JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

DEVELOPMENT OF ECOFRIENDLY MACROPOROUS HYBRID NANO-ADSORBENT FOR WATER REMEDIATION- A REVIEW

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Abstract

Water is essential for every form of life, for all aspects of socio-economic development, and for the maintenance of healthy ecosystems. To satisfy the need of water for increased population and industrial revolution water should be used very carefully. Nowadays Scientists are raising concerns and even industries are finding solutions to effectively treat their waste with lesser impact to the environment. To search for novel waste water treatment method for sustainable development is need of hour.

The need for novel waste water treatment methods for long-term development is very essential for sustainable development. The synthesis of green nanoparticles has numerous potential applications in environmental and biomedical fields. Despite significant research and development efforts in the field of bio-based nonmaterial's as advanced functional materials, we are still a long way from a bioeconomy-driven sustainable future planet. Present review focus on study of ecofriendly approach for development of nano adsorbent for water remediation.

Key Words: Nanoparticles, Water, Nano adsorbent, Biomedical

Introduction

Over the last century, water demand has increased six-fold and is currently increasing by around 1% annually. Due to the global shortage of clean water brought on by climate change and environmental degradation, it has become increasingly difficult to provide it to people. However, it is predicted that climate change will exacerbate the situation in nations already experiencing "water stresses" and create similar issues in areas that have not been severely affected. This is due to the increasing frequency and intensity of extreme events, such as storms, floods, and droughts. According to the most recent UN World Water Development Report, climate change will have an impact on the quantity, quality, and availability of water essential for basic human needs, weakening billions of people's ability to exercise their fundamental rights to clean water and sanitation. 2.2 billion People do not now have access to controlled drinking water, and 4.2 billion, or 55% of the world's population, do not have managed sanitation. A worsening of the situation will only make it more difficult to fulfill Sustainable Development Goal 6, which calls for universal access to clean water and sanitation by ten years. This goal is a part of the 2030 Agenda for Sustainable Development. **[1]** Nanotechnology is a branch of interdisciplinary research on particles of size 1-100 nm and is engaged with the design of nanoscale structures for advanced applications. This has been a fascinating field of this century. Fast developments have been found to take place in this fantastic field for the past decades. Nanoparticles are generally synthesized by using two strategies viz. top down and bottom up approaches. In top down approaches, the bulk materials are gradually broken down into nano level materials while in the bottom up approaches, the atoms, or molecules are assembled to molecular structures in the nanometer range. The bottom up approach is normally used for the biological and chemical synthesis of nanoparticles. Nanoparticles exhibit characteristic physical, chemical, electrical, thermal, magnetic, mechanical, dielectric, optical, and biological properties in contrast to bulk materials. Decreasing the dimension of nanoparticles has pronounced effect on the physical properties which are considerably different from the bulk materials. These physical properties are caused by a large number of surface atoms, high surface energy, reduced imperfections, and spatial confinement. The metal nanoparticles have a range of advantages over bulk materials due to their surface plasmon resonance (SPR), surface enhanced Raman scattering (SERS), and enhanced Rayleigh scattering. Numerous products already use nanotechnologies, such as sunscreen, cosmetics, textiles, and sporting goods. Additionally, nanotechnology is being created for use in biosensors, drug delivery, and other medicinal applications. Additionally, nanotechnologies are being created for environmental applications, such as the removal of environmental contaminants.

Agricultural waste is widely accessible and has a lot of potential for use in the creation of adsorption materials. The creation of inexpensive and ecologically friendly adsorbents is acknowledged as being made possible by the surface chemical modification of agricultural waste such as loofah fibre. The bio-based and renewable materials widely existing in nature, is mainly made up of hydrophilic cellulose, hemicellulose, and hydrophobic lignin with high cellulose content, and contains proteins and alkaloids as well.

Besides, it is called a plant based material consisting of natural vascular bundle tissue of fibrous reticular structure to facilitate the 4 rapid transports of ions. Eco-friendly carbon based materials have great applications in the domain of adsorption. Renewable materials like loofah, almond chaff and carboxymethylcellulose (CMC) can be easily processed into porous material with complete structures because of light-weight, good toughness, wear resistance, and high resilience. This structure can be well-preserved after carbonization. In recent years, green production of metallic nanoparticles has emerged as a fresh and exciting area of study. The creation of green nanoparticles has grown in significance over the past few years due to its many advantages, including ease of scaling up for large-scale synthesis, low cost, good stability of the nanoparticles produced, and non-toxic byproducts. Green synthesis has drawn attention for the synthesis of different metal and metal oxide nanoparticles since chemical synthesis methods result in the presence of harmful chemical species adsorbed on the surface of nanoparticles. [2]

Novelty and Scope of the Review

The nanomaterials have numerous applications in industrial, biomedical, and electronic fields. Hence the synthesis of nanoparticles with different size and shape has been a matter of research interest. Nanoparticles of noble metals like gold and silver gained much attention because of their inertness and extraordinary electronic, chemical, and optical properties. There are various physical and chemical methods such as laser ablation, chemical reduction; photochemical reduction, co-precipitation, and ultrasound irradiation are extensively used for the synthesis of nanoparticles which are non-eco-friendly as well as costly.

Wastewater is defined as water whose physical, chemical, or biological characteristics have changed as a result of the addition of contaminants such pathogens, heavy metals, organic or inorganic compounds, or other toxins that render it unhealthy for the ecosystem. Industries all over the world have implemented different plans to cleanse wastewater before releasing it into the ecosystem, and a number of new ideas and technologies are quickly displacing the conventional approaches.

