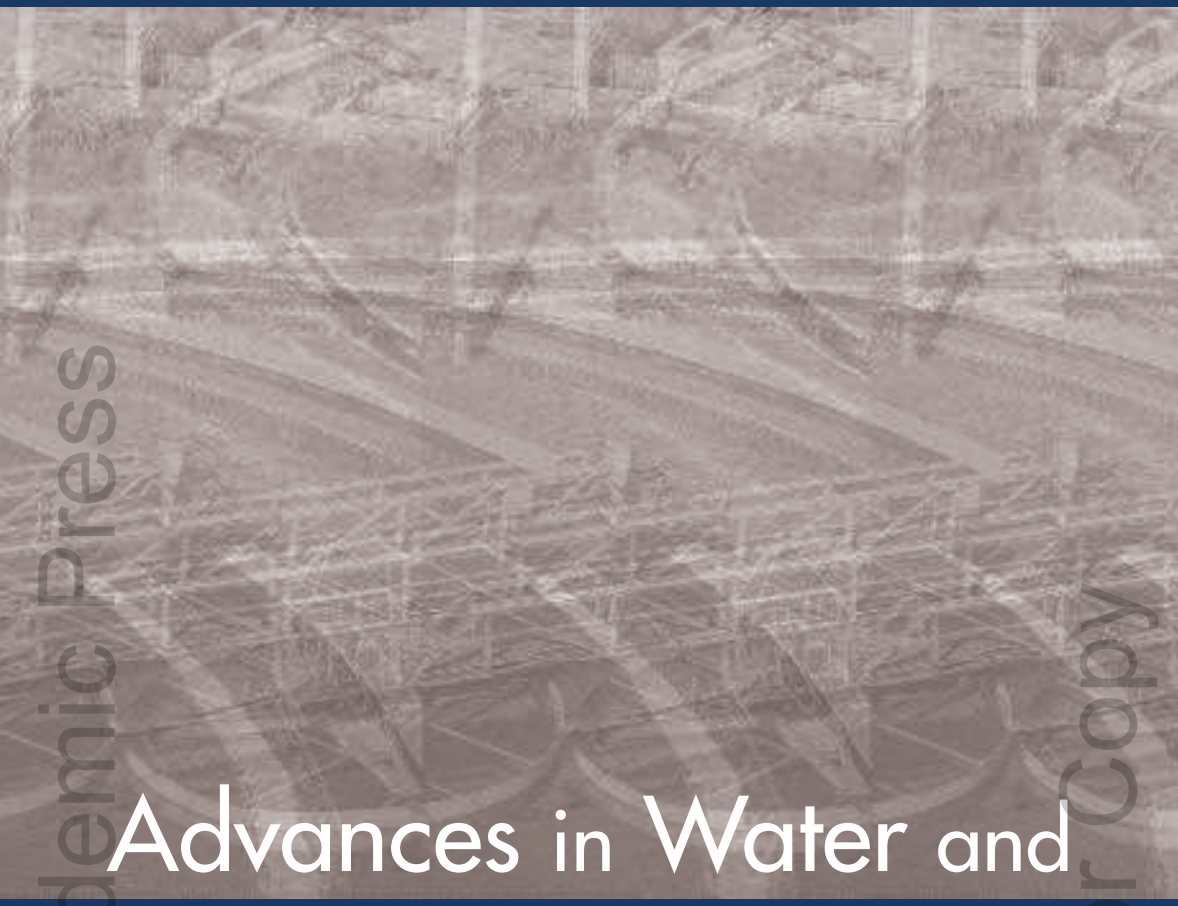


Advances in Water and Wastewater Treatment

Theoretical and Experimental Approaches

Pranav Deepak Pathak
Himanshu J. Patel
Anuja R. Jadhav
Editors

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CHAPTER 9

Treatment of Pharmaceutical Wastewater by Adsorption Using Functionalized Carbon-Based Adsorbents

SAMSUDEEN OLANREWAJU AZEEZ, ISMAILA OLALEKAN SAHEED, AKEEM ADEBAYO JIMOH, and YUSUF OLORUNTOYIN AYIPO*

Department of Chemistry and Industrial Chemistry, Faculty of Pure and Applied Sciences, Kwara State University, Malete, Nigeria

ABSTRACT

Pharmaceutical wastewaters contain evolving contaminants recognized in the environment even at low concentrations and have adversely impacted human health and the biotas. Efficient removal of pharmaceuticals from wastewater requires advanced treatment technologies, and as such, adsorption is useful. There are various investigations on the release, prevalence, consequences, and treatment of wastewater from pharmaceuticals. Carbon-based adsorbents have been recognized as excellent adsorbents for pharmaceuticals; meanwhile, functionalization of these adsorbents has been utilized for improving their adsorption features including morphology, surface properties, and chemical and thermal stabilities. Activated carbon, graphite, graphene, graphene oxide, carbon nanotubes, and fibers are a few examples of various carbon-based adsorbents that have been recently designed for the treatment of wastewater containing pharmaceuticals. The functionalization of these named carbon-based adsorbents has improved their effectiveness, and their performance is also a function of adsorption parameters (pH, initial concentrations, dosage, contact time, agitation

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speed, and temperature). The physical and chemical properties of functionalized carbon-based adsorbents together with adsorption features are mainly determined by the type of precursor and preparation methods. In this chapter, the recent synthetic routes and characterization of functionalized carbon-based adsorbents (graphite, graphene, graphene oxide, activated carbon, and carbon nanotubes and fibers), and their applications concerning their adsorption performance for the adsorption of pharmaceuticals are emphasized and outlined.

9.1 INTRODUCTION

There is a rising apprehension caused by the presence of pharmaceutical wastes in water bodies and the environment. These pharmaceuticals enter the environment during production, consumption, and disposal (Ojha et al., 2021; Wilkinson et al., 2022). Pharmaceutical wastewaters contain evolving contaminants such as antibiotics, analgesics, etc., recognized in the environment even at low concentrations and have adversely impacted human health and the biotas (De Andrade et al., 2018). Table 9.1 shows typical pharmaceuticals found in wastewater. The surge in the usage of pharmaceutical products by human beings and animals results in their increase in the environment (Luján-Facundo et al., 2019), which could be a result of one or more of the following paths: effluents produced by drug manufacturing industries, chemicals runoff, disposal of expired products, flushing off body wastes, leaching off chemicals from landfills, and agricultural wastes (Ojha et al., 2021). Among the most commonly consumed pharmaceuticals discovered in wastewater are not limited to anti-inflammatories, antibiotics, analgesics, contraceptives, beta-blockers, lipid regulators, and neuroactive compounds (Quesada et al., 2019). Figure 9.1 shows the path by which pharmaceuticals enter the environment. Although the amount of pharmaceutical contaminants in wastewater is very low (ng/L to mg/L), their existence, persistence, and endless discharge into the environment portend great danger to aquatic and human life (Quesada et al., 2019), some of which are antibiotic resistance, hormonal alterations, endocrine disruption, and chronic diseases that affect the excretory system (Duarte et al., 2022). These negative impacts of pharmaceutical contaminants in wastewater must not be overlooked. It is yet very challenging to determine their long-term effects on the environment (Quesada et al., 2019; Wilkinson et al., 2022).

