pollutants can be taken up by rooted aquatic macrophytes and other aquatic organisms. Diatom structure has been affected by high levels of metals in rivers (Grazulevicieneet.al. 2009). Once HM is accumulated by an aquatic organism, it can be transferred through the upper classes of the food chain, which is the cause of concern. Based on the impact of HMs on living beings HM can be broadly classified into two categories: Essential and Nonessential HM. Essential HMs are required by living organisms for carrying out fundamental processes like growth, metabolism, and development of different organs.

Common Physico-Chemical and Biological Methods for Removal of Heavy-metalsfrom water

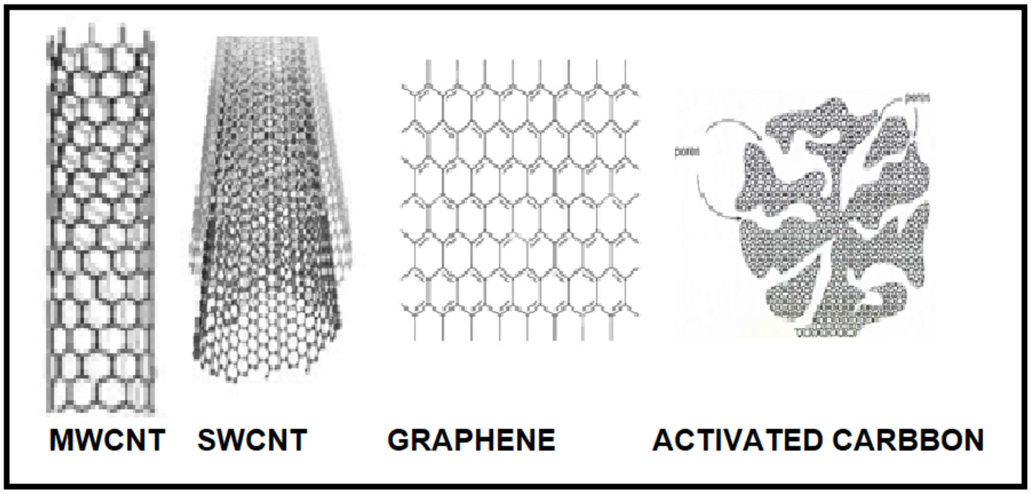
There have been efforts to develop many suitable methods for their removal from the environment e.g. (i) Chemical-Precipitation(ii) Ion-Exchange, (iii) Electrolytic-Recovery or Electrowinning, (iv) Electro-Coagulation, (v) Cementation (Chemical-Oxidation and Advanced-Oxidation),(vi) Reverse-Osmosis and Electrodialysis, (vii) Photocatalysis, (viii) Membrane-filtration, (ix) Bioremediation using Microbes, (x) Bioremediation using Algae, (xi) Phytoremediation, (xii) Rhizofiltration, (xiii) Phytovolatilization, and (xiv) Phytostabilization.

Nano Forms of Carbon-based Adsorbents

Carbon (C) atomic number 6, belongs to group 14 of the periodic table and has the electronic structure of

1s22s22p2. Factors involved in adsorption processes are adsorbent structures, fluid properties, contaminant structures, operating conditions, and system configuration.The adsorption phenomena depend on the interactions between adsorbate molecules and adsorbents. The absorption capacity of a carbon-based adsorbent for HM depends on the nature ofthe adsorbate (pKa, polarity, functionality, size, and molecularweight), the adsorbent (functional groups, pore size, andstructure), and solution conditions (pH, ionic strength andtemperature).

The aspects like the chemical and physical nature of various carbon materials and their adsorption ability by increasing their surface area and their possible modification are being extensively tried. Carbon due to its strong tendency to form a bond with its atom leads to the formation of a long network of carbon structures. At the nano-level, the carbonaceous structures that have found umpteen applications encompass fullerene, graphene, carbon nanotubes (CNT), carbon nanobeads (CNB), carbon nanocones, carbon nano onions, activated carbon (AC), biochar and carbon nanofibers (CNF).They have been tried either as raw material or after surface modification. The carbon surface charges can be enhanced by surface functional groups such as carboxyl, phenyl, and lactone to improve the HM uptake(Demiral et.al. 2021).Other modifications of carbon can be nitrogenation, oxidation, and sulphuration to enhance the specific surface area, pore structure, adsorption capacity, thermal stability, and mechanical strength(Qasem et.al. 2021).The use of adsorption to remove HM from water is a low-cost, high metal-binding capacity, but it often offers low selectivity, therefore, functionalization and doping are being tried to enhance the selectivity of HB.To measure the adsorption capacity Adsorption equilibrium isotherm,the Adsorption kinetics model, and the Adsorption mechanism are considered(Sabzehmeidani et.al. 2021).Most of these studies were done on (i) CNT, (ii) Graphene, and (iii) AC. AC is produced by pyrolysis of organic materials of plant origin, i.e. the same way as the CNF is produced from the plant parts (Figure-1).



Figure–1: From left to right, Schematic diagram of - Single wall Carbon Nanotube, Multi Wall Carbon Nanotube, Graphene sheet, Activated Carbon

Is Carbon Nanofiber Suitable for the Removal of Heavy Metals?

Prior to the use of CNF as an adsorbent, AC, Biochar, Graphene, CNT, etc. had been extensively studied for the removal of HM. Although the MWCNTs have received more interest for HM removal (Owalude et.al. 2016),they are highly hydrophobic and suffer from rapid aggregation in aqueous solution due to large Van der Waals forces, decreasing the adsorption potential. The results based on the above-mentioned nanoforms of carbon have given impetus tothe useof CNF for adsorption/filtration. Moreover, CNF being a cousin of CNT, with higher surface area and porosity is considered an alternative for the removal of HM, especially as it can adsorb and desorb.

The earliest reference to the production of Carbon fiber (CF) was in 1860 by Joseph Swan; he used it as a wire-filament that glows under electric current. Lots of activities mushroomed in the fabrication of CF in the 1960s from different precursors. Probably the first patent of CNF was by Hughes and Chambers (1889). However, the first electron microscopic morphology of CNF of 50 nm diameter was shown by Radushkevich and Lukyanovich (1952) (Figure–2).

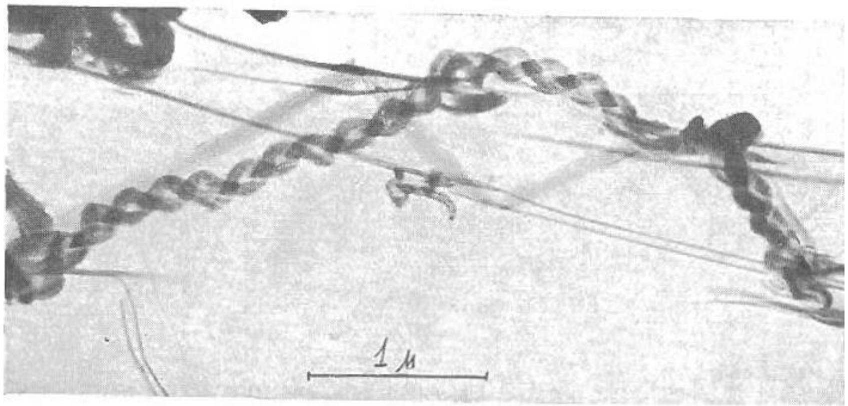


Figure -2: First published electron microscopic image of CNF (Source: Radushkevich and Lukyanovich)

Structure/Morphology of CNF

CNF is graphitic in nature. Intrinsically, the structure of CNF is similar to the CNT, which is composed of single or multi-layers of graphene sheets rolled into a cylindrical shape; whereas, CNF is composed of multi-layers broken graphene sheets rolled into a not-so-organized cylinder or other cylinder derived structures; organized as packed cones, onion, cups, beads or plates, etc (Figure-3,4). The surface area of CNF is much larger compared to MWCNT of the same dimension because the former has many broken graphene sheets which are not aligned with that of MWCNT. CNFs have average diameters of 50–150 mm and lengths from 50–100 μm; depending on the precursors and technique used to manufacture them.

POROSITY is one of the unique features of CNF morphology. Very small pores of CNF have a small size effect and offer a high surface area. Small pores are formed with turbostratically disordered graphene sheets. The unique structure of porous CNF has resulted in good electrochemical performance such as high reversible capacity and good cycle stability when used as anodes for rechargeable lithium-ion batteries (Ji and Zhang 2009). Pore size influences the surface area of the CNF. Spongy-porous CNF with ultrahigh porosity of >80% and outstanding conductivity of 980 S cm−1 was synthesized and used for preparing multifunctional flexible membranes and suggested to be a promising CNF for environmental and energy applications (Yan et.al. 2019) (Figure–4). The spongy-porous CNF with substantially reduced mass transfer resistances exhibits multifunction in terms of gas adsorption, sewage disposal, liquid storage, supercapacitors.

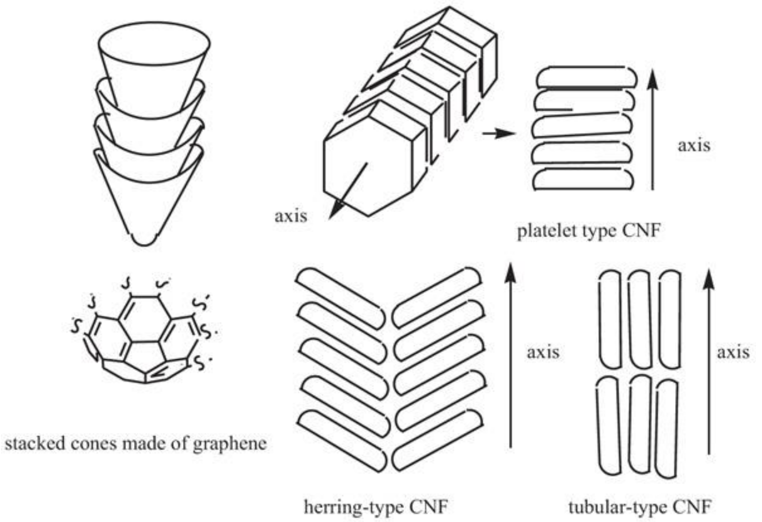


Figure-3: Schematic diagram of different morphologies of CNF (Source: from Bentham Open)