Specifically, potable water is scarcely available in regions with rapid industrialization and population growth, such as large cities, as the water is polluted in some or the other way and is not of drinking quality. It has been reported that over seven hundred organic and inorganic micro pollutants are found in water. Some of these micro pollutants are highly toxic and carcinogenic while some have long residence times in the environment and are neither biodegradable nor bio-transformable. Most toxic organic pollutants include pesticides, polynuclear aromatic hydrocarbons (PAHs), polychlorinated 9 biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), plasticizers, phenols, and drug residues while toxic metals include arsenic, lead, cadmium, mercury, chromium, etc. Attempts have been made in the known art to remove these and other micro pollutants from water and industrial wastewater. Some methods and/or processes include chemical precipitation, conventional coagulation, reverse osmosis, ion-exchange, electro dialysis, electrolysis and adsorption. It has been observed that the techniques such as the reverse osmosis, ion-exchange, electrolysis and electrodialysis are exorbitantly expensive techniques. Therefore, the developing countries cannot employ these techniques.[3] Adsorption is now one of the alternate approaches for treating wastewater that has heavy metal contamination. In essence, a substance or contamination is transferred from the liquid phase to the surface of the solid phase and bound to physical and/or chemical interactions during the adsorption mass transfer process. Numerous low-cost adsorbents made of natural materials, modified biopolymers, agricultural waste, and industrial by products have used to remove heavy metals from recently analysed and wastewater with metal contamination.[4] The materials that are nanoparticulate have been investigated as potential heavy metal adsorbents. The surface area of the nanoparticles rises due to their reduced size, which enhances their chemical activity. And the nanoparticles' ability to absorb substances, such as metals visible at the surface. [5]

Water pollution and types of contaminant-

Water pollution is a global concern that demands effective and sustainable solutions for water remediation. Our survival on our planet is dependent on three essential resources: water, air, and soil, which are three of nature's most significant gifts to humanity. Water is the most vital component, as it is the primary channel for the emergence of life. Water contamination caused by numerous hazardous substances has become one of the world's most severe issues.

Water pollutants have been linked to a variety of acute and chronic ailments all around the world. An increase in human population and activity in recent decades has not only increased the amount of garbage discharged into water bodies, but has also introduced new contaminants like pharmaceuticals, hormones, endocrine disrupting compounds, toxins, and pathogens). In addition, when analytical technologies develop, new pathogens or chemicals (e.g., viruses, algal toxins, disinfection byproducts) may be found in natural or treated water bodies, according to numerous recent studies.[6]

Water contaminants are classified as
Organic
Inorganic
Biological
radiological

Organic contaminants

Natural products of aquatic microorganisms, as well as manufactured contaminants from industrial chemicals or human wastes, pollute the aquatic environment with organic compounds. Organic pollutants in rivers, lakes and ponds, reservoirs, groundwater, and drinking water, on the other hand, have different consequences depending on the contaminant. Agriculture (pesticides, herbicides, chemical fertilisers), industries (chemical), military activities (explosives, chemical weapons), spills (oil, solvents), urbanisation, and wood treatment are the primary anthropogenic sources of organic pollutants in the environment. [7]

The WHO Guidelines for Drinking-Water Quality, the EPA National Primary Drinking Water Regulations, water quality standards in waterworks law, environmental standards, and wastewater standards are all examples of legal restrictions that affect human health. The following are the estimated organic contaminants:

- Organic chemicals produced by algae or Actinomycetes which growing in the natural aquatic environment.
- Organic pollutants of industrial chemicals, from industrial activity;
- Water contamination by pesticides from agricultural or other uses;
- Organic chemicals from unintentionally produced contaminants during combustion or burning of organic materials such as polynuclear aromatic hydrocarbons (PAHs);
- Pollutants in waste from the human environment such as domestic effluent, and Newly produced materials during the water purification process of drinking water.

Synthetic organic pollutant- (SOC)

Elements like **Carbon,Hydrogen,Nitrogen, Halogens ,Phosphorus,Oxygen** and there deriatives forms SOC . for eg- Pesticides, detergents, food additives,drug residues from pharmaceuticleindustries fibres from textile industries ,different types of synthetic plastics . SOCs make water carcinogenic. Industrial waste including synthetic chemicals is discharged into the environment. phenolic chemicals, phthalates, and nitrogen-containing compounds.
Eg- **Acrylamide**
Residual acrylamide monomer occurs in polyacrylamide coagulants used in the treatment of drinking-water. In general, the maximum authorized dose of polymer is 1 mg/l. At a monomer content of 0.05%, this corresponds to a maximum theoretical concentration of 0.5 µg/l of the monomer in water. Acrylamide is easily absorbed and broadly dispersed in body fluids. Acrylamide has the ability to cross the placenta. It's neurotoxic, damages germ cells, and makes it difficult to reproduce. In mutagenicity tests, acrylamide passed the Ames test but caused gene mutations and chromosomal abnormalities in mammalian cells in vitro and in vivo. Acrylamide caused scrotal, thyroid, and adrenal tumours in men and breast, thyroid, and uterine tumours in females in a long-term carcinogenicity study in rats exposed via drinking water. [8]

Alachlor is a Herbicide used to control annual grasses and many broad-leaved weeds and it has been reported as a carcinogen that causes benign and malignant nasal turbinate tumours, malignant stomach tumours, and benign thyroid tumours.

Persistent Organic Compounds(POPs)

There are many chemical toxic chemicals generated by modern society. The chemicals that persists in environment from many decades are called **POPs.** Exposure to POPS cause damage to nervous system,Endocrine system. when thousands of synthetic chemicals were commercially available Many of these chemicals have proven useful in pest and disease control, crop production, and industrial applications. However, these same chemicals have had unanticipated consequences for human health and the environment.

Eg- aldrin and dieldrin, chlordane, DDT, endrin, mirex, heptachlor, hexachlorobenzene, polychlorinated biphenyls PCBs, toxaphene, dioxins and furans, polycyclic aromatic hydrocarbons

Volatile organic compounds (VOCs)

Because of their high volatility, volatile organic compounds (VOCs) were frequently detected in the environment; they permeate into the environment when solvents are employed. The environment's scattered contaminants contaminate both the atmosphere and aquatic bodies. Benzene, toluene, xylene, dichloroethane (used as solvents), trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane (used in dry cleaning), and carbon tetrachloride (used as a raw material for chlorofluorocarbons) are among the volatile organic chemicals identified in diverse water locations. After employing industrial raw materials, dichlorobenzene, trichlorobenzene styrene, and vinyl chloride are discovered in the water as contaminents.

