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Review Article

Carbon-Based Nanoadsorbents for the Removal of Emerging Pollutants

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Emerging contaminants (ECs) are substances that have been detected in water but have not been thoroughly tested or regulated. Pesticides, cosmetics, pharmaceuticals, and other medications are examples of compounds in this category. Even at low quantities, these pollutants can harm human health and the environment; therefore, avoiding them is critical. The consequences of EC pollution on the endocrine, hormonal, and genetic systems are causing significant concern. Even with current best practices and available technology, it is difficult to totally eliminate ECs from municipal and industrial wastewater treatment plants. Adsorption has been the method of choice for EC removal since it is less costly, more effective, and easier to use. To treat ECs, newer generation nanoadsorbents are employed. Adsorption was greatly enhanced by functional changes to the adsorbent surface. Carbon nanostructures are widely used as adsorbents because of their outstanding surface properties, adaptability, large surface area, adjustable structural changes, and high chemical stability. This review reviews and examines recent research on the production and use of carbon-based nanoadsorbents. The emphasis is on carbon nanotubes, graphene, and graphene-derived adsorbents. It is being investigated if these adsorbents can be used to extract hormone-disrupting chemicals and other emerging pollutants. The sources and classification of these pollutants, treatment knowledge gaps, and novel prospects for increasing carbonaceous nanoadsorbent utilization were all explored. The environmental and health problems associated with EC use are also studied.

1. Introduction

Water consumption is rising as a result of population growth and rising living standards [1–5]. The accumulation of noxious substances makes it more difficult to maintain the quality of the water supply. Personal care products, home cleansers, perfluorinated compounds (PFCs), endocrine-disrupting compounds (EDCs), prescription drugs, and other commodities emit a wide range of chemicals into the environment [2, 3]. Emerging contaminants (ECs) are chemicals (synthetic or natural) and microorganisms of any sort that are not routinely monitored, have not previously been examined, and may pose harm to ecosystems, human health, and safety [6–8]. Hormone activity; damage to the skin, brain, and neurological system; cancer; and ecological toxicity are some of the most important health and environmental problems linked with ECs. Because of their androgenic or estrogenic actions, endocrine-disrupting chemicals (EDCs) can cause damage to the body's hormonal system even at low doses [9–11]. These contaminants may increase the number of cancers and antibiotic-resistant microorganisms [12]. The concentration of ECs may vary substantially from one location to another depending on the country's manufacturing procedures. Because their presence has harmed the water's physicochemical qualities, immediate action is essential. Water samples have been shown to include antimicrobials, steroid analgesics, profens, antidiabetic drugs, antidepressants, cytostatics, gastrointestinal meds, and lipid controllers [13, 14].

The treatment of these contaminants is critical owing to their environmental impacts. Some ECs may go undetected in water and wastewater treatment systems due to their extremely low concentrations. The ecotoxicological effects and behavior of ECs have yet to be validated by a global routine checking effort [5, 15]. The standard water treatment methods are intended to eliminate only the normal contaminants while preserving basic water quality parameters [16]. There has been limited investigation towards removing ECs from aquatic environments. Traditional biological removal of these contaminants in wastewater treatment plants is time-consuming and not necessarily successful since not all emergent pollutants can be eradicated. Photolysis, sonochemistry, ozonation, ultrasound, solar-powered processes, photo-Fenton, photocatalysis, and electro-Fenton have all been studied recently [17]. These technologies, however, are costly to operate and maintain, and they require a lot of energy [17]. As a result, there is a need to provide efficient and cost-effective solutions.

The adsorption approach may efficiently cure a wide range of contaminants. This technique is regarded as the most cost-effective, efficient, practical, and ecologically friendly of the wastewater treatment technologies now in use [18–22]. Adsorption is a well-known surface phenomenon that may remove organic and inorganic micropollutants effectively. It is used to remove contaminants from water after it has been treated chemically or biologically. Adsorption is becoming more used as a method of eliminating dissolved pollutants that have withstood chemical oxidation or biological treatment. Several scientists have spent the last decade studying the adsorption of ECs on activated carbon (AC). Activated carbon (AC) is a porous carbonaceous substance that may be produced chemically or by pyrolysis from bamboo, coal, wood, nutshells, and other organic materials. The source material as well as the method of activation has a large impact on the surface functional groups of ACs. Adsorption using granular activated carbon (GAC) is demonstrated by Rao et al. as a viable tertiary treatment for the simultaneous removal of five PPCPs from an aqueous solution, including three hydrophilic (ciprofloxacin, acetaminophen, and caffeine) and two hydrophobic (benzophenone and Irgasan) PPCPs [23]. Using batch sorption studies and commercial granular activated carbon as an adsorbent, the adsorption of six emerging pollutants from aqueous solutions was investigated. Caffeine, clofibric acid, diclofenac, gallic acid, ibuprofen, and salicylic acid were chosen as typical pollutants [24]. However, the problems in regeneration and higher pricing of activated carbon restrict its practical usefulness. Even regenerated AC's efficiency is inferior to that of fresh AC [1]. As a result, the quest for new adsorbents has risen in recent years [1, 6, 7]. Nanotechnology is being applied in a range of scientific sectors, including water purification, as it advances. The usage of nanoscale adsorbents aids in the removal of water pollutants. These innovative adsorbents can remove pollutants down to the atomic level, in addition to having a remarkable adsorption capacity. Recent studies have concentrated on the development of nanoscale adsorbents for EC removal [6, 25, 26]. The adsorbent's capacity to remove a wide spectrum of pollutants is enhanced by the surface functional groups [27–31]. The optimal adsorbent would have a large surface area and specialized adsorption sites with high porosity. A substance's porous structure enhances its surface area and adsorption capabilities. Carbon nanomaterials are a type of porous nanoadsorbent that has a great deal of potential for EC removal. They may have been used in place of commercial activated carbon to remove various pollutants.