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TABLE 9.1 Typical Pharmaceuticals Found in Wastewater

Pharmaceuticals	Chemical Formulae	Therapeutic Class	References
• Paracetamol	• $C_8H_9NO_2$	Analgesics and anti-inflammatories.	Duarte et al. (2022); Elamin et al. (2019); Luján-Facundo et al. (2019)
• Diclofenac	• $C_{14}H_{11}C_{l2}NO_2$		
• Ibuprofen	• $C_{13}H_{18}O_2$		
• Acetaminophen	• $C_8H_9NO_2$		
• Aspirin	• $C_9H_8O_4$		
• Amoxicillin	• $C_{16}H_{19}N_3O_5S$	Antibiotics	Ahangaran et al. (2020); Burns et al. (2018); Nazal (2020); Turku et al. (2007)
• Erythromycin	• $C_{37}H_{67}NO_{13}$		
• Sulfapyridine	• C_5H_5N		
• Sulfamethoxazole	• $C_{10}H_{11}N_3O_3S$		
• Tetracycline	• $C_{22}H_{24}N_2O_8$		
• Carbamazepine	• $C_{15}H_{12}N_2O$	Anticonvulsants	Asghar et al. (2018); Dehdashti et al. (2019); Mutiyar et al. (2018)
• Caffeine	• $C_8H_{10}N_4O_2$	Stimulating	Asghar et al. (2018); Beltrame et al. (2018); Luján-Facundo et al. (2019); Quesada et al. (2019)
• Amphetamine	• $C_9H_{13}NO$		
• Methamphetamine	• $C_{10}H_{15}N$		
• Diazepam	• $C_{16}H_{13}ClN_2O$	Anxiolytic	Luján-Facundo et al. (2019); Mutiyar et al. (2018)
• Benzodiazepine	• $C_9H_8N_2$		
• Lorazepam	• $C_{15}H_{10}Cl_2N_2O_2$		
• Atenolol	• $C_{14}H_{22}N_2O_3$	Beta-blocker	Dehdashti et al. (2019); Marques et al. (2018); Quesada et al. (2019)
• Bisoprolol	• $C_{18}H_{31}NO_4$		
• Betaxolol	• $C_{18}H_{29}NO_3$		

9.2 TREATMENT TECHNIQUES FOR PHARMACEUTICAL WASTEWATER

Presently, the treatment of pharmaceutical wastewater has attracted global interest owing to the enormous influence it has on the environment and human health. The conventional methods of wastewater treatment such as chemical oxidation, coagulation, reverse osmosis, membrane filtration, photo-degradation, etc., do not completely remove the active pharmaceuticals from wastewater at low concentrations as these techniques generate secondary wastes, are not eco-friendly, and are very expensive to operate (Azeez et al., 2022; De Andrade et al., 2018; Luján-Facundo et al., 2019; Nazal, 2020). However, efficient removal of pharmaceuticals from wastewater requires advanced treatment technologies, and as such, adsorption is beneficial due to its advantages

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FIGURE 9.1 Paths by which pharmaceuticals enter the environment.
Source: Modified from: Nazal (2020).

including ease of operation, cost-effectiveness, low energy consumption, environmental friendliness, and does not generate toxic secondary byproducts (Azeez et al., 2022; De Andrade et al., 2018; Luján-Facundo et al., 2019).

9.2.1 ADSORPTION AS A TECHNIQUE

Adsorption as a treatment technique is extensively utilized to remove substances (contaminants) from the liquid or gas phase (adsorbate) to the solid phase called the adsorbent, which can involve chemical and/or physical interactions (Singh et al., 1985). This process has been experimented with and considered for the efficient removal of several contaminants such as pharmaceuticals (Azeez et al., 2022; De Andrade et al., 2018; Luján-Facundo et al., 2019; Quesada et al., 2019). Adsorption is accomplished in batch or fixed bed columns having a definite quantity of adsorbent. Interactive

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forces occur between molecules of the adsorbate and the adsorbent surface, usually described by an isotherm. This interaction may follow physisorption (due to weak cohesive forces existing between the adsorbate molecules and the adsorbent) or chemisorption, which involves the transfer or sharing of electrons (chemical bond formation) (Tan & Hameed, 2017). The adsorption process involves three stages, namely (Azeez & Adekola, 2016):

- **Stage 1:** External Diffusion: This involves the transfer of the adsorbate molecule present in the solution to the outer surface of the solid adsorbent material.
- **Stage 2:** Diffusion of Pores: Transfer of the adsorbate molecule from the surface of the adsorbent into the pores of the adsorbent.
- **Stage 3:** Surface Reaction: Adhesion of the adsorbate on the surface of the adsorbent pores.

Adsorption techniques have been demonstrated to be an outstanding and favorable method for the effective removal of pharmaceuticals in wastewater due to their various benefits as highlighted above. Therefore, the choice of material as an adsorbent should be essential. The material must have the potential to remove the contaminant from wastewater. The efficiency of adsorption of pharmaceuticals is a function of adsorption operation and optimization parameters (pH, initial concentrations, dosage, contact time, agitation speed, and temperature) as well as the properties of the adsorbent, which include pore size, surface area, moisture content, bulk density, ash content, and functional group (Nazal, 2020; Quesada et al., 2019).

9.3 FUNCTIONALIZED CARBON-BASED MATERIAL AS ADSORBENT

Several adsorbents have been employed by various scientists for the treatment of pharmaceutical wastewater, including clay minerals (Genç & Dogan, 2015; Khazri et al., 2017; C. J. Wang et al., 2010; Wu et al., 2010), silica materials (Turku et al., 2007; Vu et al., 2010), polymeric adsorbents (Coimbra et al., 2018; Cychosz & Matzger, 2010), and carbon-based materials. Carbon-based materials such as graphite, graphene, graphene oxide, carbon nanotubes and fibers, and activated carbon have been recognized as superior and excellent adsorbents for pharmaceuticals due to their low cost compared to other adsorbents, larger specific surface area, high adsorption capacity, high porosity, and efficiency (Cao & Yang, 2018; Coimbra et al., 2018; Duarte et al., 2022). The following sub-sections discuss different functionalized carbon-based

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adsorbents for pharmaceutical wastewater treatment, including activated carbon, graphite, graphene, graphene oxide, and carbon nanotubes and fibers.

9.3.1 ACTIVATED CARBON

Activated carbon is a carbonaceous substance resulting from charcoal with an amorphous and extremely porous structure. It is prepared via pyrolysis of organic materials usually of plant origin and can also be produced from nonconventional materials (Dias et al., 2007; Nazal, 2020). Commercial activated carbon was first produced in the early 19th century from wood (Pierson, 1993). Some sources of plant materials used in the production of activated carbon currently are bamboo, coal, peat, agricultural wastes (coconut shells, flamboyant seeds, and shells, *Jatropha curcas* seed coat, nutshell, sugarcane bagasse, and wood), bones, etc. (Azeez et al., 2022; Azeez & Adekola, 2016; De Andrade et al., 2018; Luján-Facundo et al., 2019). Activated carbon is predominantly considered an adsorbent for efficient removal of organic and inorganic contaminants, including pharmaceuticals, from wastewater primarily due to some inherent properties such as high surface reactivity, large porosity, high specific surface area, and being largely available, abundant, and cheap (Akhtar et al., 2016).

9.3.1.1 PRODUCTION AND CLASSIFICATIONS OF ACTIVATED CARBON

Activated carbon may be produced from environmental wastes with great carbon contents and is classified according to the method of activation or based on its properties. There are two common types of activation of carbon based on the method of production, namely: physical (thermal) and chemical activation methods.

1. **Physical or Thermal Activation:** This method of activated carbon production involves two stages; stage one is by subjecting the precursor raw materials to carbonization at a temperature range between 400 to 800°C to remove volatile organic matter, and the second stage is performed by employing activating agents such as vapor, CO_2, or air at a very high temperature ≥800 °C.
2. **Chemical Activation:** This method of activated carbon production involves performing the two steps above together by impregnating the already carbonized materials in chemical agents such as acids (H_2SO_4, HNO_3, HCl, H_3PO_4acetic acid, citric acid, and formic acid), bases ($Ca(OH)_2$, KOH, NaOH and Na_2CO_3), salt solution (NaCl and

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$CaCl_2$, $ZnCl_2$), oxidizing agent ($K_2Cr_2O_7$, $KMnO_4$, and H_2O_2) and many others (Abdolali et al., 2014; Quesada et al., 2019).