Surface water is contaminated by naturally occurring organic substances produced by aquatic bacteria, such as 2-methylisoborneol and geosmin (trans-1,10-dimethyl-trans-9-decalol) are two volatile metabolites that generate an earthy/musty odour at extremely low levels (ng L-1), may be present in provided drinking water. hylisoborneol and geosmin, both of which have an anti-inflammatory effect [8]

Inorganic contaminants

include inorganic acids, alkalis, salts, anions, cations, free chlorine, ammonia, and other similar substances. They are introduced as a result of industrial effluents, sewage, household cleaners, and surface run-off from urban and agricultural areas, among other things. They have an impact on the physical and chemical quality of water.
For eg-Phosphoric acid, sulfuric acid, hydrochloric acids, Sodium hydroxide, lime cations of Calcium, magnesium, sodium, potassium, ammonium, iron, manganese, aluminium, mercury, lead and anions of Phosphates, sulphates, chlorides, nitrites, nitrates, cyanides,carbonates, bicarbonates
On the basis of the sources inorganic contaminats can be classified as

a**) Naturally occuring Substances**- From earths crust materials such as arsenic, fluoride and boron are entered in groundwater and contaminate it.
Arsenic- Arsenic is a metalloid that is abundant in the earth's crust, with an average concentration of 2 mg kg-1. Arsenic has four valency states: -3, 0 (+3), +3, and +5. Under reducing conditions, arsenite (As (III)) is the dominant form; in oxygenated environments, arsenate (As (V)) is the stable form. Water does not dissolve elemental arsenic. Chronic arsenic disease has been reported in several countries as a result of arsenic-contaminated well water. According to a recent epidemiological study, approximately 1 billion people use arsenic-contaminated wells for drinking water, including 47 million in India (West Bengal) and Bangladesh, 3 million in China, 0.3 million in Chile, and various numbers in other countries (including Thailand, Nepal, Vietnam, Cambodia, Mexico, and Argentina), and this figure is growing year by year.

Boron

Boron is a naturally occurring element found in the ocean, sedimentary rocks, coal, shale, and some soils as borates. It is found in abundance in nature, with a the Earth's crust has a concentration of about 10 mg kg-1 (range: 5mg kg-1 in basalts to 100 mg kg-1 in shales) and the ocean has a concentration of about 4.5 mg L-1. Boron enters the environment primarily through the weathering of rocks, the volatilization of boric acid from seawater, and volcanic activity. Boron is also released by anthropogenic sources such as agricultural waste, wood burning, glass production, the use of borates/perborates in the home and industry, borate mining/processing, and sewage/sludge disposal. Chronic exposure to boric acid and borax causes gastrointestinal and kidney problems, as well as loss of appetite, nausea, vomiting, and the development of an erythematous rash. Boron is suspected of being an endocrine disruptor based on animal studies in which it caused severe testicular atrophy and spermatogenic arrest.[9]
Fluoride Due to High reactivity fluorine does not occur in its elemental form. It makes up about 0.3 g kg-1 of the earth's crust and can be found in the form of fluorides in a variety of minerals, the most common of which are fluorite, cryolite, and fluorapatite. The fluoride ion has an oxidation state of -1.excess intake of fluoride fluoride primarily affects skeletal tissues (i.e. bones, teeth). Low concentrations protect against dental caries, particularly in children. This protective effect, which is associated with surface contact with enamel, increases with fluoride concentration up to about 2 mg L-1 of drinking water; the minimum fluoride concentration required to produce it is approximately 0.5 mg L-1. Fluoride, on the other hand, can harm tooth enamel and cause mild dental fluorosis at fluoride levels in drinking water ranging from 0.9 to 1.2 mg L-1. Elevated fluoride intakes can also have more serious effects on skeletal tissues.[10]
b)Inorganic substances in the industrial waste- Heavy metals are elements that are found in relatively low concentrations in water and have been found to endanger health when they enter the food chain via plants and biological life. Untreated or ostensibly treated industrial effluents frequently contain varying amounts of heavy metals. These toxic metals not only contaminate crops but also endanger aquatic biota.[11]
eg- Antimony,Barium,Cadmium,Chromium,Mercury,Nickel,Cyanide
Heavy metals present in varying quantities in treated sewage water are capable of contaminating crops grown and irrigated with the water. The problem of heavy metal pollution in water has gotten worse as a result of bio-accumulation and bio-magnification.the other examples of industrial waste contaminants are-
Acids Phosphoric acid, sulfuric acid, hydrochloric acids etc.
Alkalis Sodium hydroxide, lime etc.
Cations Calcium, magnesium, sodium, potassium, ammonium, iron,
manganese, aluminium, mercury, lead etc.
Anions Phosphates, sulphates, chlorides, nitrites, nitrates, cyanides,carbonates, bicarbonates etc.
c) **Inorganic substances in the agricultural waste-**
Nitrogen -Dissolved nitrate is most common contaminant in groundwater. High level can cause blue baby disease (Methamoglobinamia) in children, may form carcinogens & can accelerate eutrophication in surface waters. Sources of nitrates include sewage, fertilizers, air pollution, landfills & industries [12]

Biological contaminants

The introduction and growth of micro and macro organisms in water bodies causes biological pollution, which has a inverse impact on water quality, human health, and the ecosystem.
For eg -Bacteria, algae, weeds, viruses, protozoa, and worms

Pathogenic Microbes :-. Pathogenic microbes are contaminants of water and are responsible for dangerous diseases such as cholera and typhoid, and while less dangerous to some extent, is responsible for high numbers of infantile diarrhea. Diarrhea diseases and other internal infections are the main cause of death among people who live in the cities and villages of developing countries.

for eg-Cholera by Eltor , Typhoid by Salmonella typhi Leptospirosis through different kinds of leptospira

Parasitic and Protistas(Protozoa):-

A swarm of protistas and parasites can also enter the human body through direct consumption of contaminated water, causing disease.

for eg-Amoebic dysentery by Entamoba histolytic , Giardiasis *Giardia lamblia,* Balantidiasis by Balantidium coli , Daracunculus by Deracunculus

Worms are also contaminants in water causing various diseases. Eg- Round worms, tape worms, flukes etc.Weeds Hydrilla, potamogeton, ceratophyllum etc[13]

Bacteria *E. coli, Salmonella, S. typhi, Vibrio cholera, Clostridium botulinum* etc.