Adsorption-friendly features of carbon nanoadsorbents include ordered structure, high porosity, homogeneous pore size distribution, high specific surface area, chemical and thermal stability, and nontoxicity. Furthermore, these materials' surfaces may be altered, making them into functional materials with a greater capacity to remove different contaminants. The essential components of the adsorption mechanism include interactions, hydrogen bonds, and electrostatic interactions. The presence of oxygen-containing functional groups in adsorbents also promotes adsorption. Carbon nanotubes (CNTs), graphene, and graphene derivatives are the principal carbon-based nanoadsorbents identified which have been researched and critically appraised in this article. This paper also includes a discussion on EC categorization, as well as their history, impacts, and potential futures.

2. Potential Sources and Impact on Health and Environment Due to ECs

Sewage, solid waste generated by municipal solid waste collection and treatment facilities, and urban runoff are all important sources of ECs [1]. There are several ECs in both surface and groundwater. The concentrations of ECs in surface water are typically lower than those reported shortly after wastewater treatment facilities discharge. This is caused by dilution and other natural processes. Groundwater concentrations may worsen if the aquifer is contaminated. Environmental and water-related physicochemical factors, as well as longitude and latitude, may all influence how ECs migrate, where they go, and how they appear in the environment. The chemical purity and exposure dosage are influenced by the source type. Many human actions contribute to the destruction of the environment. ECs were discharged in large quantities into wastewater treatment facilities (WWTPs) from industrial, commercial, and residential sources. The EC sources and paths are depicted in Figure 1. Heavy metals and organic compounds are present in sludge produced by physical and chemical processes in WWTPs. Excreta from the human body, as well as

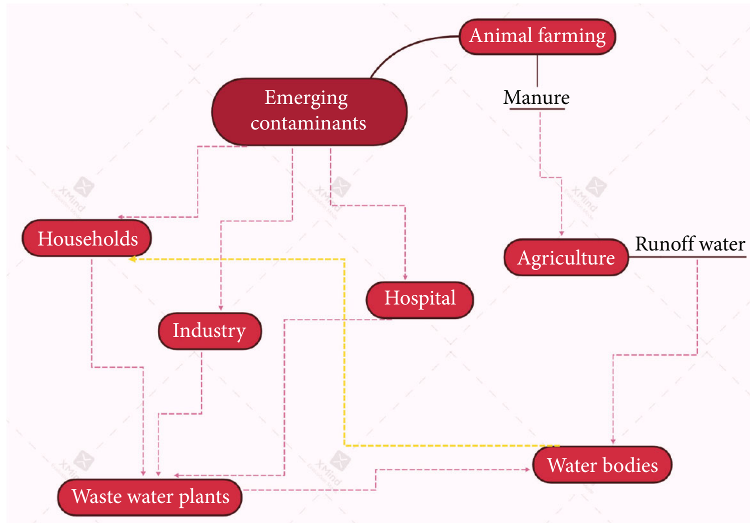

Figure 1: EC origin and pathways.

abandoned, expired, or unused medications and medicine, made their way into the environment. A variety of chemical and microbiological components are non-biodegradable long-term contaminants. These pollutants can be found in industrial, agricultural, and municipal effluents, as well as industrial smoke [32]. When pharmaceutical waste and organic matter disintegrate in neutral conditions, microcontaminants that might be toxic are produced. These micropollutants are present in the distribution of drinking water. Organic contaminants in wastewater rise as leaching increases. This is harmful to people's health. Pesticides in groundwater can be reduced by replacing ecologically acceptable materials for pesticides in fertilizer. Human excretion, residual medicine disposal, and agricultural usage were the chief sources of pharmaceuticals entering the atmosphere. These drugs were identified in both groundwater and surface water. 90% of pharmaceutically active chemicals (PhACs) reach water bodies, according to research [33]. Pesticide and insect-repellent compounds, lipid regulators, and steroid and sunscreen components are all found in our homes and personal care items. Fluoride is a bactericide that is commonly found in toothpaste, shampoo, soap, mouthwash, and even skin creams. Triclosan, an antibacterial agent, is commonly included in deodorants and cosmetics [33]. Benzophenone and its 2,4-dihydroxybenzophenone derivatives are used in sunscreen and UV cosmetic products. Because they are designed for outdoor use, most self-care products may be cleaned without affecting their structure or quality. Toxins have a bigger impact at wastewater treatment plants because they are more easily transferred into aquatic habitats [14]. Pesticides are used in farming operations to reduce the spread of potentially harmful insects, weeds, and microorganisms such as fungi and bacteria [6]. Inequity in the use of antibiotics, biocides, and pesticides must be eliminated. Pesticides must be used in order to safeguard the food supply. Biocides and insecticides are commonly used on farms and in cities. Pesticides and biocides may readily permeate the water supply and affect aquatic life with proper drainage, soil, and topography [14]. Pesticide risks are often overlooked by people in developing nations. Pesticide usage and ineffective management are to blame. Pesticide and biocide concentrations will be higher in the absence of monitoring data.