The chemical treatments are essentially performed to enhance the adsorption capacity of the carbonaceous materials of contaminants as well as alter the electrical property of the adsorbent surface. The chemical attack is anticipated to possess the ability to distort the bonding of functional groups to the adsorbent surface. Thus, increasing pore size affects the interactions with other functional groups of the contaminants (Módenes et al., 2017).

Recently, a different method of carbon activation (microwave-assisted pyrolysis) is being explored. This process is more beneficial compared to the traditional two-step procedure, which includes a reduced time of heating, less energy and gas consumption, and gives simplicity of process control. However, this method promotes the development of more pores, it is quite expensive leading to finding better, simplified, and efficient treatments of adsorbent materials (Quesada et al., 2019; Yuen & Hameed, 2009; Zbair et al., 2018).

Commercial activated carbon can be categorized into the following (Oubagaranadin & Murthy, 2012):

i. **Powdered Activated Carbon (PAC):** This consists of fine powder with a particle size < 1.0 mm and average diameters of 0.15 to 0.25 mm.

ii. **Granular Activated Carbon (GAC):** Relatively characterized by larger particle sizes than powdered activated carbon and thus, a smaller surface area. It has a particle size of about 5 mm in diameter. They are mostly used in water treatment to adsorb vapors and gases due to their ability to disperse faster.

iii. **Extruded Activated Carbon (EAC):** It is formed when activated carbon powder combines with a binder and forms a cylindrical or spherical shape. It has a diameter between 0.8 to 130 mm. It is mainly applied in gas purification.

iv. **Bead-Activated Carbon (BAC):** It is a typical activated carbon made from petroleum pitch. It has a diameter ranging from 0.35 to 0.80 mm. It is circular and mostly applied in water treatment.

9.3.1.2 PROPERTIES OF ACTIVATED CARBON

The properties of activated carbon are a function of the type of precursor utilized and the method of preparation. The choice of raw materials should

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be based on the following factors: availability of material, percentage of carbon and oxygen in the material, hazardousness, thermal stability, pore diameter, abrasion resistance, and high adsorption efficiency and regeneration capacity. Characteristically activated carbons have a large specific surface area (600 – 2000 m^2/g) and a distinct microporous structure (average pore diameter ~1.5 nm) (Ali et al., 2012). These qualities are pointers to their chemical, structural, textural, and morphological characterizations. The most widely used instrumental analyses in determining the properties of activated carbon are the Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Brunauer-Emmet-Teller (BET) surface analysis, and Energy Dispersive X-ray spectroscopy (EDS). Other analyses include Point of Zero Charge (PZC), zeta potential, moisture content, and ash content (Akhtar et al., 2016; Ali et al., 2012; Quesada et al., 2019).

9.3.1.3 TREATMENT OF PHARMACEUTICAL WASTEWATER BY ACTIVATED CARBON

The most extensively researched adsorbent for the removal of pharmaceuticals from wastewater is activated carbon, primarily due to its large specific surface area and accessibility (Akhtar et al., 2016). For instance, 185 mg g^{-1} of sulfamethoxazole and 144.9 mg g^{-1} of metronidazole were removed by a commercial activated carbon with a BET surface area of 851 m^2 g^{-1}. While the adsorption of metronidazole, ronidazole, and tinidazole under coequal operating situations by another commercial activated carbon with BET surface area (1,225 m^2 g^{-1}) adsorbed 328, 338, and 394 mg g^{-1} of each of the adsorbate respectively. Relating these two activated carbons, it is evident that the surface area is critical for the adsorption process as the activated carbon with BET 1,225 m^2 g^{-1} adsorbed nearly twofold of metronidazole than the one with BET 851 m^2 g^{-1} (Akhtar et al., 2016; Çalişkan & Göktürk, 2010; Rivera-Utrilla et al., 2009). Additionally, Lujan-Facundo et al. (2019), Beltrame et al. (2018), and Portinho et al. (2017) utilized different activated carbon prepared via different activation methods with surface areas of 1961.26, 155.50, and 19.58 m^2 g^{-1} respectively to adsorb caffeine. The adsorption capacities obtained were 1961.26, 155.50, and 19.575 mg g^{-1}, respectively. Table 9.2 highlights the adsorption capacities of some commercial and various activated carbon for different pharmaceuticals. According to Table 9.2, the type of adsorbate (pharmaceutical) influences the activated carbon's ability to adsorb it. Marques et al. studied the removal of atenolol from wastewater by activated carbon prepared from apple tree

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small branches through an activation with K_2CO_3 and KOH. The activated carbon produced with KOH has a better surface area (2472 $m^2 g^{-1}$) compared with the activated carbon obtained with K_2CO_3 (1963 $m^2 g^{-1}$). Hence, a better removal efficiency of 556 mg g^{-1} to 346 mg g^{-1} was achieved (Marques et al., 2018). Also, Chakraborty et al. investigated the uptake of ibuprofen using raw and steam-activated biochar of *Aegle marmelos* shell. The raw and steam biochar has 4.4 and 308 $m^2 g^{-1}$ BET surface area with 5.0 and 12.66 mg g^{-1} adsorption capacities respectively (Chakraborty et al., 2018).

TABLE 9.2 Adsorption Capacities of Some Activated Carbons for the Adsorption of Various Pharmaceuticals in the Literature

Pharmaceuticals	Precursor for Activated Carbon	Activation Method	BET Surface Area (m^2g^{-1})	Removal Efficiency (mg g^{-1})	References
Metronidazole	Commercial activated carbon	–	1,225	328	Rivera-Utrilla et al. (2009)
Metronidazole	Commercial activated carbon	–	851	144.9	Çalişkan & Göktürk (2010)
Sulfamethoxazole	Activated carbon	–	851	185	Çalişkan & Göktürk (2010)
Penicillin G	Commercial activated carbon	Chemical/ HCl	1000	290	Aksu & Tunç (2005)
Acetaminophen	Granular activated carbon	Thermal	1,100	87.50	Luján-Facundo et al. (2019)
Diazepam	Granular activated carbon	Thermal	1,100	466.40	Luján-Facundo et al. (2019)
Caffeine	Granular activated carbon	Thermal	1100	1961.26	Luján-Facundo et al. (2019)
Caffeine	Pineapple plant leaves	Pyrolysis/ H_3PO_4	1031	155.50	Beltrame et al. (2018)
Caffeine	Grape stalk	Thermal/ 85% H_3PO_4	1099.86	19.575	Portinho et al. (2017)
Tetracycline	Macadamia nutshell	NaOH	1524	455.33	Martins et al. (2015)
Ibuprofen (IBP)	*Aegle marmelos* (wood apple) shell	Raw steam	4.4 308	5.00 12.66	Chakraborty et al. (2018)
Ranitidine	*Aegle marmelos* correa fruit shell	Microwave	910.31	72.86%	Sivarajasekar et al. (2018)
Atenolol	Apple tree small branches	K_2CO_3 KOH	1963 2472	346 556	Marques et al. (2018)

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9.3.1.4 MERIT AND DEMERIT OF ACTIVATED CARBON AS ADSORBENT FOR PHARMACEUTICALS

The merit of Activated carbons as adsorbent for pharmaceuticals include high adsorption capacity in the removal of pharmaceuticals which could be due to their disordered pore structures, larger porosity, and relatively high surface area. It can be reactivated and reused. Its demerits include: It is relatively expensive, Non-selectivity, and problematic to isolate from the effluent.

9.3.2 GRAPHITE

Graphite is a pure form of carbon, typically appearing as flakes of black crystal and masses, and is a soft, crystalline, low-density allotrope of carbon (Tamashausky, 2006). Thanks to its remarkable properties, which include thermal stability, chemical inertness, lubricity, and high electrical conductivity, it is suitable for various industrial applications including electronics, lubricants, metallurgy, steelmaking, and more recently pollutants are treated from wastewater via an adsorption process (Keeling, 2017). Suitable alternatives are not offered for some of these applications. The primary form of graphite can be converted into a variety of substances, including incredibly strong fibers, lubricants that are simple to shear, gas-tight barriers, and gas adsorbers (Robinson et al., 2017). The sp^2 trigonal bonding of carbon atoms serves as the basis for all these different materials, which differ in many ways.