Cyanotoxins

Cyanotoxins are fresh water toxins produced by cyanobacteria, also known as bluegreen algae. At least 19 of the more than 50 cyanobacteria genera have been identified.toxic properties have been demonstrated Approximately 60% of the Blooms caused by toxin-producing cyanobacteria are a concern.

Eg-Anabaena, Aphanizomenon, Microcystis, and Oscillatoria are all toxic.

Blooms of toxic cyanobacteria have occurred worldwide for many years and have led to illness in humans and to the death of animals

Viruses Some viruses have been found to grow in the human alimentary canal, as well as the mouth and larynx. These elements will be expelled via faeces, which can be found in waste water and contaminated waters. Hepatitis A virus, Poliovirus etc.[14]

Radioactive contaminants

Any pollutant that emits radiation in excess of that naturally released by the environment is classified as radioactive waste. Uranium mining, nuclear power plants, military weapon production and testing, as well as colleges and hospitals that use radioactive materials for study and medicine, all produce it. Radioactive waste can last thousands of years in the environment, making disposal a serious concern. Consider the cleaning of 56 million gallons of radioactive waste at the decommissioned Hanford nuclear weapons production site in Washington, which is anticipated to cost more than $100 billion and take until 2060. Contaminants that have been released accidentally or inadequately disposed of pose a threat to groundwater, surface water, and marine resources.

Eg-^{60}Co, ^{137}Cs, ^{192}Ir, ^{241}Am, ^{226}Ra, ^{3}H, ^{14}C, ^{131}I, ^{99}Tc^{m} ^{234}U, ^{235}U, ^{238}U

Many of the contaminants found in public drinking water supplies are naturally occurring. Radioactive radium and uranium, for example, are found in trace amounts in almost all rock and soil and can dissolve in water. Radon, a radioactive gas produced by the decay of radium, can also occur naturally in groundwater.The most common radioactive elements found in sewage treatment plant sludge are ^{40}K and ^{7}Be. Mining for radioactive elements such as uranium and thorium pollutes surface and groundwater.Nuclear reactors produce radioisotopes ,Cobalt-60, Iridium-192, Strontium-90, Caesium-137[15]Human tissues absorb radiation through contaminated water posing serious health risks. Acute radiation syndrome or cutaneous radiation injury can result from high doses of radiation. Radiation exposure causes a variety of physiologic disorders in humans, including cancer, leukaemia, genetic mutations, osteonecrosis, cataracts, and chromosomal disruption.[16]

Sources of Nano-adsorbents

Natural-based Nano-adsorbents

Since the beginning of Earth's history, nanoparticles have existed in nature. A wide range of nanoparticles have been introduced into the system by various geological and biological processes. Naturally occurring peptides, celluloses, chitins, and many more similar biological nanoparticles have been researched. By utilizing nano adsorbents, modern adsorption techniques have advanced. High chemical reactivity and adsorption capability of these nanomaterials are made possible by their reduced size and bigger surface. Nano adsorbents are made up of magnetic NPs, mixed oxide NPs, metallic NPs, etc. Carbon nano sheets (CNTs), silica nanotubes (SiNTs) are having various industrial applications. [17]

Natural zeolites have the capacity to conduct ionic exchanges are being used as adsorbents more frequently. A significant degree of selectivity for the adsorption of Cu2+ ions and heavy metals was demonstrated for clinoptilolite, one of the most frequently studied natural zeolites. Conditioning increases clinoptilolite's capacity for ion exchange and increases the effectiveness of heavy metal removal. The ability of clinoptilolite to exchange cations is dependent on the pretreatment process. [18] The biosorption of copper(II) ions in batch reactors has been explored using the brown alga Fucusserratus (FS) as a low-cost sorbent. This suggests that biomass may be an appropriate sorbent for the removal of heavy metals from wastewaters. [19]

Nano-clay has drawn increased attention because of its distinct qualities and properties. Clay minerals used as adsorbents as they are very significant naturally occurring minerals that are crucial to protecting the environment. Clay is essentially made of raw minerals and has a variety of geometry and morphology. These clay minerals have been utilized for cleaning up contaminated water as well as for the storage and disposal of dangerous compounds. Due to their widespread availability and low cost, clay minerals have been employed as raw materials in a variety of sectors for hundreds of industrial applications. In many adsorption procedures, clay is used as a nano-adsorbent due to its distinct characteristics and high removal effectiveness. For the purification of water, nano-clays have been proven to be a highly effective and efficient property enhancer. [20]

Natural biomass-

The most promising biopolymers in nanotechnology are cellulose nanoparticles. They are the ideal material for nanomembranes due to their high mechanical strength and toughness. It is simple to functionalize the surface of cellulose. In order to improve the ability to remove heavy metal ions from wastewater, bagasse-based ion adsorbent was created by chemically altering bagasse using acrylonitrile and hydroxylamine.[21] Itaconic acid-grafted-magnetite nanocellulose composite [P(MB-IA)-g-MNCC], a new adsorbent, was created to selectively adsorb mercury(II) [Hg(II)] ions from aqueous solutions. The adsorbent was characterised using Fourier transforms infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and thermo gravimetric investigations. [22] The task of removing harmful mercury ions from aqueous solutions using a green biosorbent is challenging. By functionalizing high surface area cellulose nanocrystals with l-cysteine through periodate oxidation and reductive amination reaction, l-cysteine modified cellulose nanocrystals (Lcys-CNCs), a new biosorbent, was created in the current study. [23] Chitosan is a naturally occurring substance that is derived from the shells of crustaceans, algae, fungi, and arthropods. It has been shown to have antibacterial properties. It ranks as the second-largest organic biopolymer after cellulose. These mucoadhesive polymers are non-toxic and produced by chitin deacetylation. Chitosan is chemically identical to cellulose beta-(1-4) glycoside bonded 2-amino-2-deoxy-D-glucose monomers. The chitosan is promising bactericide, particularly against Gram-negative bacteria**.** Due to its low cost compared to activated carbon and its high amount of amino and hydroxyl functional groups, which exhibit excellent adsorption capability for diverse aquatic contaminants, chitosan has attracted particular attention as an effective biosorbent. Due to its favourable physico-chemical properties, natural biomasses are an appealing replacement for conventional biomaterials. [24]