Polychlorinated biphenyls are largely suspended solids because of their low vapor pressure, poor water solubility, and high octane-water coefficient [33]. As body fat levels rise, their half-life lengthens from weeks to months. These pollutants have been associated with neurological and endocrine system malfunction in addition to increasing tumor development [33]. The presence or absence of aryl hydrocarbon receptors influences the toxicity of dioxin-like compounds. As a result of increased environmental awareness, industrially related synthetic dyes and hazardous wastewater effluents including colors have garnered more attention. The most efficient approach to avoid harmful contaminants is through environmental laws and regulations. Synthetic dyes with structurally diverse molecular structures, such as anthraquinone and anthraquinone-based dispersions and metal complexes, are among the most commonly used and ecologically hazardous dyes [1]. Surfactants are synthetic substances that are widely used in the production of cleaning agents, emulsions, paints, insecticides, and cosmetics across the world. Surfactant toxicity is mostly determined by their capacity to permeate marine cell membranes. Large-scale surfactants include linear alkylbenzene sulfonates, lignin sulfonates, fatty alcohol ethoxylates, and alkylphenol ethoxylates.

ECs have been demonstrated to be hazardous to both human and environmental health. Mistakes in glucose metabolism and infertility have been related to a wide range of health issues. Infertility, pregnancy difficulties (such as excessive cholesterol, fetal obesity, and low sperm quality), memory loss and anemia, high blood pressure and apoptosis, and a range of other disorders are among these [34]. Medication usage has been associated with an increased risk of birth defects and developmental delays, as well as hormone imbalances and endocrine system malfunctions. ECs may be accumulating in humans and/or wildlife. To protect both human health and the environment, ECs and their adverse consequences must be studied and handled further. The deliberate or inadvertent dumping of dangerous chemicals into large bodies of water endangers the environment and human health.

3. Adsorption for EC Removal

In order to remove ECs, physical, biological, and chemical methods are used. Physical treatment with no biological or chemical materials has no influence on the biochemical characteristics of the ECs. Enzymatic breakdown and live organisms are both included in biological treatment. Chemical treatment entails the use of chemical compounds. Adsorption, advanced oxidation processes, biological treatments, and membrane separations are some of the most successful EC removal methods [35–37]. Because of its simplicity of use and minimal environmental impact, biological methods are the most extensively utilized technique. However, they are less effective due to limited biodegradability. High selectivity, high efficiency, simple processing, no need for harsh chemicals, high productivity, cost-effectiveness, easy posttreatment, and less disruptive are a few of the advantages of adsorption [38–41]. Adsorption is a surface phenomenon where pollutant molecules cling to an adsorbent owing to the van der Waals forces and electrostatic interactions. Adsorbents and adsorbates interact in two ways: chemically and physically. Through pores in the adsorbent, the adsorbate diffuses and interacts with the active sites when it comes into contact with the outer surface [13]. In the adsorption process, the adsorbate and the adsorbent's physical and chemical properties play a major role. For example, changes in pH can affect adsorbent surface groups and pollutant charge [10]. The presence of functional groups such as hydroxyl and carboxyl groups makes the adsorbent highly effective [13, 14]. Natural adsorbents like clay and sand are ideal for adsorption since they are abundant and cheap. Industrial waste adsorbents can encapsulate a material in another substance.

Activated carbon (AC) has been extensively studied for EC removal. However, adsorption using AC is expensive since activated carbon is seldom recovered. Normally, less than 40% of the AC impregnated is reused. These factors significantly limit the use of AC [42]. Biochar (BC) is a stable source of carbon that is produced by thermal or aqueous processes in low- or no-oxygen environments. It increases the surface activity, porosity, and utility of biochars. Some biochars may be confused with activated carbon due to their similarity. It is said that BC composites treated with nanoparticles enhance pollutant absorption. BC's corrosive treatment promotes oxygenated surface groupings [43]. ECs (like tetracycline and endocrine-disrupting compounds) can be taken up by modified biochar through hydrophobic, electrostatic, hydrogen bonding, and functional groups [1].