Graphite offers a carbonaceous structure, is very homogeneous and nonporous, and is perfect for researching basic adsorption mechanisms, although it is not a good adsorbent for wastewater treatment (Ivancev-Tumbas et al., 2020). According to reports, graphite has been employed as a prototype adsorbent to remove organic contaminants from the aqueous phase; however, the virgin material in an ozone stream was oxidized to produce near-surface oxygen graphite for the determination of the mechanism of the organic compounds' adsorption in aqueous solutions (Ivancev-Tumbas et al., 2020). In another report, natural graphite was exfoliated with $KMnO_4$, $HClO_4$, and $(CH_3CO)_2O$ for its functionalization as expanded graphite for adsorption (Hoang et al., 2019). In addition, Li et al. (2014) reported the use of the deposition-precipitation method to create a composite of nano-graphite/Fe_3O_4 for the adsorption of methyl violet in an aqueous solution (Li et al., 2014). In another study, the hydrothermal method of decorating expanded

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graphite (EG) with manganese oxide nanoparticles (MONPs) was used to create a new graphitized adsorbent which was then used to remove heavy metals from aqueous solutions (Do et al., 2019). Alshabanat worked on the production of a nontoxic and cheap graphitic-polymer composite (GPC) thin film for the degradation of organic pollutants via photocatalysis (Alshabanat, 2019). All of these studies indicate that natural graphite can be functionalized only by chemical, physical, or thermal processes or both to serve as adsorbents for wastewater treatment.

9.3.2.1 PRODUCTION AND PHYSICOCHEMICAL PROPERTIES OF GRAPHITE

Most adsorbents are characterized by transmission electron microscopy (TEM), structural morphology using scanning electron microscopy (SEM), material crystallinity with X-ray diffractometer (XRD), surface functionality with Fourier transform infrared analysis (FT-IR), surface area with Brunauer-Emmett-Teller machine (BET) or TEM, and elemental composition with energy-dispersive spectroscopy (EDS). Researchers have reported several important physicochemical properties of graphitic adsorbents. Thuong and co-workers reported the synthesis of exfoliated graphite (EG) as an adsorbent using H_2O_2 as the oxidant and H_2SO_4 as the intercalant, and the morphology of the EG was observed by SEM. The structure of the graphite consists of rigidly stacked multilayers after intercalation and microwave exfoliation. The synthesized EG showed worm-like particles, layered aggregate, and multi-porous structures with interconnected open pores. The FTIR spectra of ions on the EG surface revealed the characteristic peaks of O-H (stretching vibration) at 3445 cm^{-1}, C-H (stretching vibration of in CH, CH_2, and CH_3) at 2967 cm^{-1}, C=O (stretching vibration) at 1635 cm^{-1}, and C-O (stretching vibration) 1048 cm^{-1} (Thuong et al., 2019). In another report by Do et al. (2019), expanded graphite (EG) coated with MONPs-EG for adsorption purposes was synthesized. The morphologies of EG and MONPs-EG showed no significant difference as both showed a rough and leaf-like surface structure. The MONPs-EG sample's XRD results revealed fairly poor crystal properties in their structural details when compared to those of EG; the additional peaks at $2\theta = 18.0°$, 29.0°, 31.1°, 32.7°, 36.1, 50.2°, and 60.0° are characteristic Mn_3O_4 (hausmannite) peaks that were deduced from the XRD pattern of Mn_3O_4 nanoparticles. BET analysis showed that the EG possesses a slightly larger surface area but smaller pore size than

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MONPs-EG, which is attributed to the insertion and trapping of MONPs in the narrow pores between the graphene layers of the EG (Do et al., 2019). Alshabanat (2019) also reported the fabrication of a nontoxic and cheap graphitic-polymer composite (GPC) thin film for visible-light activated photocatalytic degradation of organic contaminants. The result of the GPC characterization showed an irregular and rough surface of the material. The pure graphite XRD patterns showed three notable diffraction peaks for graphite at $2\theta = 26.5°$, $2\theta = 45.5°$, and $2\theta = 54.5°$. It was reported that these peaks either broadened or disappeared after the formation of the GPC film (Alshabanat, 2019).

9.3.2.2 TREATMENT OF PHARMACEUTICAL WASTEWATER BY GRAPHITE

Several reports have been published in reputable outlets on pharmaceutical wastewater treatment by graphite. Owing to its devastating impact and consistent detection in the environment, ciprofloxacin is one of the most important pharmaceutical pollutants. Egbedina et al. (2022) examined the ability of coconut shell graphite (CHG) to adsorb ciprofloxacin from an aqueous solution. The operating conditions for the adsorption behavior were obtained at pH 10, 5 mL min^{-1} flow rate, 5 cm bed height, and 1.9 cm diameter via the column adsorption method. The Sips isotherm model's predictions were shown to be followed by the adsorption experiment, with a maximum adsorption capacity of 124 mg g^{-1}. According to kinetic studies, the pseudo-second-order kinetic model ($R^2 = 0.99$) best describes the experimental data. Additionally, the regeneration studies showed that 70% efficiency of ciprofloxacin was retained by CHG after three cycles. The desorption study confirmed the assumption that multilayer adsorption took place at heterogeneous active sites for adsorption (Egbedina et al., 2022). Khalil et al. studied the effectiveness of porous graphene (PG) synthesized at relatively low temperatures as a prospective material for the adsorption of six commonly used pharmaceuticals from their aqueous solutions viz-a-viz: diclofenac (DCF), carbamazepine (CBZ), ibuprofen (IBP), atenolol (ATL), ciprofloxacin (CIP), and gemfibrozil (GEM) via batch adsorption method. The findings showed that several of the environmental contaminants (ECs) had adsorption capacities greater than 100 mg-EC/g-PG rapidly, as well as exceptional removal efficiencies at low concentrations of all the ECs studied (>99%) and at a low PG dosage (100 mg/L). The unfavorable

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interferences that affected the efficient removal of mixed ECs in water and wastewater samples were controlled by increasing the PG dose. Adsorption mechanisms were heterogeneous and physisorption-controlled. The results further corroborated the exothermic feature of the enthalpy-driven adsorption process and the potential for PG recycling. It is possible to consider the application of PG as an excellent candidate for the effective treatment of polluted water with ECs from the pharmaceutical category (Khalil et al., 2020). Divyapriya et al. (2020) utilized graphite felt electrodes to study ciprofloxacin's enhanced electrosorption removal. Optimizing the capacity of graphite to adsorb ciprofloxacin molecules, the effects of adsorption variables including applied voltage, pH, electrolyte concentration, and initial ciprofloxacin concentration were investigated. Additionally, the adsorption process's isotherm and kinetics were examined. The operating experimental parameters did not result in any notable redox peaks on the cyclic voltammogram. The adsorption capacity was raised from 0.617 mg g^{-1} at an open circuit voltage to 1.915 mg g^{-1} at 1.0 V, while the related pseudo-first-order kinetic rate constants were raised from 0.069 min^{-1} to 0.111 min^{-1}. At pH 3.0 and 10.0, as compared to pH 7.0, it was discovered that the adsorption capacity and kinetics were high. With higher applied voltages and lower electrolyte concentrations (0.1–1.0 M Na_2SO_4), the electrosorption process improved performance (0 to 1.5 V). To the experimental data, models for the Freundlich and Langmuir adsorption isotherms were fitted. According to the electrosorption data, electrochemical polarization can greatly increase the rate of adsorption and adsorption capacity due to the increased affinity of the ciprofloxacin-charged species for graphite felt. Based on experimental findings, a proposed mechanism for the electrosorption treatment of ciprofloxacin at various pH levels was suggested (Divyapriya et al., 2020). Investigations on the removal of diclofenac from aqueous solutions by adsorption onto thermoplastic-expanded graphite were carried out. The adsorption capacity was tested in the pH range of 1-7 and kinetic and isothermal studies were used to elucidate the adsorption mechanism. Pseudo-2nd-order and Dubinin-Radushkevich models proved to be the best fits for the experimental kinetic and isotherm data, and they were also consistent with the theoretical adsorption capacity values (400 and 433 mg g^{-1}, respectively). Additionally, adsorbent regeneration study was examined and compared to two different remediation methods. A 0.2 M NaOH solution was used to perform a solvent wash, and an oven temperature cycle of 105°C for 2 hours and 200°C for 4 hours was used for the heat treatment. Adsorbent performance was maintained after four cycles of use and regeneration (Cuccarese et al., 2021). The