Nanofiber (NFs) - According to the qualities of the item samples, several polymers with a high enough molecular weight can be electrospun. Due to their large specific surface area, high porosity, and superior functionality, electrospun nanofiber membranes are significant in a variety of applications. Electrospun nanofibers have widespread uses of removing organic and inorganic pollutants, such as oil, heavy metal from industrial waste water. [25]

Researchers have recently looked into many factors that affect nylon6 nanofiber. With their high surface-to-volume and length-to-diameter ratios, nylon6 nanofibers can attain a bigger specific surface and more adsorption sites. [26]

3.2Carbon-based Nano-adsorbents

Due to their inherent dimensionality, textural, and electrical features, nanomaterial's, in particular carbon nanostructures are intriguing systems for a variety of applications, particularly for molecule adsorption. Nanomaterial's primary component is carbon, which can be found in a wide range of forms, including hollow tubes. The coordination number of the carbon atoms varies between the carbon allotropes or in the order in which the layers are packaged in a crystal lattice environment. Carbonaceous nanomaterial's are produced via various levels of sp2 hybridization having unique atomic boundaries and configurations. [27]

Examples for carbon nanostructures are -

Fullerene, C60-The curvature effect causes sp2-like hybridization in the fullerenes, which are carbon-based, zero-dimensional (0D) materials. The C60 molecule is made up of 12 pentagons and 20 hexagons of carbon atoms, and it has a diameter of about 7. A fullerene can have anywhere between 20, 60, 70, 82, 100, 180, and 960 carbon atoms (always an even number [28]

Carbon nanotubes- When the carbon atoms are wrapped up in a tubular form in a sp2-like hybridization, the resultant carbon allotropes are known as carbon nanotubes (CNT), which have an aromatic surface (1D system). [29] This particular carbon allotrope is a fascinating nanostructure whose chirality and dimension directly influence its outstanding electrical and mechanical capabilities. [30]The creation of energy storage and adsorption devices with high sensitivity, selectivity, and efficiency is just one example of how these outstanding qualities paired with unconventional shape make materials incredibly appealing for many practical applications. [31]Single-walled Carbon Nanotubes (SWNTs, SWCNTs) the majority of single-walled nanotubes (SWNT) are about 1 nanometer in diameter, although their lengths can be millions of times longer. A seamless cylinder of grapheme, a one atom thick layer of graphite, can be used to visualise the structure of a SWNT. These SWCNTs can be used as polymer additives, catalysts, electron field emitters for cathode ray lighting components, flat-panel displays, gas-discharge tubes in telecommunication networks, electromagnetic wave absorption and shielding, energy conversion, lithium-battery anodes, hydrogen storage, nanotube composites (by filling or coating), nanolithography nanoelectrodes, drug delivery, sensors, reinforcements in composites, and super capacitors. [32] Multi-walled carbon nanotubes (MWCNTs) have received a lot of attention as a promising support for nanomaterials because of their excellent mechanical and chemical stability and mesoporous nature, which encourages the diffusion of reactive species [33] Wastewater Treatment by CNT/TiO2 Composites Prepared from Multi-Walled Carbon Nanotubes with Different Organo-Titanium Precursor can be done. Wastewater was treated to remove the heavy metal Cr $^{+3}$ ions using functionalized MWCNTs. MWCNTs at 25 mg and pH 6 were found to be the ideal conditions for batch adsorption of Cr^{3+} ions and the highest adsorption efficiency. The outcomes demonstrated that MWCNTs, due to their greater surface area, had a significant capability for adsorption. [34]

Graphene– A honeycomb-shaped lattice of carbon atoms is organised in two dimensions to make graphene. Since its discovery, the graphene family, including graphene, graphene oxide (GO), and reduced graphene oxide (rGO), have seen much research because of their distinctive physical-chemical features, [35] The viability and acceptability of exploiting this diverse family of nanomaterials, which largely consists of carbon atoms, as a potential option for the prevention, control, and reduction of water pollution adsorbents are being explored in light of the rising demand for potable water. [36] Although graphene inherently repels water, it can allow rapid water absorption when narrow pores are created in it. This gave rise to suggestions that graphene might be used for desalination and water filtering, particularly once the technology to create these micro-pores is developed. Because they allow water molecules to pass but obstruct the passage of impurities and pollutants, graphene sheets (perforated with tiny pores) are being researched as a technique of water filtration. Due to its light weight and small size, graphene can help create water filters and desalinators that are energy-efficient, lightweight, and environmentally friendly. [37] For the elimination of cobalt (Co(II)), fluoride, and iron (Fe(II)), graphene is a potential adsorbent. For cationic contaminants like copper, nickel, zinc, palladium, etc.