Nanoadsorbents are adsorbents with a diameter of a few nanometers. Despite its limited application in industrial adsorption, nanotechnology has great promise for improving water treatment systems used to remove EC. Materials like graphene, carbon nanotubes (CNTs), clay minerals, siliceous adsorbents, and polymers like polyethylene terephthalate can replace AC in EC removal. Chemical or thermal modification of the adsorbent's surface can result in a multifunctional nanoadsorbent with improved capacity for EC absorption. Even at low concentrations (mg/L), nanoadsorbents were able to remove ECs. To top it all off, the nanoadsorbent dosage was small, and the removal time for ECs was quick (1–15 min). Figure 2 presents the overview of the EC adsorption.

3.1. Carbon Nanotubes (CNTs). Carbon nanotubes (CNTs) are a potential adsorbent for the remediation of several ECs due to their large surface area, tiny size, and tremendous porosity [11]. Carbon nanotubes (CNTs) have significant potential to replace activated carbon in water treatment technologies and are likely to do so in the near future. Because of their open structure, CNTs have a larger surface area, faster access to reactive sites, faster kinetics, and improved adsorption capacity [6]. Cost and development of sustainable production procedures, on the other hand, are hindering the widespread use of carbon nanotubes. The most common CNT forms are single-walled CNTs, multiwalled CNTs, and functionalized CNTs. When it comes to adsorption, the morphologies of carbon nanotubes, such as tube diameter and bundle shape, are crucial. Smaller carbon nanotubes with bigger specific surface areas and distinctive hollow and layered structures have a better potential for adsorption than larger carbon nanotubes [6]. As a result, single-walled carbon nanotubes (SWCNTs) are less effective than multiwalled carbon nanotubes (MWCNTs) at adsorbing the adsorbate. The capacity of pollutants to adhere to surfaces is determined by how they interact with one another. This implies that each pollutant has a unique capacity to adhere to surfaces.

Carbon nanotube surfaces' wettability and hydrophilicity are improved by adding functional groups [44–46]. Oxygen-containing groups, such as hydroxyl, carbonyl, or carboxylic, are found in functionalized carbon nanotubes. To add functional groups to carbon nanotubes, sulfuric acid (H_2SO_4) and nitric acid (HNO_3) can be utilized. Carbonyl groups and oxygen levels on the surface of MWCNTs have been shown to have a significant influence on their maximal adsorption capacity [45]. As a consequence, researchers created modified carbon nanotubes for use as an adsorbent. The researchers employed oxidized MWCNTs in conjunction with a range of oxygen molecules to adsorb the antibiotic medication tetracycline from aqueous settings [46]. The Langmuir model calculated the maximum adsorption capacity (q_{max}) of carbon nanotubes with 2.0%, 3.25%, 4.75%, and 5.95% oxygen to be 217.8, 269.25, 217.56, and 210.43 mg/g, respectively. Another investigation validated the impact of raising the oxygen content from 2.0 to 5.9% on the sorption limit of carbon nanotubes for ciprofloxacin expulsion [11]. Using the Langmuir isotherm model, q_{max} was calculated to be 150.6, 178.9, 206.0, and 181.2 mg/g for carbon nanotubes containing 2.0%, 3.2%, 4.7%, and 5.9% oxygen, respectively [43]. Adsorption of anti-infection medicines

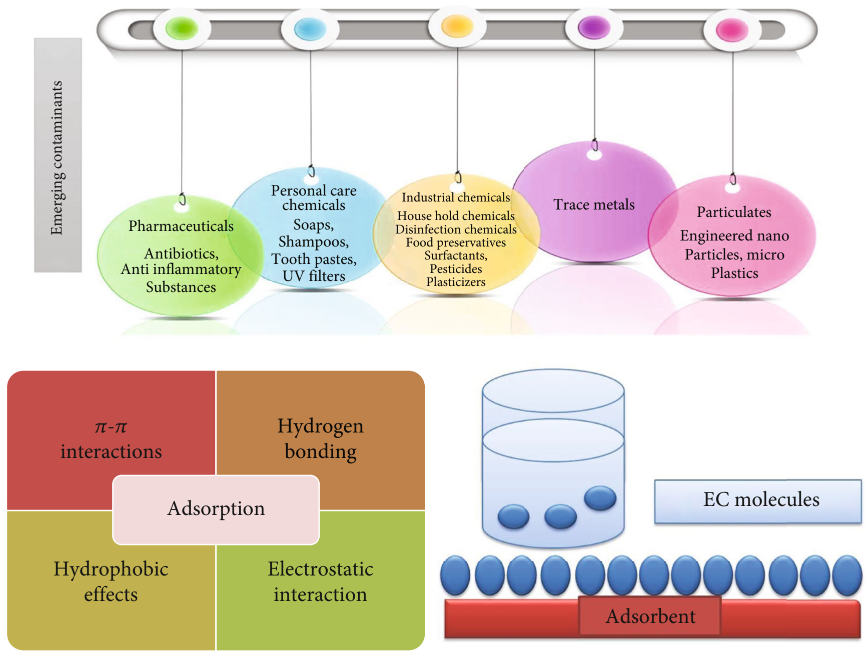

Figure 2: Overview of EC adsorption.

norfloxacin and ofloxacin onto functionalized carbon nanotubes has been studied [47]. The MWCNT and SWCNT were altered to add beneficial groups such as hydroxyl (-OH) and carbonyl (CO).