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caffeine adsorption from an aqueous medium using graphite foil that has been electrochemically exfoliated and oxidized (G_{SEEO}-modified) has been reported. According to experimental results, GSEEO-modified caffeine can adsorb efficiently, and its adsorptivity is stronger when it is made with $KMnO_4$ than when it is made with H_2O_2 or S_2O_8 by 0.1 M acetone while maintaining high adsorptivity (81%) (Chung et al., 2017). Vedenyapina et al. reported on diclofenac sodium adsorption onto expanded graphite from aqueous solutions. The adsorption kinetics showed that the reaction rate decreases with time as the equilibrium time reaches a constant value in 30 minutes. The Langmuir isotherm with a higher regression coefficient ($r^2 = 0.9917$) was found to be more appropriate for describing diclofenac sodium adsorption on exfoliated graphite than the Temkin and Freundlich isotherms, and the q_{max} compared better to the calculated q_e. The adsorption of diclofenac sodium takes place on the energetically uniform carbon surface, with no interactions between the adsorbate molecules indicating a physical adsorption process. Diclofenac sodium recovery from aqueous solution using expanded graphite was up to 98–99% (Vedenyapina et al., 2013).

9.3.2.3 MERIT AND DEMERIT OF GRAPHITE AS ADSORBENT FOR PHARMACEUTICALS

The merit of graphite includes: It can be easily modified and functionalized into a new form as a composite, and it is chemically inert and thermally stable. Its demerit includes: less efficiency due to its low porosity and is typically not good as an adsorbent in its natural form

9.3.3 GRAPHENE

One layer of carbon atoms, called graphene, has a tensile strength greater than that of steel by 100-fold, and a thermal and electrical conductivity that are significantly higher than that of copper or silver (Novoselov et al., 2012). It consists of a honeycomb crystal structure with an atomically dense planar layer of carbon atoms with sp^2 bonds packed closely together (Geim & Novoselov, 2007). High thermal conductivity, current density, chemical stability, optical transmittance, and larger surface area are just a few of graphene's remarkable, one-of-a-kind thermal, chemical, optical, and mechanical characteristics. The demand for graphene from either natural or synthetic sources is still very low, and the effects on already-existing markets

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or the requirements for new sectors are anticipating further economic advancements (Saravanan et al., 2022). Potential applications include batteries, supercapacitors, electronics, energy storage, surface coatings, water desalination, biomedicine, and adsorbents; However, most new products are still in the research and development phase (Zolnierski et al., 2022). Graphene-based materials including their derivatives have recently drawn more attention in the field of wastewater treatment due to their outstanding features (Shams et al., 2015). Materials made of graphene have been utilized as electrodes, photocatalysts, and adsorbents to effectively adsorb hazardous contaminants from wastewater, such as pharmaceuticals.

9.3.3.1 PRODUCTION AND PHYSICOCHEMICAL PROPERTIES OF GRAPHENE

Natural graphite can be chemically oxidized and exfoliated to produce graphene oxide, which is a material made of several layers of carbon atoms similar to graphene (Tung et al., 2016). By reducing the amino acid content, nanosheets are produced that are stable in aqueous dispersions and have fewer undesirable oxygen groups (Kabiri et al., 2014). The best graphene coverings are prepared using synthetic methods (Novoselov et al., 2012). Alatalo et al. reported the use of $FeCl_3$ and multilayer graphene for Fe/graphene fabrication. A two-step process involving absorption of $FeCl_3$ into the graphene matrix, reduction of the carbothermal treatment by induction annealing at 900°C in an inert argon atmosphere, and heat treatment in an inert atmosphere at 900°C to form the crystalline iron structure were used in the synthesis of Fe/graphene. Both the multilayer graphene and the Fe/graphene exhibited flake-like morphologies, with each flake being only a few micrometers in size according to SEM and TEM. In comparison to pure graphene with few layers, the Fe/graphene Raman spectra exhibited characteristic graphitic carbon peaks at Raman shifts of 1380 cm^{-1} and 1590 cm^{-1} with the peaks in the Fe/graphene being stronger and more distinct. Four chemical states were identified by XPS analysis: C=C at 284.78 eV, C-C at 285.03 eV, C-OH/C-O-C at 286.57 eV, and C=O/O-C-C at 289.2 eV. According to XRD analysis, the Fe in the Fe/graphene exists as γ-Fe has peaked at 43.6° (1 1 1), 50.8° (2 0 0), 74.6° (2 2 0), and 90.4° (3 1 1) and α-Fe with peaks at 44.6° (1 1 0), 65.1° (2 0 0), and 82.4° (2 1 1). The paramagnetic properties of Fe/graphene were revealed by the magnetization study owing to the existence of γ-Fe, a feature beneficial in real magnetic separation processes for wastewater treatment (Alatalo et al., 2019).

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Song et al. examined the effectiveness of a nanocomposite made of MnO_2 and graphene using a modified hydrothermal technique for water treatment processes. The FTIR and Raman spectra of MnO_2/graphene composite powders showed stronger peaks at 1746 cm^{-1}, 1335 cm^{-1}, and 1026 cm^{-1}, which are attributed to the stretching of the bonds of C=O, C-O-H, and C-O, respectively, compared to pristine and pretreated graphene. TGA profiles of all samples showed that the MnO_2/graphene composite was quite stable at temperatures below 320°C. The good crystallinity of the graphene composite was demonstrated by the XRD patterns of the MnO_2/graphene, showing the successful synthesis of the material. The introduction of oxygen-containing functional groups through synthesis made MnO_2/graphene highly hydrophilic, as shown by the XPS spectrum, which identifies the amount and type of functional groups present in the composite as C-O, C-O-C, C=O, and O-C=O identified at 284.22, 285.07, 286.58, 288.19, and 291.43 eV, respectively. The EDS study revealed an even distribution of Mn, C, and O on the surface of the composite (Song et al., 2019).

9.3.3.2 TREATMENT OF PHARMACEUTICAL WASTEWATER BY GRAPHENE

Although there are limited studies on the application of graphene for drug adsorption, graphene-based composite materials have shown potential for adsorbing organic pollutants such as pharmaceuticals from wastewater (Song et al., 2019). Alatalo et al. devised a simple method for fabricating composite materials consisting of Fe/graphene embedded in zero-valent iron for the adsorption of tetracycline from wastewater. Under optimal conditions, the Fe/graphene composite demonstrated excellent tetracycline adsorption with the removal of 422.1 mg g^{-1}. Additionally, the Fe/graphene showed self-regenerating properties that extended its lifetime and increased its total removal capability up to 660 mg g^{-1} of tetracycline (Alatalo et al., 2019). Comparative investigations into the adsorption of antibiotics onto biochar and graphene in aqueous solutions were conducted by Peng et al. The adsorption of 7 different antibiotics was performed on three types of carbon materials using liquid chromatography-tandem mass spectrometry (LC-MS-MS) detection. It was revealed that the small specific surface area of graphene had a stronger adsorption rate than the other two types of biochar because of the π-π interactions between graphene's aromatic rings and those of the adsorbed material (Peng et al., 2016).