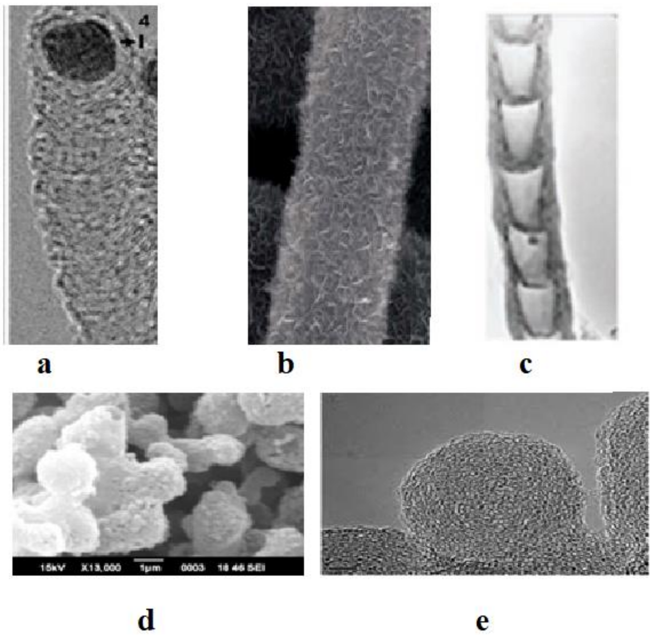
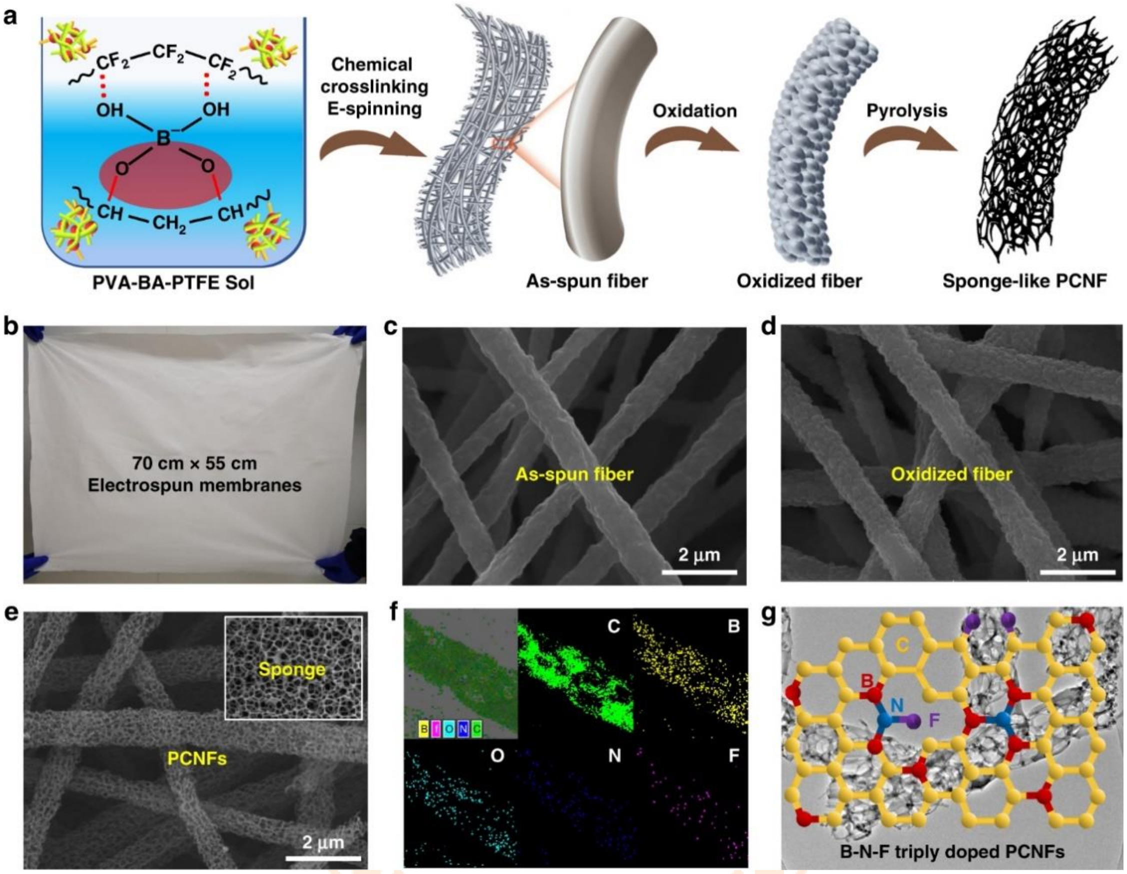


Figure-4: Electron microscopic images of different forms of CNF (a) Tubular with a lumen (b) Tubular showing broken graphene surface (c) Stacked cone-like structure (d) CNF-Onion



Figure–5: (a) A general picture of using the chemical crosslinking electrospinning method to synthesize PCNFs. (b) A digital photo of the as-spun film with a size of 70 cm × 55 cm. (c–e) Scanning electronic microscopy (SEM) images of the as-spun fibers, the oxidized fibers, and the PCNFs. (f) EDS mapping spectrum of PCNFs. (g) The proposed chemical model of B-N-F doped PCNFs. (Source: Yan et.al. 2019)

Properties of CNF

The mechanical, electrical, and thermal properties of CNF have made it a potential material for its multifarious use in aerospace, civil engineering, defense, military, motors, sports, environmental sciences, electronics, and health care.

(i) Physical Properties – CNF has high mechanical strength due to good tensile strength; can stand stress while stretched or pulled, has a very high surface area, high porosity, very high aspect ratio, and low densities.

(ii) Thermal Properties- CNF is a good thermal conductor having high thermal conductivity, high-temperature tolerance, chemical stabilities, and low coefficient of thermal expansion.

(iii) Adsorbent Property – CNF because of high specific surface area and high porosity are used for adsorption/separation of liquids, gas, and solids.Its high surface area is directly proportional to arsenic uptake, and not the morphology of the CNF (Tripathi et.al. 2012b)

(iv) Electrical Properties - CNF possesses excellent electrical conductivity, hence, is used for electromagnetic shielding.

(v) Fire Resistance - CNF is normally fire-resistant/non-flammable in the absence of oxygen.

(vi) Non-toxic - CNFs are non-poisonous, biologically inert, and X-ray permeable., thus may find application in health care.

It can be concluded that its small size effect, excellent heat resistance, and chemical stability of inorganic nanomaterials provide a ground to form self-supporting thin films, avoiding the defects of increasing interfacial resistance which makes it a potential material for many roles in filtration, and adsorption. CNF has been used in filtration media, liquid filtration, gas filtration, and molecular filtration. Moreover, Surface Stateshelp in controlling the properties and reactivity of CNF with other chemicals, thus making it a good material for forming conjugates with polymers and other nanometals.

Table -1: Properties of CNF and CNT

Material	Specific Density	Young's Modulus (Tpa)	Strength (Gpa)	Strain of Break (%)	Thermal Conductivity	Electrical Conductivity
CNF-Pitch	2. - 2.22	0.4 - 0.96	2.2 – 3.3	0.27 - 0.6	1000	2 – 8.5X10^6
CNF-Pan	1.7 – 2.0	0.2 – 0.6	1.7 – 5.0	0.3 – 2.4	8 – 105	6.5 – 4X10^6
CNT	1.3 – 2	1	10 - 60	10	>3000	10^6 - 10^7

The reason, why CNF is a good adsorbent of metallic impurities, is that due to their large surface area, and long-range porosity, act as adsorption sites for metallic impurities. Their thermal and chemical stabilities have made them attractive adsorbents for both organic and inorganic contaminants in water. Due to non-covalent interactions like ionic interaction, hydrogen bonds, and hydrophobic effect; the metals interact directly with the surface of CNF.There are four possible sites for a molecule to get adsorbed on CNF/CNT bundles (Figure -6).

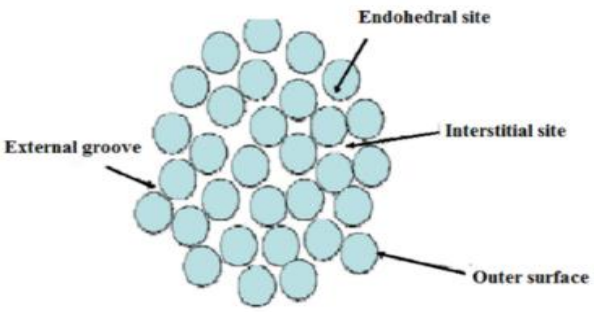


Figure 6: Schematic showing possible sites for a molecule to get adsorbed on CNT bundles

For filtration purposes, CNF mats are synthesized by electrospinning diverse precursor polymers like cellulose, followed by thermal stabilization and carbonization. Such CNF mats are often too brittle and need the incorporation of metallic nano-metals not only to increase CNF diameters but also for enhancing mechanical properties. However, such problems are not faced when CNF is prepared from agro-waste.

A cursory look at the properties of CNF such as chemical reactivity, good mobility within porous media, and high adsorption capacity; along with surface functionalization (with functional groups like -OH, -C=O, and -COOH) during synthesis increases the adsorption properties of CNFs. Functional groups are also added to CNF by oxidation using acids, such as HNO3, H2SO4, etc (Li Y. et.al. 2008, Chen et.al. 2008).

Though Laser Ablation and Arc Discharge methods are used for the synthesis of CNTs, they are not very suitable for CNF production.

Synthesis of CNF

There are two common methods of synthesis of CNF (i) Electrospinning, which requires synthetic or natural pure hydrocarbons (PAN, PVA, Cellulose), as precursors, and (ii) CVD using either pure hydrocarbons or plant parts and metabolites that are rich in hydrocarbons.

Electrospinning

Electrospinning is done by applying high voltage to a polymer solution, which creates an electrostatically repulsive force and an electric field between two electrodes so that the nanofibers can be formed (Figure 7). The important parameters of the fabrication of CNF are the viscosity and electric conductivity of the polymeric fluids, humidity, and applied voltage (Park et.al. 2008). One of the most popular precursors for the synthesis of CNF has been polyacrylonitrile (PAN); which needs pre-treatment of Acrylonitrile with a suitable plastic and a catalyst to form PAN plastic that is spun to form the internal atomic structure of the fiber and then stabilized by heat treatment. These fibers are then carbonized at 1000–3000° C in pyrolytic conditions. Finally, CNF is protected from environmental oxidation, by coating them with epoxy, polyester, nylon, urethane, etc, depending on their use.

Chemical Vapor Deposition (CVD)

CVD is a popular method of CNF synthesis under pyrolytic conditions (Figure 8). It involves a chemical process used to produce high-purity, high-performance solid materials, from the gaseous state of the precursor. If the precursors are liquid or solid, they are first heated to form gas and then deposited on a surface. The decisive parameters for CNF synthesis by the CVD include (i) Precursor, (ii) Temperature, (iii) duration of reaction, (iv) carrier gas (Argon, Nitrogen, and Hydrogen), and (v) nanometal catalysts which decides the morphology of CNF.

The large-scale production of CNF by CVD offers a low set-up cost, high production yield, ease of scale-up, comparatively low temperature, and ambient pressure. As far as the synthesis of CNF from plants and agro-wastes is concerned they are mostly done by the CVD process under pyrolytic conditions, by thermally decomposing carbon-containing material into carbon vapor.