Graphene Oxide and Reduced Graphene oxide- GO is another powerful adsorbent. In the adsorption process, the oxygen groups on GO sheets serve as anchors. While some research only looked at graphene and GO sheets, others demonstrate that rGO and composites made of graphene and GO also have high adsorption capabilities. The surface of graphene and GO is frequently embellished with various nanoparticles or oxygen-containing groups to boost the adsorption affinity for the removal of inorganic impurities. It is recommended that coating graphene and GO with magnetic nanoparticles like magnetite be used to separate inorganic impurities. [38]

Preparation and Surface-modification of Carbon Nano-adsorbents and Effect of Functionalization of Carbon on Adsorption Properties

NPs have been employed as sorbents because they have greater inherent features than traditional materials, such as chemical activity and tiny particle size. To create a new selective solid phase extractant for the preconcentration of metal ions, NPs can be chemically altered by a reagent. High surface area, high chemical activity, high adsorptive capacity, low internal diffusional resistance, and the concentration of the majority of the atoms on the surface are essential characteristics for carbon nanoadsorbent. External functionalization provides the selectivity to nanoadsorbent. MWCNT with ethylenediamine by amide bond formation via the carboxyl groups on the oxidized CNT surface are best adsorbent for Pb(II) Cd(II) ions from water. [39] For the preconcentration of analytes, a variety of carbon-based sorbents have been used, including activated carbon, carbon molecular sieves, graphitized carbon black, and porous carbon. [40] Carbon nanotube synthesis can be done by laser ablation, catalytic arc discharge, and CVD Nontubular Carbons (NTCs) are created through the catalytic dissociation of organic precursors or graphite, which is a common step in the synthesis of CNTs.Contrary to CNTs, NTCs frequently have porous architectures, which results in a unique retention/trapping process that can be controlled by diffusion. Because these NTCs lack the CNTs' superior sorbent properties, the CNTs' overall efficacy as a sorbent is significantly impacted by their purity. The most popular techniques for removing the NTCs and remaining catalysts are acid treatment and gas phase oxidation. [41] The concentration of hydroxyl and carbonyl surface groups on activated carbon is primarily increased during gas phase oxidation, and the concentration of carboxylic acids is primarily increased during liquid phase oxidation [42] Nitric acid treatment of CNT was reported to result in a greater number of carboxyl and lactone groups than the H2O2 and KMnO4 processes.[43] However, CNT fragmentation (shortening) and defect creation in the graphitic network are two of the major downsides of acid-oxidation processes [44] The high ultrasonic power normally used to disperse CNT agglomerates during oxidation has been discovered as another source of fragmentation in addition to acid concentration and exposure period [45] One of the methods for solubilization that is most frequently employed comprises oxidative acid treatment steps such refluxing in diluted nitric acid or sonicate [46] After oxidative acid treatment and numerous washing/centrifugation cycles, a black supernatant solution containing carboxylated carbon nanotubes is produced his solubilization technique, however, has the potential to cause tube shortening and surface flaws. Due to the fact that the structures and properties of carbon nanotubes are typically maintained after dispersion, numerous researchers have advocated for their non covalent stabilisation in solutions. According to this method, the carbon nanotubes are complexed or derivatized with micelles, polymers, or other aggregation systems in order to be solubilized /dispersed in an aqueous environment. [47] Adsorbent substances typically have inherent limitations, and the bulk of them have limited adsorption capabilities. This suggests that applying nanoparticles in their pure or bare forms is insufficient. In order to fully grasp the benefits of nanoparticles over traditional adsorbents, a method for removing the emphasized restrictions associated with them functionalization or surface modification is proposed. Surface functionalization refers to a process that modifies the chemistry of a material's surface to provide specific properties. various functionalization techniques such as thermal treatment, acid treatment, sonication, etc.

The particular surface area was directly impacted by surface modification as well; it shrank as functionalization increased. But it was typically found that the degree of functionalization led to higher adsorption capacities. [48] There are several methods for preparing surface modified nanoparticles, ranging from single step to multi-step processes. Grafting, hydrothermal and/or hydrothermal reduction, covalent binding, co-precipitation, co-condensation, surface coating, ligand exchange method, modified Stober method, and sol-gel method are among the available synthesis methods. A variety of modifications in the surface characteristics of nanomaterials are observed when different functional groups are used. Excellent adsorption qualities can be achieved by combining a wide range of external functionalization techniques with nanomaterials. To enhance analytical characteristics like selectivity, affinity, and adsorption capacity, the search for functionalized groups is a crucial step. For improving benzene, toluene, ethylbenzene, and p-xylene (BTEX) adsorption in an aqueous solution, carbon nanotubes (CNTs) were created using the catalytic chemical vapour deposition method and then oxidised by HCl, H_2SO_4, HNO_3, and NaOCl solutions. This involves the surface modification of CNTs for effective removal of BTEX. [38] Sulfur compounds pose some environmental risks, so it's important to remove them from hydrocarbon fuels. Different surface modifications of carbon nanostructures, including physical and chemical surface modifications, were used to achieve the adsorptive desulfurization and oxidative desulfurization processes in order to effectively remove aromatic sulphur compounds like benzothiophene and dibenzothiophene. For these surface modifications the H_2SO_4/HNO_3 acid treatment and polymer-wrapping approach were applied [49] Tetraethoxysilane and functionalized trialkoxysilane $RSi(OR')_3$ were co-condensed to create heavy metals adsorbents [50] The addition of fundamental nitrogen functionalities to the carbon surface can boost the CO_2 adsorption capability of activated carbon, [51] Commercial carbon nanofiber (CNF) shows better surface chemistry and adsorption characteristics after chemical activation using HNO_3.After the carbon nanofibers have been exposed to oxidation, both the capacity and the strength of adsorption decrease, perhaps in the case of chlorinated compounds, the specific component of surface energy exhibits a notable rise. It has been shown that the shape of the surface is the important factor in determining how n-alkanes and cyclic compounds interact, and the presence of oxygen surface groups has no effect on this. Steric restrictions on the adsorption are caused by the oxidation of the nanofiber. These materials function similarly when it comes to the adsorption of aromatic compounds due to the nucleophilic interactions between the aromatic ring and surface oxygenated groups. The chlorinated compounds can't adhere to the activated nanofibers because they lack nucleophilic groups. [52] One of the most popular adsorbents, activated carbon has low removal efficiency for polar molecules like ammonia or ions because of the lack of oxygen-containing groups in its structure. By oxidising activated carbon using HNO3/H3PO4 -NaNO2, activated carbon was changed to enhance the amount of oxygen-containing groups. The outcomes demonstrated that when reaction time and temperature increased, the carboxyl content of the modified activated carbon (MAC) also increased. [53,54]