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9.3.3.3 MERIT AND DEMERIT OF GRAPHENE AS ADSORBENT FOR PHARMACEUTICALS

The merit of graphene includes: possessing high tensile strength, being chemically and mechanically stable, and having strong electrical and thermal conductivity. Its demerit is that it should be composited with other materials to function efficiently and optimally as an adsorbent.

9.3.4 GRAPHENE OXIDE

Graphene oxide (GO) is a single-layer material with a two-dimensional (2D) structural arrangement, having a hexagonal and crystalline structure on the plates of its oxygen groups. It possesses high interactive ability with substances due to the presence of oxygen groups. This substance is not biocompatible; however, it is applicable as an adsorbent to remove a variety of contaminants (Yang et al., 2022). GO is an oxidative form of graphene with various types of oxygen functionalities (Reddy et al., 2019).

The ideal 2D substance in GO has a honeycomb lattice often processed from graphite (Mahmoodi et al., 2021). GO is broadly utilized as a prestigious and advantageous adsorbent in removing various pollutants from water, including pharmaceuticals (Salihi et al., 2021). The two interesting features of GO that justify its priority over other materials as adsorbents include:

- Relatively high surface area (theoretically ~2630 m^2/g) that gives it the tendency to provide a suitable specific area of contact for adsorption applications.
- Possession of adequately rich oxygen-containing groups such as hydroxyl, carbonyl, carboxyl, and epoxide, that provide active sites (Hu & Xu, 2020) for bonding interactions with pollutant material, and also aid GO dispersion in a polar medium.

However, despite the noteworthy features possessed by GO, the strong tendency of GO to agglomerate during sorption applications due to its π–π interactions has limited its applications for use as an adsorbent. This problem has been partly solved through the development of GO-based composites using polymers as support when considering the adsorption of pollutants from water (Mahmoodi et al., 2021). In addition, the development of a typical 2D GO nanomaterial has quite some advantageous properties including rich surface active sites, a large theoretical specific surface area for adsorption processes (Khalil et al., 2020; Rosli et al., 2021), rapid rates of attaining

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equilibrium, relatively high adsorption capacity, and a good tendency of effectiveness over a wide pH range (Rostamian & Behnejad, 2016).

9.3.4.1 PHYSICOCHEMICAL PROPERTIES OF GRAPHENE OXIDE

GO possesses interesting characteristics including hydrophilic, adsorptive, and antibacterial properties. Its hydrophilic and adsorptive properties are associated with the existence of hydroxyl, epoxy, and carboxyl functional groups on its surface, which are developed during the oxidation of graphite at a stage of the synthesis route. Interestingly, GO can be applied for the adsorption of many disturbing pollutant species ranging from metal ions, dyes, and pharmaceuticals. The mechanism of adsorption by GO significantly depends on the functional group on its surface and the nature of the compound to be adsorbed. Meanwhile, interactions of GO with specific substances via bonding occur primarily through π–bond, hydrogen bond, electrostatic interactions, and at times hydrophobic interactions (Polak et al., 2021).

GO is more hydrophilic when compared with graphene. The oxygenated functionalities on GO support its hydrophilicity, which enables it to disperse more easily in organic solvents (Mandeep et al., 2020). GO's surface is decorated with oxygen-containing groups in nanosheet form, which offers a good hydrophilic feature and increased adsorptive affinity towards a wide range of polar contaminants (Khalil et al., 2020). GO also behaves as an electrical insulator. This is due to the disturbance of the sp^2 bonding network of graphene experienced during the preparation of GO. The electrical conductivity of GO could be restored by reducing GO to recover its honeycomb hexagonal lattice of graphene (Mandeep et al., 2020). This process eliminates some oxygen functional groups on the GO, and the new substance is often termed reduced graphene oxide (rGO).

A monolayer of GO prepared through a modified Hummer's method by Sku et al. has a Young's modulus of 207.6 ± 23.4 GPa, with a drop in order of magnitude but still notably high. Similarly, in the work conducted by Gomez-Navarro et al. (Gómez-Navarro et al., 2008), a reduced GO monolayer material (prepared via Hummers' method before heat treatment under a hydrogen gas environment) has a Young's modulus of 250 ± 150 TPa. GO, especially those prepared from graphite as a precursor, have low thermal conductivity. This property has limited its potential for applications where materials with good thermal conductivities are required. However, better thermal conductivity has been observed for graphene with one of the highest in-plane thermal conductivities of ~3000–5000 W/m K. Therefore, the

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reduction of GO is necessary during the intercalation of GO into polymers for the fabrication of blends with improved thermal conductivity (Smith et al., 2019).

9.3.4.2 PRODUCTION OF GRAPHENE OXIDE

GO (Graphene oxide) with its unique physicochemical properties, which make it efficient for the removal of pharmaceuticals, has been popularly synthesized through Hummers' method (Hummers & Offeman, 1957) and several modified Hummers' methods (Khalil et al., 2020; Shu et al., 2017; Smith et al., 2019; Song et al., 2014). In the preparation of GO through Hummers' method, 100 g of graphite powder (Dixon's 8635, 325 mesh) was mixed with 50 g of $NaNO_3$ in 2.3 L of conc H_2SO_4 and stirred. The materials were subsequently cooled to 0°C in an ice-bath after thorough mixing. While maintaining continuous stirring, 300 g of $KMnO_4$ was added to the suspension at a controlled rate of addition, thereby maintaining the temperature of the suspension within 20°C. The ice bath was subsequently removed, and the temperature of the suspension medium was carefully controlled at 35 ± 3°C, and maintained for 30 min. The mixture gradually thickens, lowering effervescence as the reaction progresses. The mixture became pasty with a brownish-gray color appearance and a very small evolution of gases. Then, 4.6 L of water was slowly added, causing violent effervescence and a rise in temperature, which was controlled at 98°C for 15 min before further dilution with 14 L of warm water. The suspension was treated with 3% hydrogen peroxide, which then turned bright yellow and reduced the residual MnO_4^- and MnO_2 to colorless soluble manganese sulfate. The yellowish-brown suspension that emerged was filtered while warm to prevent the precipitation of mellitic acid (a slightly soluble salt in the medium) formed as a side reaction. The GO residue formed was dispersed in 32 L of water to ~0.570 solids. The residual salt impurities were eliminated by treating with resinous anion and cation exchangers, and the dried GO was finally obtained through centrifugation and drying over phosphorus pentoxide *in vacuo* at 40 °C.

Synthesis of GO and its derivatives into nanocomposites can be categorized into two main parts:

i. **Bottom-Up Method:** This which involves the preparation of graphene from simple carbon molecules, and

ii. **Top-Down Method:** In which graphene derivatives are extracted from a carbon source, usually graphite material.

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Meanwhile, adopting bottom-up methods (such as chemical vapor deposition, epitaxial generation on silicon carbide wafers, and electrical discharge) is time-consuming, including challenges related to scalability. Therefore, the focus on top-down methods (such as Brodie, Staudenmaier, and Hummers' methods in which GO is generated via oxidation of graphite using various techniques) for generating the nano form of GO is more popular (Smith et al., 2019).

9.3.4.3 TREATMENT OF PHARMACEUTICAL WASTEWATER BY GRAPHENE OXIDE

There are prestigious advantages attributed to GO including dispersibility in an aqueous medium, enhanced biocompatibility, colloidal stability, good optical absorptivity, relatively large surface area, and lower cost when considered in a relative comparison with other adsorbents (such as carbon nanotubes and noble metal-doped nanoparticles). These interesting features impact opportunities for GO and its composites for adsorption applications featuring the removal of pharmaceuticals (Delhiraja et al., 2019). GO has been extensively investigated for the removal of pharmaceuticals, including a large number of those with aromatic centers. There are some common features (such as aromatic rings and functional groups) in both GO and pharmaceuticals that present GO as an efficient adsorbent for eliminating pharmaceuticals from wastewater (Bhattacharya et al., 2020; Khan et al., 2017).