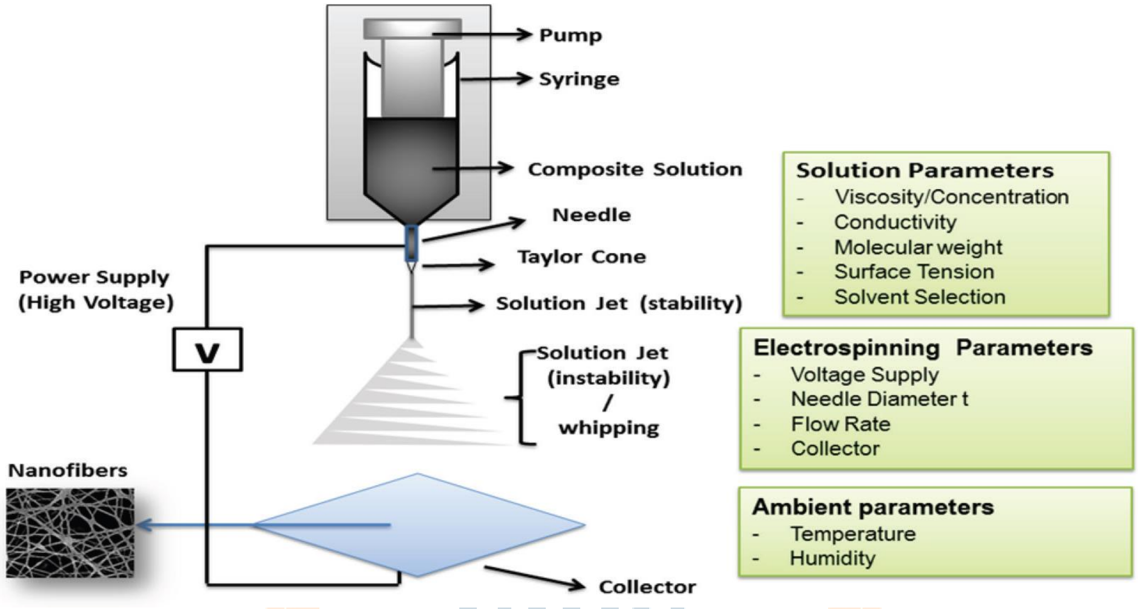


Figure -7: Electrospinning setup and controllable electrospinning process parameters (Source: Nabeel Zabar Abed Al-Hazeem, Nanofibers and Electrospinning Method. http://dx.doi.org/10.5772/intechopen.72060

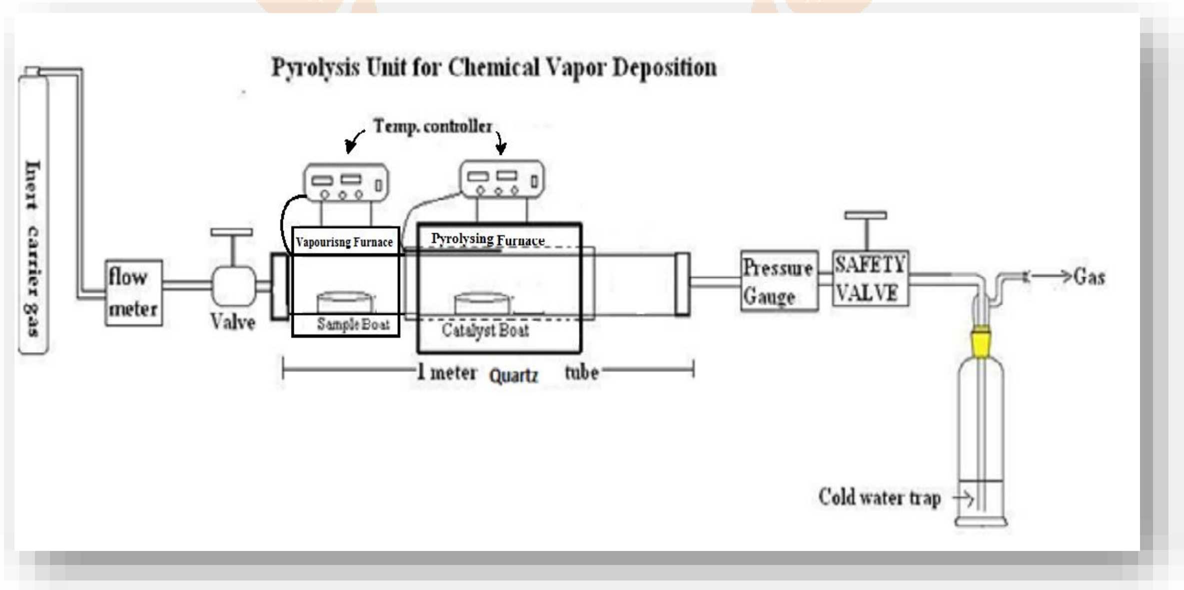


Figure 8: Schematic diagram of a Chemical Vapor Deposition Unit

PLANT PARTS AND PLANT-DERIVED PRECURSOR - Advantages of using plant parts and plant metabolites are that they are eco-friendly due to their non-toxic nature, regenerative, reproducible cheap source, and are rich in hydrocarbons. Plant parts mostly yield CNF, whereas plant metabolites yield different types of CNM including CNT, CNF, graphene, and carbon dots. Stem and root-derived CNF have highly porous CNF with hollow cores. The presence of pits in the walls of water-conducting tissues Xylem of the plant stem, roots, and leaf veinis the base in producing pores in the walls of CNF (Sharon and Sharon 2008).Fibrous plant materials have been successfully used as precursors for CNF (Sharon et.al. 2011; Shukla et.al. 2012; Zhu et.al. 2012; Deb and Chusuei 2013; Romanoviez et.al. 2013; Vishwanathan et.al. 2014). The anatomy of the precursor to a large extent determines the unique morphology of CNFs obtained, which are difficult to synthesize otherwise. The inherent anatomy of plant fibers that is composed of sclerenchyma, phloem/bast fiber, and mature xylem tissues; helps in producing unique morphology of CNF with channel-like structures which otherwise are difficult to fabricate (Sharon and Sharon 2008); SEM, TEM, RAMAN and XRD characterization (Sharon 2021) have confirmed graphitic nature of CNF Figure-9 and 10).

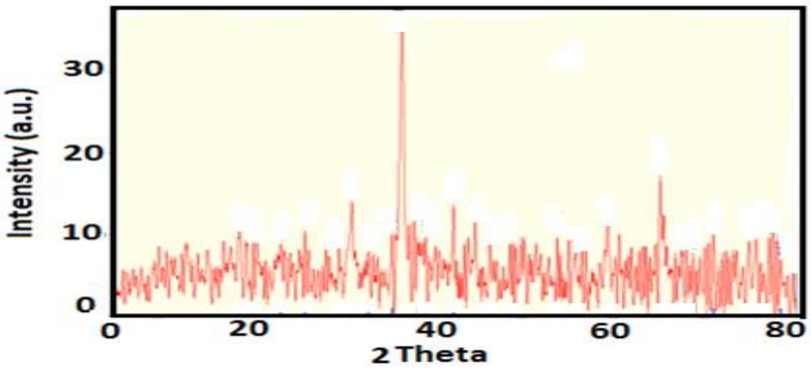


Figure-9: XRD pattern of CNM synthesized from Maize cob-hair

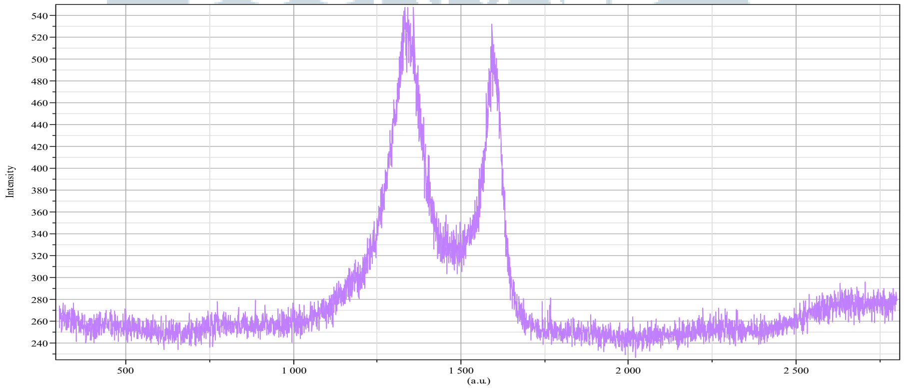


Figure 10: Raman spectrum of CNTs synthesized from Maize Hair

TEMPERATURE

plays important role in deciding the solubility of carbon. At higher temperatures decomposition of precursors is promoted and the dissolved carbon precipitates onto the surface of the catalyst. At proper temperature, carbon nucleation becomes faster than carbon diffusion resulting in smaller size and diameter with the rise in reaction temperature. Moreover, clean CNFs are produced because at a higher temperature many impurities get sublimed. High melting point and low equilibrium vapor pressure offer a wide temperature window of CVD for a wide range of carbon precursors

CATALYSTS- usually transition metals (Fe, Co, Ni, etc); are used as catalysts, because of the high solubility of carbon in these metals at high temperatures and high carbon diffusion rate in these metals. Moreover, catalystslower energy barriers for the pyrolysis of precursors, as well as help in graphitic structure formation. It acts as a nucleation seed for the growth of CNM and increases the speed of reaction during CNM synthesis.

Biogenic CNF Derived from Agro-Waste

Agro-waste is unused materials produced from agricultural operations related to the growing of crops, vegetables, fruits, grapevines, etc. Though there are planned agricultural waste management systems, up to 58% of farms and food produced is wasted in many countries.

Agro-Wasteas Precursor

Agro-waste has a rather low economic value, hence cheaper. Plant part and plant metabolites are rich in cellulose and lignin-containing polar functional groups like amino, carbonyl, alcoholic, phenolic, and ether groups having high potential for metal binding. These groups donate a lone pair of electrons and form complexes with metal ions in the solution (Demirbas et.al. 2008). The hemicellulose, lipids, lignin, water hydrocarbons, simple sugars, and starch have a variety of functional groups, it is a viable option for CNF synthesis and modification.

Plant Parts as Precursor

Nanotechnologists across the globe have directed their efforts to use agro-waste-derived plant parts such as a leaf, stems, straw, seeds, roots, etc.(Bhardwaj et.al. 2008, Shukla et.al. 2012, Mukherjee et.al. 2013, Gijare et.al. 2016, Vishwakarma et.al. 2016); as a precursor for various carbon nanomaterials e.g. CD, CNT, CNF, etc. Sharon's group has shown that the plant-derived precursors play a very important role in deciding the morphology of CNF. As can be seen in figure-11 when precursors were taken from different parts of different plant parts such as tea leaves, cotton fiber, and castor seeds they yielded different types of CNM. Whereas, when all three precursors were from the same plants but different parts (Cob-hair, calyx, and stem of Maize); and carbonized under pyrolytic conditions, yielded graphitic carbon organized into different morphologies of CNF (Figure-12). These morphologies had a base of anatomical structures of the plant parts. The impact of carbonization temperature on the increase in micropores has been observed by Kotsyubynsky t al (2021) when they synthesized porous carbon from hemp bast fiber. Which was further enhanced by doping with nitrogen

Plant Metabolites as Precursor

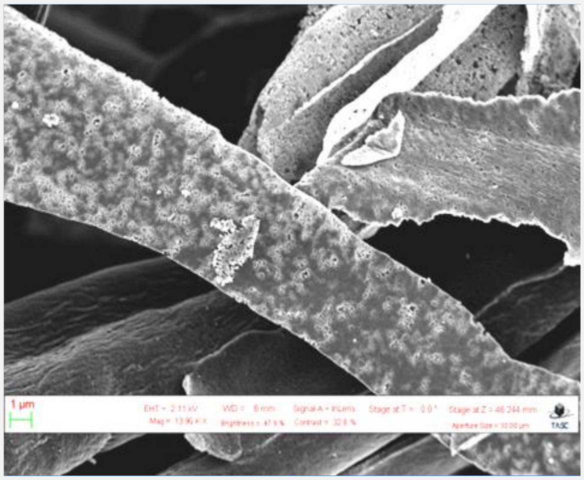
Plant metabolites such as camphor, pinene, oil, latex, etc that are rich in hydrocarbons; are used as precursors of CNF. About two decades ago, Sharon's group (Sharon et.al. 2005a; and 2005b) synthesized CNTs and CNF from camphor and observed that variations in physical conditions and catalysts, produced CNF of different morphologies (Pradhan 2003) (Figure-13).