In the adsorption of the antibiotics ofloxacin (OFL) and norfloxacin (NOR), there is a significant link between the adsorption coefficients and the specific surface area of CNTs. It is probable that structural properties had a significant influence on the adsorption of OFL and NOR on CNTs via an electron donor-acceptor mechanism [47]. Tetracycline adsorption on MWCNTs is influenced by surface characteristics and solution chemistry. The adsorption capacity and coefficient of adsorption of tetracycline increased linearly with the surface oxygen concentration of MWCNTs. Water clusters formed during tetracycline adsorption due to the dispersibility of the nanotubes. This contact is assumed to be the source of the problem. Furthermore, interparticle and boundary layer diffusion might influence total tetracycline adsorption onto 3.2% oxygen-containing carbon nanotubes. When the pH was between 3.3 and 8.0, the majority of tetracycline could adhere to carbon nanotubes. This occurred when water clusters, or H-bonds, formed on the carbon nanotubes [44].

Oxidized multiwalled carbon nanotubes were utilized as adsorbents in a study to investigate the effect of oxygen concentration on the adsorption capabilities of ciprofloxacin (CPX) [46]. The rise in oxygen content from 2.0% to 5.9% appears to be increasing CPX's adsorption capacity. The interaction of electron donors and acceptors has been identified as the fundamental reason for the lower expansion rate. The increased hydrophilicity and dispersion of the adsorbent, as well as the suppression of water clusters, enabled CPX adsorption on oxidized MWCNTs. The alkaline atmosphere was demonstrated to have a negative impact on the attachment of CPX to MWCNTs. Ionic strength, on the other hand, had no effect on CPX's capacity to adsorb onto MWCNTs. Electrostatic interactions appear to have a significant role in adsorption [46]. Single-walled carbon nanotubes were employed to remove bisphenol A (BPA) and 17-estradiol (E2) from aqueous systems without and with ammonium persulfate treatment. DFT calculations revealed that two chemicals interact with sorbent structures. According to adsorption energy estimates, both sorbents preferentially adsorb E2 over BPA. The optimum geometric orientation of molecules in contact can have a significant impact on adsorption behavior [48]. Ahmaruzzaman et al. synthesized CNTs from sunflower oil, a readily accessible bioprecursor, which was then coated with SnO_2 nanoparticles using *Coccinia grandis* extracts. The generated nanoheterojunction displayed outstanding performance against arsenic, with a maximum adsorption capacity of 106.95 mg/g. Furthermore, the SnO_2-CNT nanoheterojunctions showed catalytic activity in the reduction of 4-nitrophenol [29].

CNTs may be used to make structures such as a one-dimensional hollow tube shape. Depending on the quantity of graphene layers, single-walled and multiwalled carbon nanotubes can be created. Many pollutants are adsorbed on the surface of carbon nanotubes [11, 44–46]. CNTs can have their base or sidewalls modified with different oxygen-containing functional groups to improve the surface properties. MCNT, a magnetic material consisting of carbon nanotubes, has become a popular approach for enhancing separation and purification efficiency. For example, because of its large surface area and capacity to be regenerated, MCNT is perfect for the rapid separation of various environmental media. Sulfamethoxazole, carbamazepine, and ketoprofen were among the pharmaceutical pollutants that could be removed from water using carbonaceous adsorbents containing doped phosphorus (P). Adsorbents demonstrated high removal rates (>99%) for all substances tested. Adsorption was primarily controlled by π-π and n-EDA interactions as well as H-bonds. Metal ions were demonstrated to have no influence on the removal of pharmaceutical pollutants [34]. Table 1 summarizes the studies on CNT adsorbents used to clear up EC.

Even though carbon nanotubes are well known in many industries and have significant promise for environmental remediation, there are a number of factors that prevent them from being employed more broadly. Scientists must cope with production costs, toxicity, and environmental dangers. It is expected that CNTs can have safety criteria and risk evaluations to determine how safe they are to use, which might lead to additional CNT uses in the near future.