Salihi et al. synthesized GO for the removal of isoniazid and trimethoprim antibiotics in which equilibrium was attained for the adsorption processes in less than 1 hour. The maximum adsorption capacities (qe) were reported to be 204.08 mg g^{-1} and 13.89 mg g^{-1} for trimethoprim and isoniazid respectively (Salihi et al., 2021). The surface functional features of the prepared GO were significant for the adsorption of antibiotics, and better performance was reported in alkaline and acidic mediums for trimethoprim and isoniazid respectively. Rostamian and Behnejad worked on the adsorption of sulfamethoxazole by GO nanosheet and graphene nanosheet, and the results obtained revealed an adsorption process that is significantly influenced by pH and temperature with adsorption capacities of 127 mg g^{-1} (for GO) and 103 mg g^{-1} (for graphene) at 25°C. The GO nanosheet adsorbed sulfamethoxazole more quickly than graphene, and the adsorption capacities decreased as the temperature was raised from 25°C to 45°C. The kinetic modeling of the

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adsorption processes conforms to pseudo-second-order kinetics (Rostamian & Behnejad, 2016). In another work, ranitidine was removed from pharmaceutical wastewater using GO as an adsorbent. The maximum percentage removal of 94.1% was reported at a 10 ppm concentration, a dosage of 100 mg, 313 K, a stirrer speed of 140 rpm, and pH 6 (Bhattacharyya, 2019).

Membrane-based GO has also been prepared for the removal of pharmacological substances (Hidalgo et al., 2022; Polak et al., 2021). Polak et al. worked on the adsorption of pharmacological substances using a GO-based membrane. The polypropylene membranes' layers that contain GO on their surface were attached using dip-coating and chemical modification. The membranes possessed a better wettability property, with a contact angle of 110° measured for the unmodified membrane to ~85°–90° obtained for the modified form of the membrane. Meanwhile, for the membranes modified through dip-coating, better adsorption properties are recorded. The uptake capacity of 103.45 and 17.79 mg m^{-2} were obtained for dip-coating modified membranes and chemical methods respectively, as the observation is related to pore blocking by a new layer (Polak et al., 2021). Porous GO adsorbents having an enlarged surface area have also been made by connecting GO sheets with decafluorobiphenyl (DFB) or tetrafluoroterephthalonitrile via a nucleophilic aromatic substitution process. Favorable diffusion and adsorption of typical pharmaceuticals onto adsorbent were accomplished using the as-synthesized GO-based adsorbents. The GO supported with 20 mmol/L DFB (GO-DFB20) exhibited the highest adsorption capacities for six pharmaceuticals: carbamazepine (340.5 mmol/g), sulfamethoxazole (428.3 mmol g^{-1}), sulfadiazine (214.7 mmol g^{-1}), ibuprofen (224.3 mmol g^{-1}), paracetamol (350.6 mmol g^{-1}), and phenacetin (316.1 mmol g^{-1}). A good reusability was also reported with the spent GO-DFB20 with a slight loss in adsorption capacity at the 5^{th} adsorption cycle (Shan et al., 2017).

9.3.4.4 MERIT AND DEMERIT OF GO AS ADSORBENT FOR PHARMACEUTICALS

The merit of GO as an adsorbent for pharmaceuticals includes a relatively high surface area for effective removal of pharmaceuticals, efficient adsorbent for a large variety of pharmaceuticals due to its rich oxygen functionalities, and relatively high adsorption capacities for large varieties of pharmaceuticals. However, its demerit includes being non-biocompatible, having a high tendency of agglomerating in an adsorption medium due to π–π interactions, and being easily dispersible in a polar organic medium except for reduced GO.

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9.3.5 CARBON NANOTUBES AND FIBERS

Carbon nanotubes (CNTs) are physical forms of carbon that are cylindrical tube nanomaterials, made of graphite. Their cylindrical tubes comprise a minimum of two layers with an outer diameter ranging from about 3 to 30 nm and several millimeters in length. The length/diameter ratio could be higher than 1,000,000 (Saifuddin et al., 2013). CNTs were first discovered from carbon soot made by the arc-discharge method by Japanese scientist Ijima in 1991, in which a quasi-one-dimensional nanotube form of carbon was reported (Saifuddin et al., 2013). CNTs possess remarkable mechanical, structural, and electronic features, which are gained from their smaller size and mass, and notable mechanical strength, including relatively high electrical and thermal conductivity features (He et al., 2013). CNTs are either (i) single-walled having a one-atom-thick with a tube diameter of 1–2 nm or (ii) multiple-walled CNTs having many stacked single-layered tubes with a tube diameter of < 15 nm. Multi-walled CNT with tube diameters >15 nm are considered carbon nanofibers.

The application of activated carbon for water treatment lacks certain parameters, including unfavorable sorption kinetics and difficulty of regeneration after use. Meanwhile, the fabrication of activated carbon fibers has offered an alternative carbonaceous adsorbent to solve the problems. Activated carbon fibers' openings cover the matrix area on the carbon surface, which reduces the distance of diffusion of pollutants from the active sites to facilitate rapid adsorption. CNTs with a one-dimensional structure have similar features as the miniaturized activated carbon fibers, where the adsorption sites are situated on the surface of the interior and exterior layers of CNTs (Arora & Attri, 2020).

9.3.5.1 PHYSICOCHEMICAL PROPERTIES OF CNTS

The strength of the sp^2 C-C bonds in CNTs offers them superlative electronic, thermal, and mechanical properties among the carbon-based adsorbents. The density of CNTs is as low as 1.3 g cm^{-3} with a superior Young's modulus (a measure of material stiffness with values > 1 TPa) when compared with carbon fibers. CNTs are known to be the strongest materials discovered with the highest measured tensile strength of 63 GPa, considered to be about 50 times higher than steel (Saifuddin et al., 2013). CNTs possess good chemical and thermal stabilities, with a thermal conductivity of ~3000 $Wm^{-1}K^{-1}$. The distinct electronic properties of CNTs present them with high electrical conductivity (comparable to copper) and could be either metallic or semiconducting. The symmetry of the planar system in CNTs is broken by their cylindrical

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structure which gives them a direction relative to the hexagonal lattice and the axial path. The relationship between the axial plane path and unit vectors that describe the hexagonal lattice defines the CNTs to act electrically with either a metallic or semiconductor character. CNTs with semiconductor features possess bandgaps that are inversely proportional with a diameter ranging from ~1.8 eV for relatively small diameter tubes to ~0.18 eV for a wider plausible single-walled CNT (Arora & Attri, 2020; Saifuddin et al., 2013).

Furthermore, like activated carbon with a specific surface area as high as about 500–1000 $m^2\ g^{-1}$, a popular adsorbent like CNT having enshrined unique adsorption characteristics possesses a surface area in the range of 100–300 $m^2\ g^{-1}$ that impacts high sorption efficiency to the material. The malleable surface charge in CNTs significantly affects the adherence of the aqueous phase's contaminants onto them. Their large pore size as common to the fibrous type enables better surface exposure of the material. The aqueous phase organic-based contaminants adhered more easily onto the exterior layer and interior adsorption sites of open-ended CNTs. Meanwhile, the available surface functional groups as well as the surface area are the main determinants for enhanced adsorption (Arora & Attri, 2020).

9.3.5.2 PRODUCTION OF CNTS

The three primary techniques applicable for the preparation of single-walled and multi-walled CNTs include:

i. **Arc-Discharge Technique:** It involves the subjection of two carbon rods to vaporization through arc-discharging.

ii. **Laser Ablation Technique:** It involves the utilization of graphite as a precursor.

iii. **Chemical Vapor Deposition Process:** It involves the use of hydrocarbons (such as methane, ethylene, acetylene) and carbon monoxide.