Plant metabolites like oil, pure fatty acids, terpene-oil, latex, resins, etc have been also used as precursors to produce different types of CNM (Kshirsagar 2007, 2009, Tripathi et.al. 2013; Vishwanathan et.al. 2014) for various applications such as super-capacitor, hydrogen-storage, fuel-cell, dye-removal, H- removal, microwave-absorption, health-care, etc. Figure 14 expresses the CNF Obtained from different plant metabolites.

Plant and Microbes Derived Cellulose as Precursor

Celluloses isolated from plants, algae, or bacteria have been proven to be good raw materials in synthesizing CNF. The functions and properties of the micro-and nano-sized cellulose are highly dependent on the cellulose source and preparation process. Cellulose-rich fibers are pre-treated by acid hydrolysis (Brinchi et.al. 2013) and used for making micro-fibrillated cellulose (MFC) (Herrick et.al. 1983; Turbak et.al. 1983), which is commonly used for nanocellulose produced from wood fiber and plant fiber (Moon et.al. 2011). They have 2–20 nm diameters and lengths ranging from 100 nm to several μm (Abdul Khalil et.al. 2014). MFC is also known as nanofibrillar cellulose (NFC), cellulose nanofiber (CNF), and cellulose nanofibril (CNF). MFC contains a bundle of stretched cellulose molecules with long flexible, entangled cellulose nanofibers that are 1–100 nm in diameter and lengths of up to several tens of micrometers (Chakraborty et.al. 2006).

Xu et.al. (2018) synthesized cellulose nanofiber by extracting cellulose from corn stover (i.e. leaves, stalks, and cobs of maize plants left in a field after harvest), which yielded > 93% cellulose. The diameter of thus obtained CNF was 5-50 nm and the length was in the range of microns. Cellulose fibers extracted from sugarcane bagasse have also (Sankararamakrishnan et.al. 2014) gained attention. To enhance the adsorption capacity of Carbon Surfactant Modificationofagro-wastes is studied (Bingol et.al. 2004; Namasivayam and Sureshkumar 2008; Nadeem et.al.2009; Jing et.al. 2011). The properties of cellulose fibers have been enhanced by various chemical modifications via cross-linking. Cellulose nanofibers extracted from sugarcane bagasse and doped with Zirconium (IV) nanoparticles (ZrCNF), zerovalent Iron nanoparticles (ZVICNF), and bimetal oxide nanoparticles (zirconium and zerovalent iron) (ZrZVICNF) to produce nanocomposites; and investigated the durability of the nanostructures as adsorbents for the process of HM remediation. Cellulose serves as a good adsorbent for the remediation process and removal of contaminants from water. Carbonized powder of husks and pods of Moringa oleifera, modified by a surfactant (cetyltrimethylammonium bromide) improved the removal efficiency of the carbon powder with an adsorption capacity of 27 mg/g being reported at an optimum pH of 8. Since surfactants are amphipathic they can form self-associated clusters.. Depending on the nature of their hydrophilic group they can be cationic (positive charge), anionic (negative charge), non-ionic (no apparent charge), and zwitterionic (both charges are present); because the surfactant-modified adsorbents are superior in removal efficiency and promote selective adsorption (Rosen 2012).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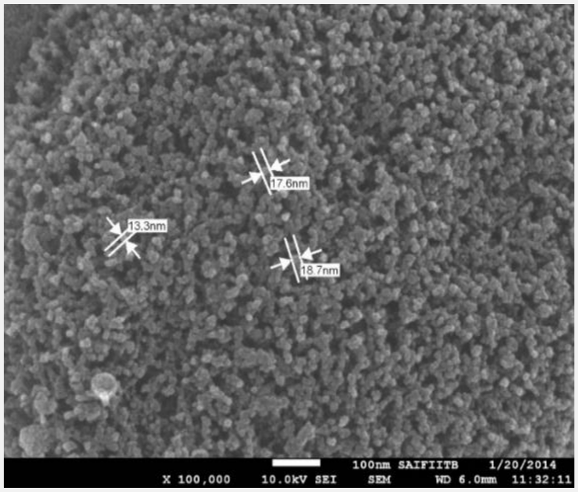
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Figure –11: CNF of different morphologies derived from different plant parts by a CVD process(a) Leaves of tea show a small plate-like structure (Source: Bhardwaj et.al. 2008)(b) Semul cotton fiber showing tubular highly porous surface (Source: Mukherjee et.al. 2013) and (c) Castor seeds yielded small tubular structures(Source: Gijare et.al. 2016)

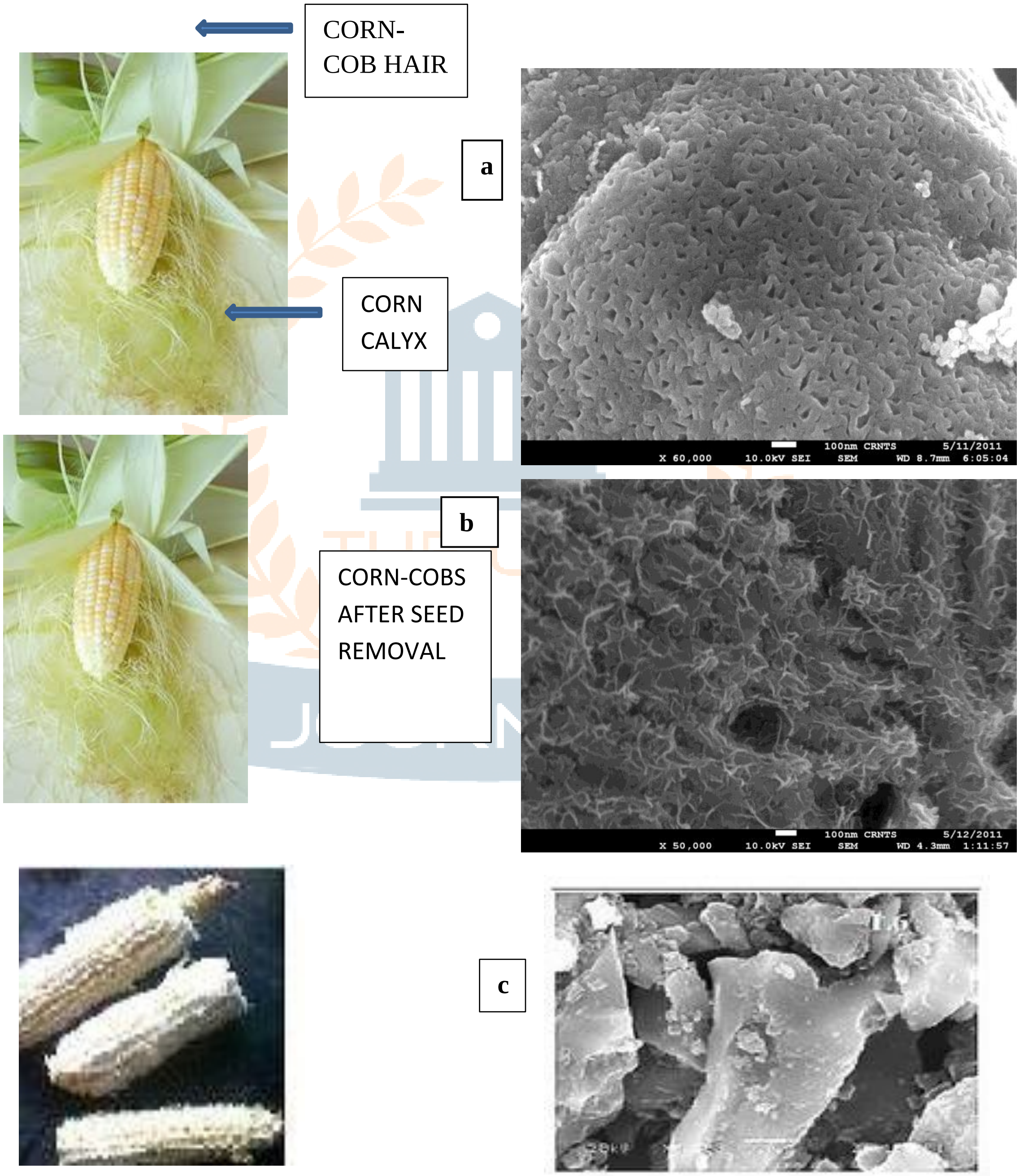


Figure – 12: CNF of different morphologies derived from different parts of Maize plant by a CVD process

(a) Calyx of corn-cob showing branched packed fibers

(b) Corn hair present on the tip of maize cob showing fibrous porous tubular (Source: a and b: Shukla et.al. 2012) and

(c) Corn-cob after removal of the seeds yielded plates like tubes (Source: Vishwakarma et.al. 2016)

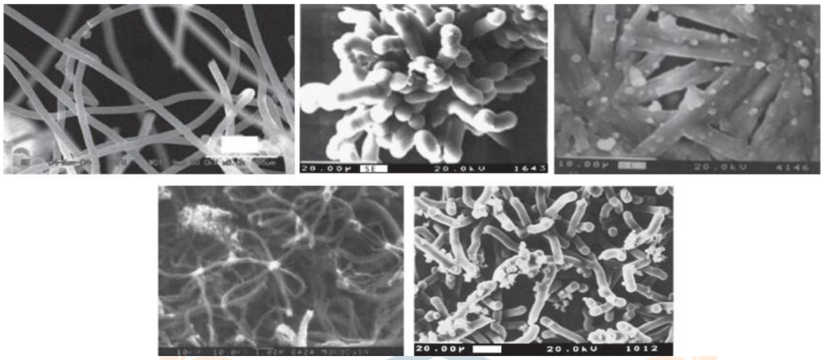


Figure- 13: SEM images of carbon fibers synthesized from camphor by pyrolyzing them at 700°C in presence of argon under varying conditions: (a) Long tubelike CF over nickel plate,(b) cauliflower-like CF over oxidized nickel plate, (c) CF grown without using any catalyst,(d) branched carbon fibers obtained at 750 °C, with Ni sitting at the center, and (e) VGCFs obtained by pyrolysis on the Ni coated quartz substrate (Source: (Pradhan 2003).

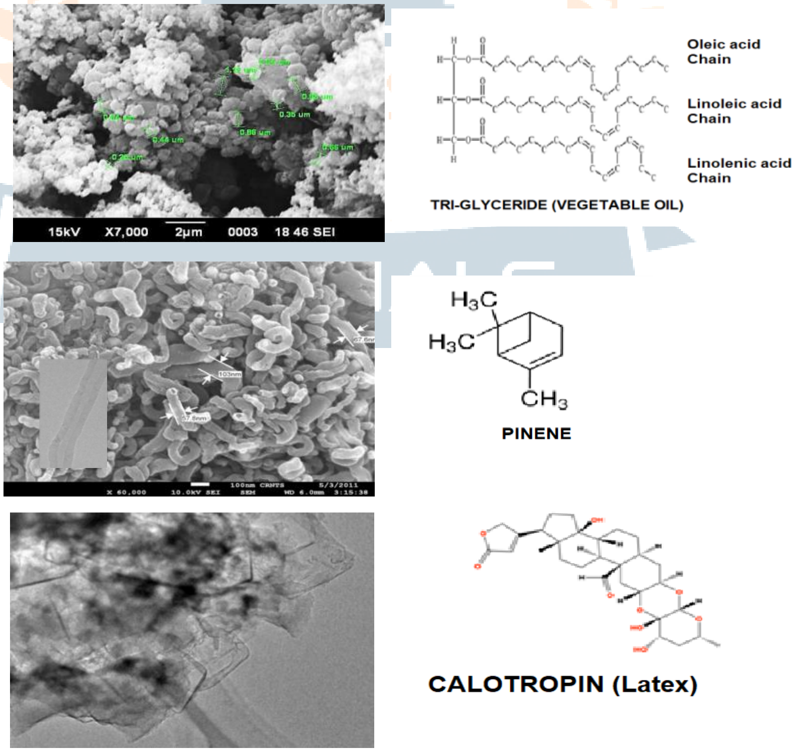


Figure – 14: SEM images of CNMs obtained from different plant metabolites along with their Molecular structure showing (a) Clusters of beaded structures obtained from typical vegetable oil composed of triglycerides (Source: Tripathi 2012)(b) Tubular structure synthesized from α-Pinene, (c) HRTEM images shows unique rectangular multi-layered graphene nano-sheets obtained from the latex of Calotropis gigantea composed of Calotropin.