3.2. Graphene-Based Adsorbents. Many scientists believe that graphene and graphene-based nanomaterials are the ideal options for water purification because of their high surface area-to-volume ratio and other physical features, such as their capacity to receive electrons and resist pollutants [35, 54]. According to the literature, nonelectrostatic interactions are the primary means by which graphene-based nanomaterials remove pollutants. Several researchers have attempted to alter the surface of graphene in order to make it more efficient and simpler to reuse [27, 35, 54, 55]. For the majority of the ECs studied, reduced graphene oxide and graphene were found to have lower adsorption capabilities than graphene oxide. This is because the surface has grown more hydrophobic, with fewer oxygen functional groups, making it more difficult for ECs in water to adhere to it. With a wider surface area, ECs may adsorb in more places. As a result, the material's adsorption capability can be increased. Because of its delocalized electrons and vast surface area, graphene is suited for the removal of organic compounds comprising benzene rings and π-π stacking. GO suspension was used to eliminate tetracycline, a prescription antibiotic. Tetracycline's four aromatic rings each have a distinct functional group, such as phenol, aldehyde, ketone, and amino. It adheres to the GO surface via two mechanisms: interaction and cation bonding. The Langmuir model predicts a maximum adsorption capacity of 313 mg/g. When pH or Na^+ concentrations were increased, tetracycline adsorption on GO was decreased [54].

Three-dimensional chitosan-gelatin aerogels containing GO are mixed in two ways: coating and embedding. Tolerance to lead (Pb^{2+}) was assessed, as well as its effectiveness against the fluoroquinolonic medications ofloxacin and ciprofloxacin. Coating and embedding techniques demonstrated only a small influence on organic contaminant adsorption capacity, which varied from 5 to 8 mg/g, whereas chitosan-gelatin control aerogels without GO showed no adsorption [27]. Kovtun et al. used coating and embedding processes to incorporate GO into three-dimensional chitosan-gelatin aerogels. The fluoroquinolonic medications ofloxacin and ciprofloxacin, as well as lead (Pb^{2+}), were used to evaluate the produced adsorbents. There was just a little variation in pollutant removal between the adsorbents manufactured utilizing both techniques [27]. The issue with graphene is that due to its hydrophobicity, it is difficult to recycle. Graphene is also ineffectual for polar component adsorption with hydrophilic chemical groups. Khalil et al. used porous graphene (PG) to extract the medicines atenolol (ATL), ciprofloxacin (CIP), carbamazepine (CBZ), gemfibrozil (GEM), diclofenac (DCF), and ibuprofen (IBP) from aqueous solutions. At trace concentrations, low PG dosages (100 mg/L) resulted in quick response times and high clearance efficiencies for all studied EC. EC mixes were examined to evaluate if PG might be utilized for tertiary therapy. Increasing the quantity of PG in water and wastewater samples can aid in the removal of mixed ECs [56]. Table 2 summarizes the studies on graphene adsorbents used to remove EC.

Toxic organic contaminants are effectively removed by graphene and its functionalized compounds. The most significant constraints of GO and GO-based nanomaterials are their high cost and difficulties in reusing. Because of the nanomaterial's high electrostatic interactions, reuse may be impossible. Only a few researchers have looked at the reusability of graphene-based EC adsorbents. More study is needed to determine how graphene impacts human health and the environment.

3.3. Miscellaneous Carbonaceous Nanoadsorbents. Fullerenes, carbon nanospheres, and carbon nanofibers are the other carbon-based nanoadsorbents that have recently been employed for EC adsorption. The major contrast between CNTs and fullerenes is the carbon form. Fullerenes are frequently found as hexagonal rings containing carbon atoms. Fullerene's properties have been effectively used to increase its utility in the environmental domain. The detection and capture of carbamazepine in an aqueous media were investigated theoretically using fullerene and its derivatives doped with B, Al, Ga, Si, Ge, N, and P. The fullerene derivatives doped with Al, Si, and Ga are the strongest candidates for serving as sensors and uptaking carbamazepine in aquatic conditions, according to DFT simulations [61]. Mesoporous carbon nanospheres (MCNs) were employed to efficiently remove methyl orange (MO), rhodamine (RhB), and p-hydroxybenzoic acid (p-HBA), with a removal efficacy of more than 95% [62]. The greatest removal efficacy for tetracycline hydrochloride (TCH) and ciprofloxacin hydrochloride (CPH) for hollow mesoporous carbon spheres (HMCSs) generated and modified for laccase (Lac) immobilization was 99.4% and 96.9%, respectively [63]. A zinc oxide-coated carbon nanofiber composite was used as an adsorbent to extract amoxicillin from ambient water matrices. The maximal adsorption capacity was determined to be 156 mg/g based on the results. Furthermore, the adsorbent was successfully tested on actual wastewater samples and shown to be reusable for up to fifteen cycles [64]. Activated carbon, multiwalled carbon nanotubes, and carbon nanofibers have been used to remove atenolol, caffeine, diclofenac, and isoproturon from ultrapure water and a municipal wastewater treatment plant effluent [65]. A magnetic carbon nanofiber (MCF) composed of bacterial cellulose absorbed diclofenac from water. MCF is a porous

Table 1: Removal of emerging contaminants by CNT-based adsorbents.