CNTs are often subjected to further cleansing treatments through refluxing in acid, sonicating under surfactant-aided conditions, or air oxidation after preparation to remove impurities like fullerenes, amorphous carbon, and transition metals added as catalysts during the preparation (He et al., 2013).

Like in AC, acid treatment using nitric acid and tetraoxosulfate (VI) acid is commonly utilized for enriching the surface functional groups of CNTs which offer two main purposes:

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- Reducing the length of the tubes by opening up the CNTs' ends – helps to increase the specific surface area of the CNTs and as well aids in homogenizing the CNTs mixture for more precise control over the physical characteristics.
- Introduction of functional groups that promote oxidation (such as alcohols, carboxylic acids, epoxides) onto the edges of the CNTs via acid treatment, principally around the openings. Functionalizing the CNTs and shortening their tube length aid the easy dispersion of CNTs in aqueous solutions (Sweetman et al., 2017). Meanwhile, an adequate extent of oxidation of CNTs towards attaining better adsorption capacity was obtained at 3.2% for effective adsorption of tetracycline antibiotics (Yu & Han, 2014).

9.3.5.3 TREATMENT OF PHARMACEUTICALS WASTEWATER BY CNTS

The adsorption mechanisms of organic species such as pharmaceuticals from water onto CNTs have been thoroughly investigated. There are various interactions such as hydrogen bonding, hydrophobic interactions at CNTs' surfaces, $\pi - \pi$ interactions, and electrostatic interactions occurring between the CNTs and these organic species. The adherence of pharmaceutical-based organic species onto CNTs via the adsorption process is majorly influenced by the morphological features, as well as the functional group characteristics of the CNTs and adsorbate species. In addition, the interaction conditions parameters such as ionic strength and medium pH, as well as the dispersion state also affect the adsorption of the pharmaceuticals onto CNTs. Meanwhile, the surface of CNTs is commonly hydrophobic with a strong affinity for non-polar groups over the polar species. However, surface functionalization helps in reducing hydrophobicity, which leads to an increase in oxygen content, a decrease in specific surface area, and a lowering of affinity for non-polar hydrocarbons. Inadequate interactions to establish effective contact between CNTs and organic species also lower the sorption efficiency of planar molecules onto the CNTs (Wang et al., 2019)

Single-walled CNTs were applied as adsorbents for the removal of carbamazepine as the primary adsorbate in a medium where bisphenol A and phenanthrene were competitors' adsorbates (Lerman et al., 2013). There exists a competitive adsorption between carbamazepine and bisphenol A for CNTs but no such effect between carbamazepine and phenanthrene. The neutral fraction of the dissolved organic species that are hydrophobically displayed the highest reductive effect for the uptake of carbamazepine, most

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probably resulting from interactions within the solution. Meanwhile, direct competition existing in the adsorption medium due to the presence of the hydrophobic acid fraction lowers the carbamazepine uptake. These findings revealed that the chemical nature of dissolved organics disturbs the adsorption of polar organic pollutants onto carbon nanotubes in an aqueous system (Lerman et al., 2013). The oxidized multi-walled CNTs prepared by Yu et al. (2016) to investigate the influence of oxygen contents on the adsorption properties of ciprofloxacin revealed an increase in adsorption capacities as the oxygen content in the CNTs increases from 2.0% to 5.9%. Though, the increment rate subsequently became slower due to π–π electron donor-to-acceptor interactions. Moreover, the enhancement of dispersibility and hydrophilicity, including the prevention of water clusters, presents a coordinated role in the adsorption of ciprofloxacin onto the multi-walled CNTs. Suggestively, electrostatic interactions were the main adsorption mechanism for the process (Yu et al., 2016).

9.3.5.4 MERIT AND DEMERIT OF CNTS AS ADSORBENT FOR PHARMACEUTICALS

The merit of CNTs as adsorbents for pharmaceuticals includes high chemical, thermal, and mechanical stabilities, and a relatively large pore size to accommodate large organic molecules. Its demerit includes a relatively low surface area for the effective removal of pharmaceuticals, a hydrophobic surface that often results in low adsorption capacities for pharmaceuticals, and poor surface interactions leading to ineffective contact with pharmaceuticals.

9.4 CONCLUSION

The surge in the usage of pharmaceutical products has led to their increase in the environment and as a result, has increased the search for better treatment technology. The treatment of wastewater containing pharmaceuticals can be achieved using the adsorption technique, taking advantage of its simplicity of design and low cost. The search for an efficient adsorbent with optimal potential for the removal of pharmaceuticals from wastewater fosters the application of functionalized carbon-based materials as adsorbents and enhances adsorption. However, the adsorption of pharmaceuticals from wastewater has also been determined to depend on process parameters such as adsorbent dosage, initial concentration, ionic strength, pH, and temperature. As discussed in this chapter, the removal of pharmaceuticals

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by adsorption using functionalized carbon-based materials such as activated carbon, graphite, graphene, graphene oxide, and carbon nanotubes and fibers is promising. Functionalized graphite and graphene have been prepared through in situ hydrothermal and reduction methods. Graphene oxide is popularly prepared by Hummer's method, while carbon nanotubes and fibers are produced via discharge, chemical vapor deposition, and laser ablation methods. Meanwhile, activated carbon and graphene oxide exhibit exceptional performance with high adsorption capacities for the removal of pharmaceuticals in wastewater due to high surface area and rich functionalized active sites. Although GO is quite unstable under an aggressive chemical environment for the treatment of pharmaceuticals from wastewater, the development of reduced GO minimizes the disadvantage. The physical and chemical properties of these functionalized carbon-based adsorbents rely solely on the type of precursor and methods of preparation. The order of adsorption efficiency towards common pharmaceutical contaminants is GO > CNTs > AC > Graphene > Graphite. Modification of activated carbon, graphite, graphene, graphene oxide, and carbon nanotubes and fibers relative to their functional groups and surface morphology gives the prospect for the treatment of pharmaceutical wastewater.

9.5 FUTURE PROSPECT

Treatment of wastewater containing pharmaceuticals by adsorption techniques using functionalized carbon-based adsorbents presents dual advantages: a cheap, simple, and efficient process owing to the adsorption technique, and efficient adsorbent characteristics concerning functionalized carbon-based adsorbents. As discussed in this chapter, several functionalized carbon-based adsorbents have been developed and applied for pharmaceutical wastewater treatments. The reports in the literature are promising towards reducing the quantities of pharmaceuticals in wastewater. Consequently, opportunity abounds in improving the adsorption efficiency and stabilities of functionalized carbon-based materials via modifications for the treatment of pharmaceutical wastewater in the near future. Furthermore, there is an assumption that the prospect of functionalized carbon-based adsorbents is very positive. Accordingly, most of the research performed involved the use of a single functionalized carbon-based adsorbent, at times composited with other adsorbent materials for the removal of pharmaceuticals from wastewater. However, since each of the functionalized carbon-based adsorbents has distinct characteristics, different kinds of suitable

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functionalized carbon-based adsorbents should be composited for improved removal efficiency and stability. Although there are concerns associated with the use of functionalized carbon-based adsorbents in the future in terms of the management of spent adsorbents. The control of the used adsorbent is a crucial problem that has not been wholly addressed. The available work in the literature has not been exclusively targeted toward controlling and management of the spent adsorbent. Therefore, modification of functionalized-carbon-based adsorbents to increase their reusability capacity and the creation of an environment-friendly and cherished end-usage of the wastes should be purposefully investigated. Finally, the practicability of utilizing functionalized-carbon-based adsorbents on a pilot and commercial industrial scale should also be exclusively studied in the future.

KEYWORDS

- **adsorption**
- **extruded activated carbon**
- **functionalized-carbon**
- **granular activated carbon**
- **pharmaceuticals**
- **powdered activated carbon**
- **wastewater**

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