Role of Nano-Catalysts in CNF Synthesis

Though it is not necessary to use nanocatalysts when plant parts are used as precursors because often plants do contain trace metals and it is expected that they may be acting as catalysts. However, when hydrocarbon-rich plant metabolites are used as precursors, nano-metal catalysts do decide the morphology of the CNM. For example, as it can be seen in the HRSEM images of CNF obtained from pyrolysis of maize cob-hair shows different types of CNMs (Shukla Thesis 2012). These CNMs were further characterized by XRD and Raman spectroscopy confirming their graphitic nature. The use of CoNP as a catalyst produced CNB; NiNP produced branched CNF and FeNP produced CNF with a broken surface(Figure –15).

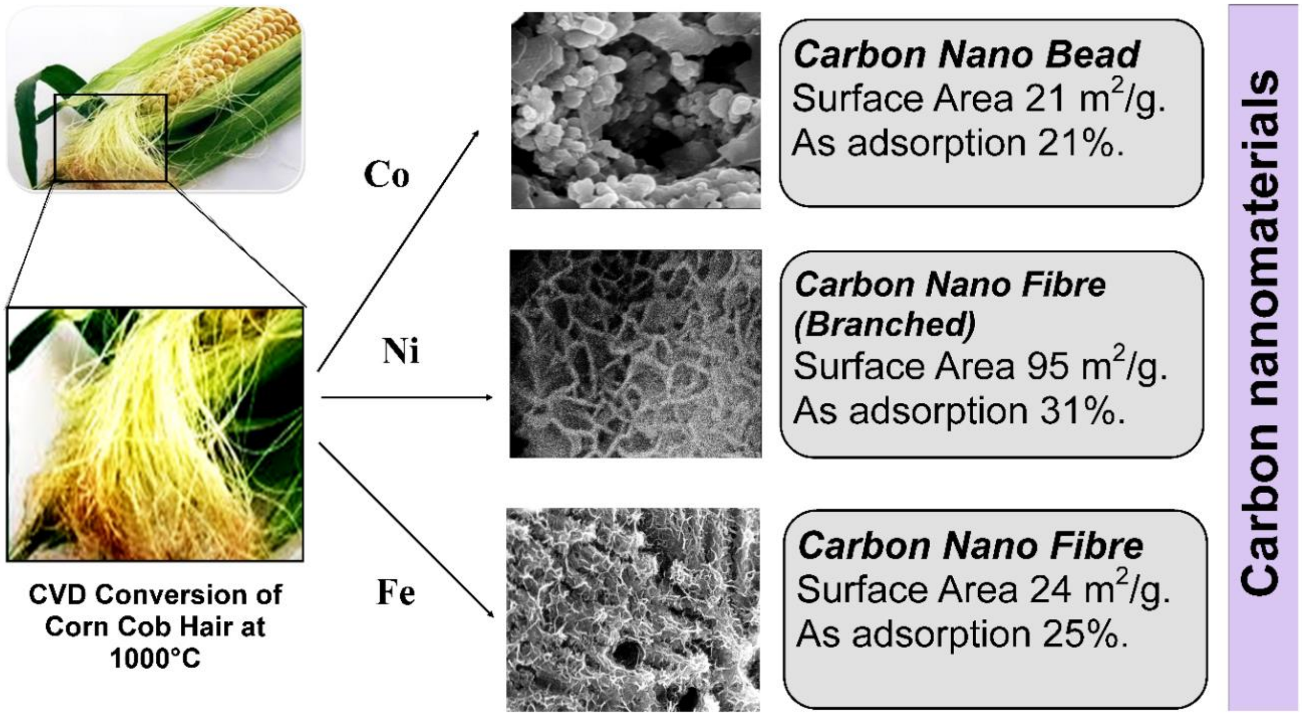
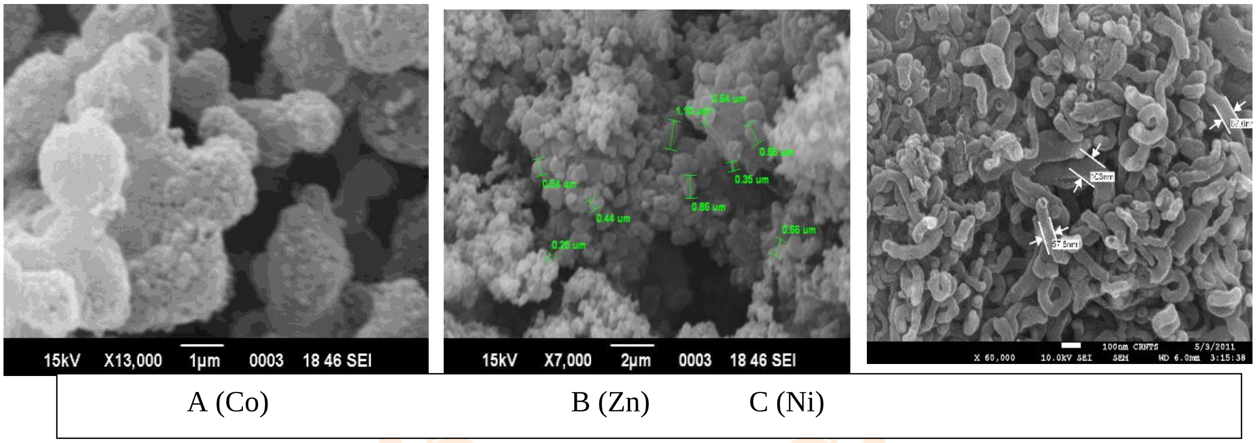


Figure 15: HRSEM images showing the impact of three different nano-catalysts (Co, Ni, and Fe) on the morphology of CNF synthesized using Corn Cob-hair as a precursor (Source: Shukla Ph.D. Thesis Solapur University, 2012)

Similarly, when neem oil was pyrolyzed using the CVD technique (Tripathi 2012)in the presence of different metal NP as catalysts it produced CNF of different morphologies (Figure-16).However, SEM images show that plant parts are a better source to get unique morphologies of CNF having high surface area and they will bea better material for the removal of HMs from the aquatic medium.



A (Co) B (Zn) C (Ni)

Figure 16: HRSEM images of CNM synthesized using the CVD method and Neem oil as precursor showing the impact of three different nano-metal catalysts (A)) CoNP yielded globular CNF having a rough surface, (B) ZnNP yielded beaded CNF (C) NiNP yielded tubular structure(Source: Suman Tripathi, Ph.D. Thesis, Solapur University, 2012b).

Suitability of CNF From Agro-Waste for Removal of HM

Many of the agro-wastes such as bagasse, non-edible seeds, post-harvest Farali, or stubble that are left in the field after grain harvestingsare burned in the field, causing air pollution (Figure-17). Such agro-wastes have been used to produce CNF by pyrolytic CVD process; which shows unique CNF structures.

Figure – 17: Showing burning of remaining wheat stubble after harvest, being burnt.

An ideal adsorbent for removal from water should have a high surface area and high adsorption and desorption capacity; should be environmentally benign, inert, and insoluble in water, non-toxic to aquatic flora and fauna at low concentration, recyclable, and economically viable at mass production. CNF suffices these needs. Because the rough surface of CNF is a dynamic system that interacts with the environment; the multi-layered graphitic structure, is helpful in its use in removing HM and other organic and inorganic pollutants from aqueous media. It adsorbs water; as well as has thermally assisted desorption properties. Moreover, the covalent chemistry of carbon with oxygen, hydrogen, and nitrogen provides facile routes for the functionalization of carbon surfaces with various molecules; thus, enhancing its capacity in its use as a filter system. CNM can satisfy most of these requirements (Machida et.al. 2006; Sharma et.al. 2009). Moreover, graphitic CNF and CNTs possess many dangling bonds on the surface and edges of CNF, which are conducive sites for adsorbing HM from water effectively Tripathi et. al. (2012) (Figure-18).

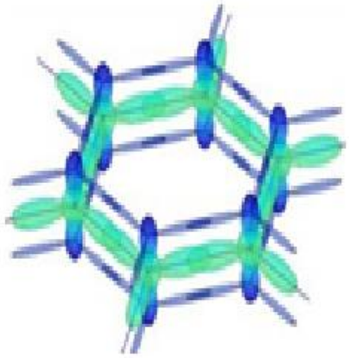


Figure – 18: Dangling bonds of a monolayer of graphene

CNF Derived from Agro-Waste for Removal of the Heavy Metals

The CNF derived from agro-waste can be envisaged, namely as (i) Adsorber, and (ii)Filter. It cancreate a linkage between adsorption and electrochemistry, thereby the synergistic interaction will be expected for enhanced HM removal.Some experimental work has shown that as compared to CNT, CNF has a better adsorption capacity for dyes(Rodriguez et.al. 2010). The CNF-based membrane has been used for oily wastewater treatment (Al-Anzi and Siang 2017).

CNF for Adsorption – adsorption is a surface phenomenon in which absorbable solute in a solution comes into contact with a solid, and due to intermolecular forces of attraction brings the solute molecules from the solution get deposited on the solid surface. The adsorption could be Physisorption i.e. when the adsorbate is bound to the surface by weak van der Waals forces; Chemisorption, which takes place through covalent bonding of the adsorbate, or Adsorption due to Electrostatic attraction.

The adsorption is assessed by (a) Adsorption isotherm models that analyze the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at a constant temperature and (b) by the Kinetic model, which analyses the rate and the mechanism of adsorption processes (e.g., mass transfer and chemical reaction). There are many Kinetic models e.g. simple-first-order, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models; using them the adsorbate-adsorption phenomenon is disclosed.

CNF for Filtration–CNF, and membrane technology are evolving as important tools for treating not only HM-polluted water by nanofiltration, but also organic pollutants, pathogens, and viruses.The main advantage of using CNF in membrane filtration is that it will help in overcoming membrane fouling, concentration polarization, hydrophilicity, and morphology. Modification and functionalization of CNM are offering advanced hybrid membranes.To be used for filtration CNFhas distinctive properties of sp2 hybridization, where carbon molecules bond with the characteristics of physical and chemical parameters at the nanoscale. The surface adsorption ofoxidized CNF becomes highly effective in removing Heavy-metal ions, from liquid wastewater.