Adsorbent	Pollutant	Adsorption capacity	Reference	Significant findings
SnO_2-CNT	As (III)	106.95 mg/g	[29]	(i) 86% removal efficiency after 5 regeneration cycles (ii) Multifunctionality: catalytic effectiveness against 4-nitrophenol, alizarin red S dye, and metronidazole pollutants. Antimicrobial activity against bacterial and fungal strains
Oxidized multiwalled carbon nanotubes with different oxygen contents	Tetracycline	Adsorption capacity of CNTs-2.0%O < CNTs-3.2%O > CNTs-4.7%O > CNTs-5.9%O.	[44]	qm/SSA continued to increase with increasing oxygen content
	Ciprofloxacin (CPX)		[46]	
SWCNT, acidified ammonium persulfate treated SWCNT (t-SWCNT)	Bisphenol A (BPA), 17β-estradiol (E2)	BPA: 19.4 mg/g and 8 mg/g, respectively, for SWCNT and t-SWCNT; E2: 27.2 mg/g	[48]	
MWCNTs with 15nm, 30nm, 50nm and SWCNTs (hydroxyl functionalized, carboxy functionalized, and pure)	Ofloxacin (OFL) and norfloxacin (NOR)		[47]	The structural and hydrophobic characteristics of OFL and NOR influenced their adsorption
SWCNTs and MWCNTs	Ibuprofen (IBU) and triclosan (TCS)	For SWCNT, IBU at pH 7: 232 mg/g; TCS at pH 7: 558 mg/g	[49]	SWCNT adsorbed more IBU and TCS than MWCNT; IBU adsorption was higher at pH 4, but TCS adsorption was higher at pH 7; CNT surface oxidation decreased adsorption
MWCNTs	Ciprofloxacin (CPX)	150 mg/g	[50]	CNT absorbed more CPX than activated carbon and carbon xerogel; however, oxidation and heat treatment had little effect on CNT adsorption
SWCNTs and MWCNTs	Perchlorate (ClO_4^-)	3.55 mg/g	[51]	DWCNTs adsorbed better than SWCNTs and MWCNTs; the presence of additional ClO_4 oxygen-containing functional groups increased adsorption
SWCNTs in the presence of natural organic matter (NOM)	Bisphenol A (BPA) and 17β-estradiol (E2)		[52]	The adsorption of BPA and E2 varied from 7.3 to 95% depending on the solution pH and the presence or absence of NOM and SWCNTs
MWCNT carboxyl functionalization	Mixture of four linear alkyl benzene sulfonates	168 mg/g	[53]	The adsorption was made possible through hydrophobic contact and the creation of hydrogen bonds

(mesopores and macropores) material having a specific surface area of 222.3 m^2/g. The diclofenac elimination was effective (93.2%) and quick (20 min) [66]. Self-assembling two-dimensional graphene oxide nanosheets and one-dimensional carbon nanotubes were used to readily construct three-dimensional macrostructures. The adsorbent was more effective at eliminating oxytetracycline (1729 mg/g) and diethyl phthalate (680 mg/g) [67]. The literature studies show that ECs can be successfully removed by adsorption tests using fullerenes, carbon nanospheres, and carbon

Table 2: Removal of emerging contaminants by GO-based adsorbents.

Adsorbent	Pollutant	Adsorption capacity	Reference	Significant findings
Embedded GO aerosols. Coated GO aerosols	Ofloxacin, ciprofloxacin, and Pb^{2+}	5-8 mg/g for antibiotics for both adsorbents. For Pb^{2+}: 11.1 mg/g for embedded GO aerogels and 1.5 mg/g in coated GO ones	[27]	Antimicrobial effects were found particularly for the GO-coated aerogel materials
Graphene oxide (GO)	Tetracycline antibiotics	313 mg/g	[54]	Tetracycline strongly deposited on the GO surface via π-π interaction and cation–π bonding.
Nanostructured porous graphene	Atenolol (ATL), ciprofloxacin (CIP), carbamazepine (CBZ), ibuprofen (IBP), diclofenac (DCF), and gemfibrozil (GEM)	8.87, 7.33, 14.63, 47.85, 91.59, and 9.26 mg/g, respectively	[56]	(i) Regeneration and reuse for four cycles (ii) Heterogeneous adsorption described by the Toth and Sips isotherm models
Graphene oxide	Metformin	96.7 mg/g	[57]	
Graphene oxide nanoplatelets	Carbamazepine (CBZ)	9.2 mg/g	[58]	Could be reused for up to 8 times
Graphene oxide composite with activated carbon and chitosan	Acetaminophen (ACP), carbamazepine (CBZ), bisphenol A (BPA), caffeine (CAFF), and triclosan (TCS)	13.7, 11.2, 13.2, 14.8, and 14.5 mg/g, respectively	[59]	According to DFT studies, the adsorption process is mostly accompanied by size-related diffusion, with a modest contribution from a synergetic mix of hydrophobic/hydrophilic, hydrogen bonding, electrostatic, and π-π interactions
Reduced graphene oxide (rGO)–cellulose nanocrystal sponge	Methylene blue	17 mg/g	[60]	

nanofibers. However, these studies provide a scant description of adsorption processes and place little focus on adsorbent reusability. These materials have the potential to be extremely useful for EC adsorption.