Examples of eco-friendly precursors and templates- Some examples of eco-friendly precursors and templates that are commonly used in the synthesis of macro porous hybrid nanoadsorbents for water remediation:

a. Cellulose: Cellulose, derived from renewable sources such as plants or agricultural waste, is an eco-friendly precursor widely used in the synthesis of nanoadsorbents. It offers advantages such as biodegradability, high surface area, and functional group modification possibilities.[55]

b. Chitosan: Chitosan, derived from chitin found in the exoskeleton of crustaceans, is another eco-friendly precursor. It possesses excellent adsorption properties, biocompatibility, and abundant availability, making it suitable for water remediation applications.

c. Lignin: Lignin, a complex aromatic polymer obtained from plant biomass, is an eco-friendly precursor that can be used to develop macroporous nanoadsorbents. It exhibits high adsorption capacity for various pollutants due to its unique chemical structure.

d. Starch: Starch, derived from crops such as corn, potato, or cassava, has been used as a precursor for the synthesis of macroporous nanoadsorbents. It offers good adsorption properties, biocompatibility, and low cost.[56]

e. Alginate: Alginate, extracted from brown algae or seaweed, is an eco-friendly precursor that has been utilized for the fabrication of macroporous nanoadsorbents. It exhibits excellent gel-forming properties and can be easily modified for enhanced adsorption performance.

f. Zeolites: Zeolites are naturally occurring or synthetic microporous minerals with high adsorption capacities. They can be modified or functionalized to form macroporous structures for water remediation applications.[57]

2. Templates:

a. Natural templates: Natural materials such as plant fibers, algae, and diatoms can serve as templates for the synthesis of macroporous nanoadsorbents. These templates can be selectively removed, leaving behind a porous structure that enhances adsorption capacities.[58]

b. Biomass-derived templates: Biomass-derived templates, such as rice husk, corn cob, or fruit peels, can be utilized in the synthesis of macroporous nanoadsorbents. These templates are abundant, renewable, and offer a cost-effective approach for developing eco-friendly nanomaterials.[59]

c. Bio-inspired templates: Bio-inspired templates mimic the hierarchical structures found in nature, such as coral, sponge, or honeycomb structures. These templates can be replicated using fabrication techniques to create macroporous nanoadsorbents with enhanced adsorption properties.[60]

d.Biopolymers: Biopolymers such as protein-based materials (e.g., gelatin, casein) or polysaccharides (e.g., agarose, pectin) have been used as templates for the synthesis of macroporous nanoadsorbents. These materials provide structural support and can be selectively removed after synthesis.[61]

e. Silica templates: Silica templates, such as silica nanoparticles or mesoporous silica, have been employed as sacrificial templates for the creation of macroporous structures. These templates can be easily removed by etching, leaving behind a highly porous nanoadsorbent.[62,63]

f. Carbon templates: Carbonaceous materials, such as activated carbon or carbon nanotubes, can be used as templates for the synthesis of macroporous nanoadsorbents. The carbon template can be selectively removed or retained to create hierarchical porosity.[64,65]

Applications of Carbon-based hybrid Nano-adsorbents

Adsorption

Adsorption is the process of molecules adhering to the exterior surface or internal surface of solids or liquids. In a one-pot hydrothermal procedure using ferrocene and no carbon sources, carbon-encapsulated Fe nanoparticle composites (Fe/C CNPs) were produced. [66] The efficient phosphate removal from aqueous solutions is crucial for environmental protection. The idea of creating hierarchical, economical aluminium functionalized melamine foam (MF) as phosphate adsorbent. The efficiency of phosphate removal from the as-prepared material at various temperatures further confirmed the endothermic character of the adsorption process. Additionally, the MF-HA sponge demonstrated good recyclability and could be easily removed from the solution. The innovative sponge's high adsorption efficiency, cost-effectiveness, preferred selectivity, environmental friendliness, and ease of water separation due to the adsorbing approach used in its design and fabrication may encourage sponge functionalization for use in large wastewater treatment areas Agricultural waste is widely accessible and has a lot of potential for use in the creation of adsorption materials. In this study, a green technique is presented for making a quick-acting adsorbent for methylene blue (MB) based on loofah fibre. In order to create the loofah fiber-graft-polyacrylic acid (LF-g-PAA) composite, enhanced Fenton's reagent (LF-loaded Fe2+/H2O2) is used to form hydroxyl radicals (OH) on the surface of the LF, which then trigger surface grafting polymerization at room temperature. When compared to traditional synthetic adsorbents (Fenton's reagent and ceric ions initiator synthesis), the proposed green synthesised adsorbent (LF-g-PAA) for adsorptive applications demonstrates less self-polymer. [67] Research conducted by Zhang et al. (2019) focused on the removal of heavy metals from water using a hybrid nano-adsorbent composed of magnetic nanoparticles and chitosan. The hybrid material exhibited enhanced adsorption capacity due to the synergistic effect between the magnetic nanoparticles and chitosan. The study demonstrated successful removal of heavy metals, such as lead (Pb) and cadmium (Cd), from contaminated water, highlighting the potential of hybrid nano-adsorbents in heavy metal remediation.[68] In a study conducted by Li et al. (2020), a macroporous hybrid nano-adsorbent composed of graphene oxide and metal-organic frameworks (MOFs) was employed for the removal of organic pollutants, specifically dyes, from water. The hybrid nano-adsorbent exhibited a high adsorption capacity and excellent selectivity for dyes due to the combined advantages of graphene oxide and MOFs. The results demonstrated efficient removal of various dyes from water, highlighting the potential of hybrid nano-adsorbents in organic pollutant remediation[69] Researchers investigated the removal of emerging contaminants, such as pharmaceuticals, from water using a hybrid nano-adsorbent composed of carbon nanotubes and activated carbon. The study conducted by Li et al. (2018) demonstrated that the hybrid nano-adsorbent exhibited excellent adsorption performance for various pharmaceutical compounds. The combination of carbon nanotubes and activated carbon resulted in synergistic effects, leading to enhanced removal efficiency. The study highlighted the potential of hybrid nano-adsorbents in addressing emerging contaminant challenges.[70] Carbon-based hybrid nano-adsorbent application is the removal of organic contaminants, such as pharmaceuticals and pesticides, from water. Carbon-based materials, such as activated carbon, graphene oxide, carbon nanotubes, and carbon nanofibers, can be combined with other nanomaterials to form hybrid nano-adsorbents with enhanced adsorption capacities and selectivity towards organic pollutants[71]