The functionalization of CNF is done by covalent bonding and non-covalent bonding. The common chemical method of functionalization is by sidewall hybridization of C atoms from sp2 to sp3 or by defect formation. Physical method of functionalization is also used, which encompasses (i) Polymer wrapping by Van Der Walls force, π- π stacking; (ii) Surfactant absorption, or (iii) Endohedral method based on capillary effect.

An account of the removal of various HM using carbon-based materials i.e. CNF and AC is discussed in this section. Like CNF the chemical structure of AC is also a disorganized graphite form. The basic chemical structure of activated carbon is closely approximated by the structure of pure graphite and CNF. The layers are held by carbon-carbon bonds. The large surface area of the AC, due to its particle size and pore configuration, allows for adsorption. Factors that decrease solubility and/or increase accessibility to the pores improve the performance of the AC filter.

Antimony (Sb)

TheEPA has approved Coagulation/Filtration, and Reverse Osmosis for the removal of antimony from water. However, efforts on using various carbon materials(Hu et.al. 2022)have been tried forthe last two decadesfor the removal of Sb; such as AC(Navarro and Alguacil 2002),CNT(Salam and Mohamed,2013), carbon nanosphere(Ren et.al. 2020), biochar(Vithanage et.al., 2015), graphene,and graphene-oxide (Leng et.al. 2012,Yang Xet.al. 2015); using their adsorption property. The use of soybean stover-derived so-called biochar by the CVD method, which exhibited CNF-likeproperties; showed that the adsorption capacity of Sb when surface complexed with acid biochar was85% forantimoniteSb(III), and only 65% for antimonate Sb(V). Further standardization of this process will lead to a higher percentage of removal of Sb(Vithanage et.al. 2015).

Luo et.al. (2015) used CNF decorated with zirconium oxide (ZCN) to remove Sb(III) and Sb(V) from water. As revealed by XPS analysis the incorporation of zirconium was helpful in forming an ionic bond with Sb(III) and Sb(V).ZCN showed a maximum Sb(III) and Sb(V) adsorption capacity of 70.83 and 57.17 mg/g, respectively. The adsorption process between ZCN and Sb was identified to be exothermic and followed an ion-exchange reaction. Moreover, based on the density functional theory (DFT) calculations, it was found that the Sb(III) formed Sb-O and O-Zr bonds on the surface of the tetragonal ZrO_2 (t-ZrO_2) (111) plane and monoclinic ZrO_2 planes (m-ZrO_2) (111) plane when it gets adsorbed. Only an O-Zr bond was formed on the surface of t-ZrO_2 (111) plane and m-ZrO_2 (111) plane for Sb(V) adsorption. The adsorption energy of Sb(III) and Sb(V) onto the t-ZrO_2 (111) plane were 1.13 and 6.07 eV, which were higher than that of m-ZrO2 (0.76 and 3.35 eV, respectively).

AC modified with $FeCl_3$ has also been used for the removal of Sb (Yu Ting-Chao et.al. 2021)

Arsenic (As)

The presence of Arsenic in water is due to arsenic-based pesticides, deposits of natural minerals, and inappropriate disposal of arsenic-based reagents or chemicals. The arsenate and arsenite form of Arsenic is lethal to living beings as it interacts with the sulphydryl group of the cells causing respiration to malfunction and affecting mitosis and cell enzymes. Moreover, Arsenic disturbs the environment also (Jaishankar et.al. 2014). Iron-impregnated into pores of AC has been found to be very effective in arsenic removal. Oxyanionic arsenic species such as arsenate and arsenite(Weifang et.al. 2007)

CNF having three different surface areas was synthesized by pyrolyzing Maize cob hair using the CVD method (Figure 12).Adsorption of Arsenic by CNF assessed by Chand Pasha et.al.'s method; showed that CNF (having a surface area of 38.007) could adsorb as much as 34% Arsenic; CNF (surface area of 31.118) adsorbed 28% whereas CNB (surface area of 21.379) could adsorb only 16% arsenic; confirming the impact of surface area on the adsorption capacity (Shukla Thesis 2012).

Carbon nanosphere synthesized from Castor oil in a thermal catalytic vapor reactor using Co nanoparticles as catalyst showed similar graphitic nature as CNF (as observed by XRD and Raman Spectroscopy). The surface area of these carbon nanospheres was30.88 m2/gm and it could adsorb as much as 49% Arsenic in 12 hr of exposure(Tripathi et.al. 2012) (Figure-19)

Since, graphitic CNF and CNTs possess many dangling bonds on the surface and edges of CNF, which are conducive sites for adsorbing HM like Arsenic from water effectively Tripathi et. al. (2012). They have attributed the high uptake of Arsenic by CNF is due to the presence of more dangling bonds (Figure-18),on the surface and more surface area. Moreover, CNFs can be tuned or manipulated by ball milling to create a broken graphitic structure, with more dangling bonds thus providing a greater number of reactive sites. Hence surface modifications led to an increase in surface area, and changes in surface morphology led to improved adsorption capabilities.

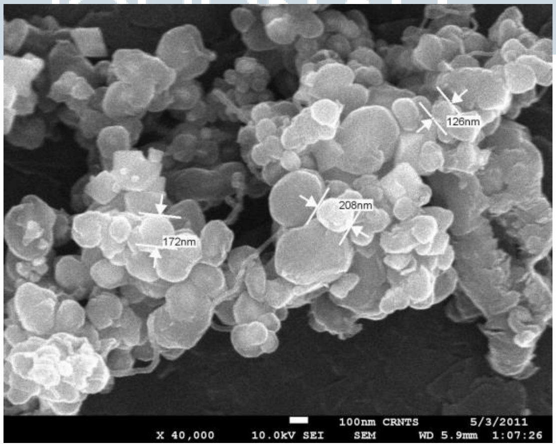


Figure – 19: HRSEM micrograph of CNMs synthesized at 9000 C, in presence of Ar gas using castor oil as precursor and Ni as catalyst; showing Ni nanoparticles entrapped in graphitic layers having almost spherical conformation, the size of the particle varies from 200 – 1000 nm.(Source Tripathi et.al. 2012)

Bismuth (Bi)

Though Bismuth is the only non-toxic HM. Butthe salt of Bi if consumed is highly toxic. In water,all bismuth salts form insoluble compounds. Bismuth is stable to oxygen and water but dissolves in concentrated nitric acid. There is a report onBi-based photocatalytic disinfection of water(Kumar Rohit et.al. 2021).There are Bi-based sorptive materials also that are used for the removal of contaminants from water. Hence the Bi remains very confused and less understood HM (Yang and Sun 2011). But looking at the data available researchers have not felt the need toremove Bi from water.

Cadmium (Cd)

As mentioned above different types of agro-waste without carbonizing have also been tried for the removal of Cde.g.,wheat-stover(Tan and Xiao 2009),saw-dust dust (Memon et.al. 2007), orange peels(Li Xet.al.2007), etc. However,phytoremediation has not been very popular because of the inconvenience of separation in multi-metal ions solution, poor performance, and low absorption efficiency.

Hema and Srinivasan (2011) investigated AC prepared from Agro-Industrial by-products (coconut and neem oilcake) for removal of Cd(II) from wastewater, and demonstrated that the adsorption process corresponds to the Pseudo-second-order-kinetic model and the Equilibrium adsorption data fit well with Temkin isotherm model. The adsorption capacity 'b' calculated from the Langmuir isotherm was 188.68 mg/g for coconut-derived AC and 23.7 mg/g for neem-derived AC. The mechanism of adsorption was ion-exchange pH played important role in adsorption. Desorption studies with 0.1M hydrochloric acid up to five cycles recovered from 99 to 89% in the case of coconut oil cake-derived AC and 97 to 86% for neem oil-cake-derived AC.

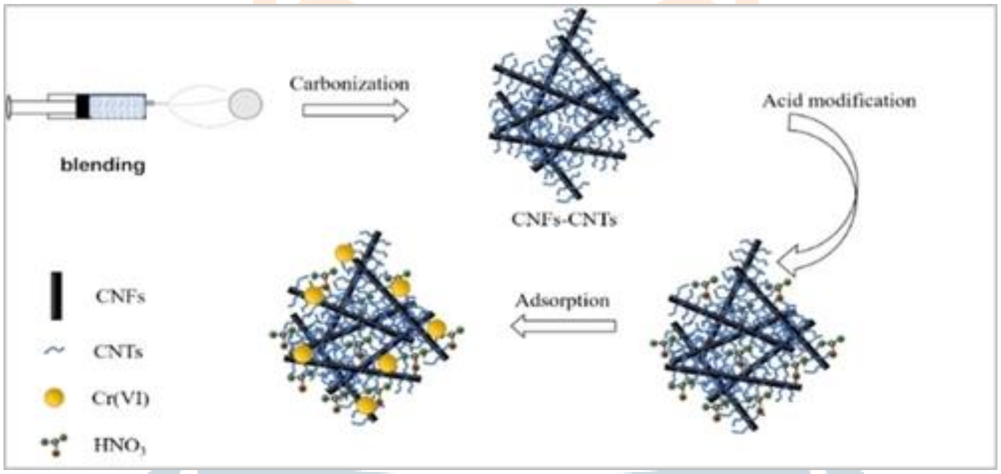
A comparative trial for assessing the Cd ion adsorption capacity from water, by four types of carbonaceous material (Fly-ash, AC, CNT, and CNF) was done (Fahadet.al. 2013). To calculate the percentage removal of cadmium adsorption isotherms were usedto find the model of the adsorption behavior. CNF showed higher absorption i.e. 34% than CNT (27%). The Correlation coefficients for kinetic models of cadmium adsorption for both CNTs, and CNFs, AC were of Pseudo-second order. CNF used were10–40 μm long and had200–500 nmouter diameter and 1–10 nm inner diameter. The surface area of CNT and CNF was not mentioned by the author, and neither was the precursor used for CNF. There is a need for choosing CNF with a higher surface area to increase the adsorption capacity as many have noted that the adsorption is directly proportional to the surface area.Chitpong, (2016) has shown thatPoly(acrylic acid) and poly(itaconic acid) modified electrospun cellulose nanofiber membranes offer a high productivity platform for selective removal of Cd, from impaired water. It is a grafted polymer, which plays a role in the membrane ion-exchange performance, with dicarboxylate groups showing higher selectivity for Cd over competing for divalent ions. He has recommended the electrospinning technique as it offers ease to control membrane thickness and thus permeability. Using this CNF membrane, it was easy to recover Cd using EDTA from membrane binding.

Though many carbon-based adsorbentshave been researched for the removal of Cd from water, however, all of them have not yet met the need to adsorb 100% Cd, restricting their use at the mass level.This has prompted many researchers to make efforts.