3.4. Adsorption Mechanism and Influencing Factors. Polar organic molecules, such as carbon-based nanoadsorbents, exhibit hydrophobic effects, π-π interactions, hydrogen bonds, covalent bonds, and electrostatic interactions [44]. The π-π interaction dominated benzene ring adsorption. Triclosan, for example, has two aromatic rings and is thus more compatible with the CNT surface than ibuprofen [49]. Electrostatic interactions can greatly aid adsorption. Depending on the pH of the solution, functional groups containing oxygen can be protonated or deprotonated [49]. Carbon materials absorb hydrophobic organic molecules as a result of hydrophobic interactions. Adsorption is most effective in carbon materials with a net charge density of zero. Furthermore, the benzene ring on the surface of carbon nanotubes can serve as an electron donor for organic molecules containing oxygen-containing functional groups [44, 49]. This enables hydrogen bonds to form. Adsorption is a good way to get rid of ECs in water because they have a lot of aromatic rings and a specific chemical makeup [18].

The pH of the solution affects the protonation and deprotonation of pollutants, which is dependent on their pKa, making it an important factor in organic molecule adsorption [10]. This can be aided by increasing the pH, which changes the interactions between adsorbents and sorbates by changing their hydrophobic and electrostatic properties [44, 49]. A higher pH may also increase the ability of the adsorbate to donate electrons, potentially improving the overall electron donor-acceptor interaction. The pH of the carbon nanotube surface can affect the protonation state of the tetracycline molecule and the hydrophobicity of the adsorbate, thereby influencing adsorption interactions [54]. The adsorption of tetracycline on GO varied greatly between pH ranges of 3 and 11. Tetracycline's adsorption capacity varies with initial concentration. When the adsorption capacity falls to 133.62 mg/g, three times as much, tetracycline is removed. Tetracycline's adsorption capacity decreased eightfold and fourteenfold over the pH range, depending on the initial concentration. Because adsorption and adsorption are electrostatically repelled, an increase in ionic strength facilitates adsorption. Increased ionic strength can make organic molecules more likely to precipitate from aqueous solutions and bind to nanoadsorbents. Different concentrations of NaCl were added to the tetracycline and GO solutions to investigate the effect of ionic strength on adsorption capacity. The adsorption capability decreases when NaCl is added. Tetracycline's adsorption capability was reduced by more than half when NaCl concentrations were increased to 100 mmol/L. The ability of NaCl to bind to tetracycline varies little between 8.33 mg/L and 33.33 mg/L in the range of 20-100 mmol/L [54].

4. Current and Future Challenges

There is a possibility that nanomaterials could remove EC from water in an effective manner. It is possible that limiting the use of adsorbents will result in the creation of new sources of pollution. It is difficult to develop adsorbents of high quality today that can be utilized in the most modern water treatment processes. The adsorbents are susceptible to change if functional groups or structures are introduced into the mix. This approach is more effective than others in the elimination of pollutants. Due to their diverse range of properties, conventional adsorbents are not capable of filtering out all of the contaminants that can be found in wastewater. It is possible that some adsorbents with multiple uses will come in handy. Because different types of pollutants compete for adsorption, special consideration needs to be given to the design of multifunctional adsorbents. Instead, we need to investigate the possibility of using one pollutant as a binding site for another pollutant by employing the process of beneficial adsorption. Obtaining an absorption rate of this magnitude ought to be the end goal. Adsorption and removal of pollutants can be significantly improved through the use of particular interactions between the pollutants and the adsorbents. Like any other method, absorption has some drawbacks that must be considered. The widely utilized arrangement of fixed beds has only been the subject of a limited number of research efforts. It is essential to reuse adsorbents after they have been recycled because of the impact that this practice has on the environment. In order to model multicomponent systems accurately, isotherms are required.

5. Conclusions

As a result of their introduction into the environment, newly discovered contaminants will pose significant new hazards to natural resources, ecological systems, and human health. The methods now in use for safety monitoring, risk assessment, preventive actions, and cleaning will become obsolete. More research is needed to develop efficient low-level detection methods as well as overall pollution eradication utilizing appropriate treatment technologies. Of course, the overall economics of an adsorption water treatment facility are important to the end customer. The use of carbon nanoadsorbents, such as carbon nanotubes (CNTs), graphene, and its derivatives, as an alternative to or substitute for activated carbon in the remediation of emerging contaminants is discussed in this article. A significant amount of research and development on these adsorbents will be necessary in the not-too-distant future in order to address some of their worries about how they are created, how they operate, and how they may be used.

Data Availability

All the data is available in the manuscript.

Additional Points

Highlights. (1) Adsorption is the most preferred method for removing ECs. (2) The use of nanoadsorbents may increase the adsorption efficiency of ECs. (3) Carbon nanotubes, graphene, and their derivatives have the potential to replace the commercially available adsorbent activated carbon, which has limitations. (4) Functional modifications will play a major role in improvising the uptake of emerging contaminants.

Conflicts of Interest

The authors declare no conflict of interest.

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