Photo catalysis

Photo catalysis has been shown to be one of the most widely used and promising tertiary treatment methods. Because of their availability, unique pore structures, and superior physico - chemical properties, carbon-based materials, particularly those based on graphene, carbon nanotubes, biochar, and hierarchical porous carbon, have received a lot of attention in antibiotic removal as green adsorbents and photo catalysts.[72] TiO2 coupled with activated carbon, carbon nanotubes, graphene derivatives are being used to degrade various pollutants found in water, such as dyes, pesticides, pharmaceuticals, phenols, and heavy metals.[73] Carbon-based hybrid nano-adsorbents have found applications in photocatalysis, where they can act as both adsorbents and photocatalytic materials Carbon-based hybrid nano-adsorbents, such as graphene-based composites, carbon quantum dots, and carbon nanotube composites, have been utilized in photocatalytic processes for the degradation of organic pollutants. These hybrid materials can exhibit excellent photocatalytic activity, high adsorption capacity, and enhanced stability, making them suitable for the removal of various organic contaminants from water through photocatalytic degradation processes[74] Graphene heterojunctions are especially favorable due to their high catalytic surface area and abundance of reaction sites, as well as the suppression of photogenerated electron-hole pairs recombination at the 2D/2D interface and facilitation of charge transfer.[75,76]

While carbon-based hybrid nano-adsorbents have shown promise in photocatalysis, there are indeed some limitations and challenges associated with their use

1. Limited Light Absorption: Carbon-based materials, such as graphene or carbon nanotubes, typically have limited light absorption in the visible or solar spectrum. This can restrict their photocatalytic activity, as efficient light absorption is crucial for initiating photocatalytic reactions. Strategies such as incorporating light-absorbing components or sensitizers into the hybrid structure can help overcome this limitation.

2. Charge Carrier Separation Efficiency: Efficient separation and utilization of photogenerated charge carriers (electrons and holes) are crucial for effective photocatalysis. Carbon-based materials, being typically electron-rich, may face challenges in achieving efficient charge carrier separation and transfer. Hybridization with appropriate materials or coupling with suitable electron acceptors can help enhance the charge carrier separation efficiency.

3. Catalyst Stability and Reusability: Ensuring the stability and reusability of carbon-based hybrid nano-adsorbents is important for practical applications. Some carbon-based materials may suffer from degradation or leaching of active species during photocatalytic processes, leading to reduced performance or difficulty in regeneration. Developing robust hybrid structures and optimizing synthesis methods can address these challenges.

4. Scalability and Cost: Scaling up the production of carbon-based hybrid nano-adsorbents while maintaining their performance can be challenging. Some hybridization processes may involve complex synthesis methods or costly precursor materials, which can limit their practical applicability. Developing cost-effective and scalable synthesis approaches is an ongoing challenge in the field.

5. Selectivity and Specificity: Carbon-based hybrid nano-adsorbents may exhibit broad-spectrum adsorption capabilities, leading to the potential removal of both target pollutants and beneficial compounds from water. Achieving high selectivity and specificity towards specific pollutants while minimizing the interference with other water components remains a challenge.[77]

Membrane separation

The use of nanomaterials as membrane modifiers in water purification is appealing due to the potential for scale-up and high efficiency. Membrane separation when compared to other separation systems is one of the most efficient separation methods. Nanomaterials are thought to be more effective due to their superior properties, which highlight their potential for use in doping membranes as a CO2 capture technique due to their thermal stability. [78] Membranes are used in both desalination processes and the treatment of wastewater from various types of pollutants such as organic pollutants, heavy metal salts, and so on. Microfiltration, ultrafiltration, nanofiltration, membrane distillation, ion exchange membranes, and direct osmosis are all membrane processes used for water purification and desalination.[79] Nanomaterials-based membrane systems have evolved with the goal of improving overall performance, such as higher flux (flow rate per unit membrane area), greater removal of targeted contaminants, and lower membrane fouling.[80]

Energy Storage

High ionic transport, superior electronic conductivity, rapid ion diffusion, high current tolerance, and so on is just a few of the numerous factors that contribute to nanomaterials' versatility.[81] It is possible to create tailor-made surfaces with unique properties by combining different allotropic forms of carbon at the nanoscale. The electrochemical properties of hybrid carbon nanomaterials are extremely fascinating. Nanomaterials have sparked interest in the field of energy storage due to their rapid recharging capability, increased durability, and large storage capacity. Nanomaterials are unique in their ability to exhibit electric, magnetic, optical, structural, mechanical, and chemical properties due to their small size and high surface area per unit volume or mass.[82]

Conclusions

From the present review work, the vital role of Nanotechnology In terms of wastewater treatment is applicable in detection and removal of various pollutants. Hybrid nanoadsorbent represents the class of emerging sustainable materials. This field of study is still brewing, with new types of materials, new scientific progress on tailor-made functionalization realized, and new application areas making their way. This review aims to summarise the lessons learned by researchers during the development and application of hybrid nanoadsorbents. The purpose of this review paper is to survey the current state-of-the-art common knowledge base and to open up new horizons in materials science and technology. Green chemistry and sustainable engineering are used to evaluate and assess the efficacy of hybrid nanoadsorbent processes and products.

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