Cerium (Ce)

Sunet.al. (2018) have used polyacrylonitrile (PAN) nanofiber-derived CNF-Blended with CNT to get the CNF films for the removal of Co and Ce(VI). It was found that the specific surface area of CNF blended with CNTs increased to 37.627 m2/g and the pore volume to 3.832cc/g. This porous adsorption material showed an adsorption capacity of 25.17mgg−1 within 20 min. At equilibrium, the adsorption capacity was 76.62mgg−1.(Figure 20)

AC synthesized from banana peel showed 98.35% adsorption efficiency (Somaia et al 2015) and the cane of Arundo donax used for removal of Cd(II) from the water showed 90% adsorption efficiency(Basso et al 2002)



Figure–20:Graphical abstract showing polyacrylonitrile (PAN) nanofiber derived CNF-Blended with CNT to get the carbon nanofiber films for removal of Co and Ce(VI).Source: Sun et.al.Chemistry Select 2018, 3(44). [Ask Wiley Journal]

Chromium(Cr)

For the removal of chromium from waterfunctionalized CNF was used, calling it a green-functionalization (Zahari 2016). The FTIR analysis confirmed the functionalization parameters for CNF to be 4hrs 25min with 150 rpm with water was suitable and optimal. The chromium adsorption capacity of water-functionalized CNF was assessed using AAS and showed 40.13% absorption capacity. If CNF with a higher surface area could be fabricated and then water functionalized, it will enhance the adsorption capacity. However, selectivity to HM will still remain a concern with this method.

Magnetic nanoparticle (cobalt Ferrite) decorated CNF (PG-C) and graphene (PG-C), synthesized by solvothermal method; was used for the removal of cationic lead and anionic Cr(VI) ions (Chella Santhosh et.al. 2017). The optimized adsorption performance parameters were time, pH, adsorbent dosage, and initial ion concentrations. Kinetic and isotherm models were examined to elucidate the adsorption process; which revealed that pseudo-second-order and Langmuir models, respectively explained the sorption mechanisms for both the studied pollutants on CNF and Graphene. The adsorption capacity of PG-C and CNF-C for Pb(II) ions was 131.40 and 42.90mg g−1, respectively. adsorption capacity of PG-C and CNF-C for Cr(VI) ions, was 68.85 and 51.07mg g−1 respectively. The spontaneous and endothermic nature of the reaction was suggested by thermodynamic analysis. Cr(VI) ions adsorption was higher at acidic pH and decreased with the increase in pH. Whereas Pb adsorption was found to be low at acidic pH and reached a maximum at pH 4.0–7.0. The stable reusable capacity of the adsorbents was noted for five cycles.

A CNF web was synthesized byelectrospinning of PAN and PVP (5:5) at 4500 C thermal treatment and then hydroxylating it with NaOH. It was used for the adsorption of Cr(VI) under different parameters such as pH, contact time, and temperature. The results show that it efficiently adsorbed 56.9 mg/g for Cr(VI) ions. Moreover, the adsorption capacity remained up to 55%after five cycles, indicating that this modified CNF webis apromising material for application in Cr(VI) ions adsorption(Xinying et.al. 2018).

Cobalt (Co)

For Co removal, MWCNT and AC have been used. The effects of contact time, pH, ionic strength, foreign ions, temperature, humic substances (HSs), and the addition sequences of Co(II)/HSs on Co(II) sorption on magnetic MWCNT/iron oxide composites (magnetic MWCNT/IO composites) have been noted under ambient conditions(Qi Wanget.al. 2011). Adsorption of Co(II) increased with increasing pH. The main sorption mechanism of Co(II) at low pHwas ionic strength and foreign ion-dependent and outer-sphere surface complexation, whereas the ionic strength and foreign ion independent of Co(II) sorption at high pH values indicated that inner-sphere surface complexation was predominant sorption mechanism. It fitted the Langmuir model. The temperature-dependent sorption isotherms suggested that Co(II) sorption was a spontaneous and endothermic process. The removal of Co(II) by the magnetic MWCNT/IO composites was affected evidently by the presence of HSs and by the addition sequences of Co(II)/HSs. The authors suggested the interactions between Co(II) and HSs to determine the mutual effects of inorganic and organic matter on the removal of metal ions in environmental pollution management.Activated carbon from apricot stone along with H_3PO_4 has been studied forthe removal of Co^{2+} (Abbas et.al. 2014).The adsorption system is described by the pseudo-second-order kinetic model. The Freundlich model fits the data with a monolayer adsorption capacity of 111.11 mg/g at pH 9. Moreover, the enthalpy and free energy indicate an endothermic and not spontaneous process. Adsorption was found to be due to interaction between functional groups of Carbon and Co^{2+}. Success with AC and MWCNT has opened the way to study the use of CNF for Co removal from water.

Copper (Cu)

Removal of Cu from water is being efficiently done through reverse osmosis, distillation, precipitation, ion exchange filtration, and adsorption on activated carbon. Nowadays CupriSorb is available in the market for rapidlyremoving Cu, it extracts all types of copper, including chelated copper, and remains effective until it turns a deep blue-black color. Such efficient methods of removal of Cu has not prompted to useof various types of CNM. However, Rao et.al. (2006) have used activated carbon prepared from Ceiba pentandra hulls, an agro-waste, for the removal of copper and cadmium from water. Adsorption was measured under different parameters (equilibrium time, effect of pH, and adsorbent dose).Functional groups C O and S O present on the surface of carbon were the reason for good sorption potential for both copper and cadmium at pH 6.0. The maximum adsorption capacity of copper and cadmium as calculated from the Langmuir isotherm were 20.8 and 19.5 mg/g, respectively and sorption kinetics of the copper and cadmium have been analyzed by Lagergren pseudo-first-order and pseudo-second-order kinetic models. The desorption studies using 0.2 M HCl,showed that the maximum desorption of copper was 90% and for cadmium, it was 88%.

A helical CNF was shown to be a potential material for the adsorption of Cu2+, having an isoelectronic pH of 1.9(Garcia-Diaz et.al. 2018). The influence of parameters on adsorption considered wasstirring speed, temperature, pH, and adsorbent concentration.The pH has a great influence on Cu2+ maximum adsorption capacity reached at a pH of 10. The experimental data fitted well to pseudo-second-order kineticand Langmuir isotherm models at T = 298 Kand pH = 4. Endothermic and physical nature adsorption was noted. Metal elution was carried out with 4 M H2SO4 solution, at 30 min, reaching an elution percentage of 96%. The Cu2+ adsorption is explained by the particle diffusion model. It was interesting to note thatan increasein the temperature did not influence the adsorption capacity.

Gallium (Ga)

A study using tea waste to investigate its adsorption potential for Ga, under different parameters (initial concentration of gallium ions, adsorbent dose, and temperature on adsorption performance) revealed that itfitted satisfactorily with the Freundlich isotherm model; and pseudo-second-order kinetic model with correlation coefficients >0.99. Thermodynamic parameters, including the Gibbs free energy, enthalpy, and entropy, indicated that the gallium adsorption of aqueous solutions onto tea waste was feasible, spontaneous, and endothermic in the temperature range of 288 K to 318K (Wei-Lung et.al. 2010).CNT and mesoporous AC has also been used as adsorbent for the removal of Ga from wastewater(Ying Xiong et.al 2020 and Bernabé et.al. 2013).

Iron (Fe)

As for other HM, for Fe also MWCNT has been successfully used. The optimum removal of98.97% total Fe is reported at pH 8.2 andD/C= 5.00 (Alimohammadi et.al. 2017).OxidizedMWCNT has also been studied as a filterfor iron removal from water.The efficiency of filtration was directly affected by the concentration of metals in the aqueous solution, pH, and the filter mass. The regression analysis data showed there wasan ion-exchange mechanism involving surface functional groups of oxidized MWCNTs(Elsehly et.al. 2018).

AC prepared from corn cobs (CAC) and luffa sponge (LAC) modified with aluminum chloride (Al-CAC and Al-LAC) were investigated for the adsorption of Fe(III) from aqueous solution (Nohier El-Bendary 2021), in batch experiments mode. It showed maximum removal efficiencies of 99.1%, at pH 8 by aluminum chloride (Al-CAC) and 96.7% by Al-LAC.The maximum adsorption capacity was 366.7, and 348.8 mg/g for Al-CAC, and Al-LAC, respectively. The adsorption data fitted well with the Langmuir model for Al-CAC, and the Freundlich model for Al-LAC. The experimental data fitted well with the Pseudo-second-order model (R2 = 0.999). The thermodynamics showed spontaneity with increased randomness of the adsorption process.

Granular AC was also found to bean effective low-cost adsorbent for Fe(III) removal from aqueous solutions.

Lead (Pb)

There had been many studies on the use of CNF and its composites for the removal of lead from the water. Ahmed et.al. (2010) attempted to study the sorption of Sb from water using CNF grown of powdered AC (synthesized from palm kernel shell). The optimum pH was noted to be 5.5. The interesting result was that the adsorption capacities of the CNF to uptake Pb increased from 16 to 89 mg/ g-l with increasing the initial Pb concentration from5 to 70 mg L-l. Sorption process fitted well by Langmuir isotherm and the equilibrium sorption capacity of Pb ion was found to be 100 mg g-l,

For the removal of Pb(2+), Chakraborty et.al. (2011)used a multiscale web of micron-sized activated carbon fibers (ACF)and CNF which was prepared by growing CNFs on activated ACFs via catalytic CVD and sonication, to remove catalytic particles from the open pores of the CNFs. This ACF/CNF had a total pore volume of 0.537 cc/g;

Hossein et.al. (2012) used CNF synthesized by the CVD method from cyclohexanol a toxic secondary alcohol. The substrate used was Kaolin and Ferrocene as catalysts. CNF thus produced was modified with a mixture of nitric acidand sulfuric acid to enhancethe adsorption capacity of Pb2+. The nature of the surface changed after acidic treatment, there was an increase in surface functional groups oxygen-containing positive and negative charges, which made CNF adsorb more positive ions, which significantly increased after the oxidation process. The surface activity as estimated by Boehm's titration was 211m/g–1 was obtained. Kinetic and thermodynamic reaction studies concluded that the adsorption process is spontaneous and endothermic. Equilibrium data fitted well to theLangmuir model and the pseudo-second-order kinetic model.

In a trial, activated carbon nanofibers (ACNFs) fabricated from PAN and zinc oxide (ZnO) via electrospinning (ACNFs/ZnO), hada specific surface area of 163.04 m2/g as compared to 67.6 m2/g of only ACNFs. The FESEM analysis exhibited that composite ACNFs possessed more compact fibers with the presence of ZnO beads and smaller fiber diameters whereas neat ACNFs possessed more aligned nanofibers with larger fiber diameters. The composite ACNFs hada higher adsorption capacity of Pb (120.3mg/g) than that of the ACNFs(77.6 mg/g). The adsorption mechanism is best fitted with the Freundlich model(Norfadhilatuladha et.al. 2017).

In another attempt, the surface modification of the electrospun CNF (ECNFs) successfully enhanced the adsorption capacity and the adsorption rate of Pb2+ ions from aqueous solutions. The efficiency of ECNFs in removing Pb2+ ions was improved via a surface modification to increase their hydrophilicity. (Thamer et.al. 2019). Efforts were made to controlthe properties (surface area, porosity, diameters) of electrospun CNFs during fabrication, to increase the hydrophilicity and in turn its efficiency in removing lead ions (Pb2+)from water. The surface modification was done by oxidizingpristine ECNFs, followed by covalently bonding melamine, andpoly(m-phenylene diamine) for forming melamine-functionalized ECNFs (melam-ECNFs) and poly(mphenylenediamine)-functionalized ECNFs (PmPDA-ECNFs), respectively. Adsorption ability was studiedunder different parameters(pH solution, contacttime, initial concentration, and temperature) and the adsorption process was analyzed isothermally, andkinetically. The values of the thermodynamic parameters suggested that the adsorption of Pb2+ ionsonto the functionalized ECNFs was endothermic and spontaneous, except with melam-ECNFs wasexothermic.

Mercury

In 1989 Bourke and Mazzoni had given a presentation during Gas Conditioning Conference and said that under normal operating conditions, a properly designed activated carbon bedis being used to remove mercury for many years.

Ahmad Mudasiret.al. (2020) fabricated what they called a magnetic mercury trap (MSTT) for removing Hg(II) from wastewater. Fabrication was done in two steps; first, a polymer tubular fiber (PTF) was prepared using Polydimethylsiloxane (PMS), 1,2-dichloroethane (DCE), and α,α,0-dichloro-p-xylene (DCX). This PTF was then carbonized in pyrolytic conditions to get carbon tubular fiber (CTF), which was sulfonated using sulphuric acid. The product had high surface area with dense andflexible chelating arms (-SO3H groups). It showed Hg(II) adsorption capacity of 970.87 (mg/g) as obtained from the Langmuir isotherm model. Maximum adsorption (>99 ± 0.5)occurred at pH 6.8. Moreover, this adsorbent showed good regenerationpower and adsorption capacity greater than 90 ± 0.5% in the fifthcycle. In another study removal of nitrogen-doped porous CNF for Hg2+ ions was demonstrated byBae and Hong (2021) using a simple adsorption test apparatus and 5, 10, 15, 20-tetraphenyl porphine tetrasulfonic acid (TPPS) as an indicator, at pH 7.AC has been accepted as the material for the removal of Hg. Calgon Carbon – a Kuraray company has a patent for mercury removal using AC and is producing granular and powder AC for Hg removal.

Nickel (Ni)

Activated carbon cloth (ACC) is known to be used in water filters. Using ACC a study was made to coat it with benzo-crown ethers and use it for the removal of three HM ions Cr(III), Co(II), and Ni(II). A comparison of adsorption on ACC and ACC modified with benzo-crown ethers. Anenhancement in adsorption capacity was noted in modified ACC for the three ions, which was found to be due to the type and cavity size of crown ethers, the size and the form of the ions, and their interactions with adsorbate species on the ACC surface. All the isothermsfitted better withthe Freundlich model(Duman and Ayranci 2010).

Chitpong (2016) and Chitpong et.al. (2017)developed high-productivity cellulose nanofiber cation-exchange membranes for the removal of cadmium and nickel from wastewaters, this nanofiber-based macroporous ion-exchange membraneshas high surface area-to-volume ratios and highcapacities based on ligand chemistries that are selective for the target Heavy-metal ion(s).Cellulose-based nanofiber membrane was produced by the electrospinning method. A polymeric ligand with carboxyl functional groups was incorporated on membrane fiber surfaces so as to achieve high grafting densities bythe “grafting to” method. poly(acrylic acid) and poly(itaconic acid) modified electrospun CNF, which showed 6 to 15 times higher than commercial ion-exchange resins. Moreover, these membranes were reused at least five times without a decline in performance. The functioning of polyacid-modified CNF cation-exchange membranes was not diffusion limited, as it was shown by flow rate-independent dynamic binding capacities. The ion-exchange performance of the membrane was affected by the graftedpolymer, e.g. the membranes with dicarboxylic acid functional groups exhibited a higher Cd staticbinding capacity than the monocarboxylic acid functional groups, they exhibited alower Cd dynamic binding capacity. The swelling and collapse behaviorof polymer onmembrane pore surfaces between monovalent and divalent ions binding causedan increase in mass flow rate in the dynamic system. Thus, this polymer behavior is envisaged to be used incontrolling the binding and regeneration cycles of metal removal and recovery processes.

Tellurium (Te)

Mal et.al. (2017), studied the continuous removal of tellurite (TeO32-) from synthetic wastewater and subsequent recovery in the form of elemental tellurium using an up-flow anaerobic granular sludge bed (UASB) reactor operated at 30°C; which was fed with lactate as carbon source and electron donor at an organic loading rate of 0.6g CODL-1d-1. The process involved feeding the stabilized reactor with 10mg TeO32-L-1 for 42 d before increasing the influent concentration to 20mg TeO32-L-1. 98 and 92%, Tellurite removal was obtained respectively, from 10 and 20mg TeL-1. Various analysis methods (XRD, Raman spectroscopy, SEM-EDX, and TEM) confirmed the association of tellurium with the granular sludge, typically in the form of elemental Te(0) deposits. Later they applied an extracellular polymeric substances extraction method to the tellurite-reducing sludge and recovered up to 78% of the tellurium retained in the granular sludge. This is a continuous tellurite removal process from tellurite-containing wastewater coupled to elemental Te(0) recovery.

Thallium (Tl)

There are reports of the use of Biochar for the removal of Tl. Biochar does display CNF-like properties. Li Huosheng et.al. (2019) have reported the removal of Tl (I) from wastewater using hypochlorite oxidation coupled with magnetite-based biochar as adsorption.The biochar was derived from watermelon rinds The hypochlorite addition enhanced the Tl(I) removal under the normal pH range (6-9) to 1123 mg/g.The advantage of magnetic biochar is that it can be regenerated using 0.1 mol/L HNO3 solutionsin 5 min, with a Tl desorption efficiency of 78.9%. The Tl removal efficiency was constantly higher than 98.5% during five consecutive recycle tests. Oxidation, surface precipitation, pore retention, and surface complexation were the main mechanisms for Tl(I) removal. The re-dissolution of Tl compounds and ion exchange of Tl cations with proton were the main mechanisms for adsorbent regeneration.

Later Liu Juanet.al.(2021)also tried to use biochar for the removal of Tl from wastewater. They used a composite of MnFe2O4-Biochar (MFBC). This composite was fabricated by the coprecipitation method. The specific surface area of MFBC was187.03 m2/g, At pH range of 4-11, it exhibited170.55 mg/g Tl(I) removal capacity, based on the Langmuir model (pH 6.0, a dosage of 1 g/L). The removal mechanisms included physical and chemical adsorption, ion exchange, surface complexation, and oxidation.

Xu Haiyin et.al. (2019) has reported that though there are many reported methods (adsorption, oxidation-reduction precipitation, solvent extraction, and ion exchange processes) for Tl removal, none of them suffice the need to remove it to a trace level of "µg L-1". Therefore, he has recommendedtryingto usethe combined multi-technology approach to enhance the removal efficiency. However, several fundamental issues, such as the comparative toxicity of Tl(I) and Tl(III), the confliction of hydrolysis constants, the interference of complexant ligands as well as the influence of redox potential, are still needed to be addressed for large-scale experiments and economic assessment for real Tl polluted wastewatertreatment.

Uranium

The technologies used for the removal of U(VI) from aqueous solutions are flocculation(Linand Harichund 2012), electrolysis(Fischer et.al. 2005),membrane separation(Qiu and Mao 2013),photocatalysis(Sarvanan et.al. 2014), precipitation(Alvarez et.al. 2007), and adsorption(Li M et.al. 2017). It is suggested that adsorption is a better method as it has high selectivity and is easy to operate(Santos et.al. 2011)even at low U(VI) concentrations from large-scale water(Li Let.al. 2015). Therefore, Ahmad et.al. (2020) experimented withhollow tubular nanofiber, having a good number of functional groups and high surface area, for adsorption of U(VI) fromwater. It showed quick iontransport capacity. A tubular hyper cross-linked polymer was fabricated in a single pot using α,α-dichloro-p-xylene (DCX) as a monomer. After carbonization, hollowtubular nanofibers (HTnFs) were obtained, which were modified with carboxylic (COOH) and sulfonic(SO_3H) groups toobtain HTnF-SO_3H and HTnF-COOH. Both showed U(VI) of greater than 90 ± 0.5% adsorption efficiencies under seawater conditions over a short period of10 min. The adsorption results were in agreement with theLangmuir model. Themaximum adsorption capacities of HTnF-COOH and HTnF-SO_3H were1928.59 and 1827.57 mg/g. These adsorbents act as good U(VI) adsorbents from large-scale water.

Earlier when the adsorption of U(VI) onCNFs was investigated by Sun et.al. (2016),it was found to be pH-dependent adsorption and the adsorption of U(VI) on the CNFs was significantly higher than theadsorption of U(III) at pH < 7.0. The maximum adsorption capacity of theCNFs calculated from the Langmuir model at pH 4.5 and 298 K for U(VI) was 125. Moreover, the CNFs displayed goodrecyclability and recoverability. It was suggested that theabundant adsorption sites (e.g., –OH and COOH groups) were responsible for higher absorption especially the–COOH groups were more responsible forU(VI) adsorption. Other findings were that the reducing agents of the RCH_2OHgroups were responsible for the highly efficient adsorption of U(VI) on the CNFs; at pH 4.5 the adsorption mechanism of U(VI)on the CNFs shifted from inner- to outer-sphere surface complexation with increasing initial concentration,whereas the surface (co)precipitate (i.e., schoepite) was observed at pH 7.0 by EXAFS spectra.

Vanadium (V)

Removal of Vanadium has been tried by different types of CNM e.g.MWCNT,Fullerenes, other Carbon Nanostructures(Yaqi Uet.al. 2017),and biomass of seagrass Posidonia oceanica (Pennesi et.al. 2013),

Palm fruit husk a lignocellulosic agro-waste was surface modified with a cationic surfactant Cetyl Trimethyl Ammonium Bromide (CTAB) and used for C removal (because the raw fruit does not absorb V). At pH 4 it showed high adsorption capability for V(V). The Adsorption equilibriumfitted to Langmuir, Freundlich, and Duminin Radushkevich (D-R) isotherm models; and the second-order kinetic model. Moreover, desorption was also feasible to recover V(V) from the spent adsorbent(Thamilarasi et.al. 2018).

Zinc

Earlier trials for the removal of Zinc (II) from the water was using purified MWCNT and SWCNT (Lu et.al. 2006), however, later plant-derived material such as hornbeam wooden sawdust(Kovacova 2019) has also been used.The use ofacid-treated CNF (COOH-CNFs) having 100-200 nm diameter and 30 μm length at pH 7 was later reported (Ali Atieh 2011). The simple adsorption process involved stirring zinc-containing water at 150 rpm for 2 hours;toremove 97% zinc from the water. This high removal efficiency was attributed to the strong affinity of zinc to the physical and chemical properties of the CNFs.

Concluding Remarks

Agro-waste-derived carbonaceous materials (AC, Biochar & CNF) have shown a potential for more efficient wastewater treatment due to their unique properties.The challenges associated with adsorption efficiency, toxicity, fouling, etc, are being met by modification/functionalization; which not only enhances the adsorption capacity but alsohelp in good dispersion insolvents and polymer matrices. This has led to the improvement of membrane properties and membrane performance. The progressive development of modified/functionalized carbonnanomaterials-based membranes is expected to arise as the best technology in wastewater treatment and many otherfields.However, more knowledge is needed to produce desired CNF, about their surface morphology and properties while functionalizing them. One consideration is the lack of literature on quantitative assessment of functional groups' role in HM ions sorption. Moreover, the current surface modification techniques demand high heat/pressure, strong acid/base, or intensive oxidation/reduction reactions. Even though biogenic CNMs are considered cost-efficient, there is a need to develop an efficient carbon nanomembrane. Further research is necessary for testing their efficiency for large-scale applications.Thus, innovative, low-cost, and environmentally friendly surface modification techniques and the use of agro-waste-derived CNF is one such proposal for the removal of HM from water.

CONFLICT OF INTEREST

Authors have no conflict of interest

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