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# Carbon-based composites for removal of pharmaceutical components from water

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## ABSTRACT

Carbon-based materials. including carbon nanotubes, graphene, and activated carbon, are among the most effective materials for pharmaceutical components removal from water. Despite the severe effect of pharmaceutical micropollutants in the aquatic environments and the effectiveness of carbon-based composites for water treatment, only a few studies has reviewed carbon-based materials for the removal of pharmaceutical components. Carbon-based materials with special properties like tunable surface functions, abundant pore structure, and high specific surface are used in different water treatment mechanisms such as adsorption and advanced oxidation processes. Graphene, activated carbon, and carbon nanotubes have been widely studied for pharmaceutical components removal. Herein, we have introduced carbon-based materials and reviewed recent studies on their properties, application in water treatment, and possible mechanism for removal of pharmaceutical components from aquatic environments.



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## 1. Introduction

There are many concerns about the effect and presence of active pharmaceutical compounds in water in recent years, additionally, cost-effective and efficient technologies have been developed to treat groundwater, surface water, and industrial effluents and remove these compounds [1]. About 100 different substances of pharmaceuticals up to various milligrams per liter have been discovered in water environments including drinking, surface, and underground water [2]. Direct toxicity to environmental media, endocrine disorders, antibiotic resistance spread in microorganisms, genetic toxicity, and potential risks for human health are the effects of the contamination of these medicinal substances for the aquatic environment [3]. Antibiotic residues reduce the quality of drinking water because they affect the structural metal ions' properties. Therefore, when residues of antibiotics are received from the environment through drinking and eating, they may affect the gut microbiota due to the effect of potential biomagnification. More than 700,000 deaths per year are reported due to drug resistance-related diseases, which, if the main reasons are not addressed, could reach 10 million annually by 2050 [4].It is worth mentioning that unfortunately medicinal substances with aromatic structures are resistant or difficult to decompose in nature.

The destruction of pharmaceuticals in waters has been accomplished through the use of a variety of techniques, the majority of which are classified as advanced oxidation processes (AOPs). These techniques include electrochemical oxidation, ozonation, ultrasound radiation and sonolysis, Fenton and photo-Fenton, photolysis and photocatalysis and other similar processes [3, 5-7]. As a result, a number of techniques for removing antibiotics from systems have been created, such as membrane procedures, chlorination, improved oxidation technology, electrochemical processes, ultrasonic cavitation, and adsorption,[8]. chitosan[9], polymeric compounds [10]metals and their oxides, Carbon, and clay minerals [9, 11]are among the substances that have been developed to remove antibiotics from aqueous solutions. Because of its high specific surface area, plentiful pore structure, and adaptable surface functions, carbon materials have been widely utilized to remove antibiotics [12, 13].

This study focuses on carbon composites for the removal of pharmaceutical from water. Variety of this composites, mechanisms is discussed herein.

## 2. Removal Mechanism

### *2.1. Adsorption Mechanism*

Traditional biological wastewater treatment methods are unable for removing antibiotic residues effectively and need a significant amount of additional energy. Duo to high removal efficiency, comparatively low prices, global applicability, and its simplicity of operation, adsorption is regarded as a highly promising technology [14]. The process of adsorption involves the pharmaceutical compounds accumulation on the surface of the adsorbent [8]. Capturing molecules of interest is driven by the interaction between the adsorbent and adsorbate. Therefore, adsorbent selection must be judicious [15]. The pore size, functional group composition, surface area, and ash concentration all have a significant impact on how effective this method is. In addition to this, it is dependent on the chemical factors such as the other competing solutes availability, pH, polarity, concentration of the adsorbate, and temperature [16, 17]. Additionally, the process of adsorption is dependent on the pore size of surface, adsorbate molecules mobility toward the adsorbent exterior boundary layer, and active surface sites [18]. The functional groups (-NH2, -OH, and -COOH) of carbon-based adsorbents have a significant impact on the adsorption efficiency and adsorption process [19]. The fundamental adsorption process between antibiotics and AC is electrostatic interactions, which include attraction between the adsorbents as well as an oppositely charged adsorbate [20]. In addition, the antibiotics adsorption onto carbon-based adsorbents is facilitated in large part by π - π electron donor-acceptor (EDA) interactions, hydrogen bonds, π - π interactions and hydrophobic interactions [8].

### *2.2. Advanced Oxidation Processes*

Due to the following benefits among these AOPs, heterogeneous photocatalysis looks to be one of the most appealing technologies: (1) Heterogeneous photocatalysis does not generate residues and secondary sludge during the pharmaceutical residues breakdown from complex molecules into simple, nonhazardous substances; (2) Because catalysts and activity of photocatalyst during the treatment procedure stay essentially constant , heterogeneous photocatalysis can be re-usable; (3) owing to the nanoscale catalysts' enormous surface area and the pharmaceuticals' strong adsorption to the catalyst surface, the photocatalyst concentration utilized to break down residues of pharmaceutical in water is extremely low; (4) Heterogeneous photocatalysis is an alternate solution to environmental cleanup and remove pharmaceutical residues that is both effective and inexpensive [21]. In the process of photocatalysis, a semiconductor material is employed for generating hydroxyl radicals (OH•), which play the principal oxidant function. In addition, several reactive oxygen species that have a high level of reactivity are also engaged in the degradation of pharmaceutical residues [22]. stimulation of the catalyst by a photon with an energy which is equal to or greater than the semiconductors band gap energy is required for the initiation of photocatalytic processes [23]. In semiconductors, the production of electron-hole pairs (e/h+) in response to light stimulation with a wavelength that is less than 400 nm, as shown in Equation (1),

$$TiO_2 + hv = h^+_{vb}\left(TiO_2\right) + e^-_{cb}\left(TiO_2\right) \quad (1)$$

Where conduction band or cb is the lowest available energy and valence band or vb is the greatest available energy. According to pH and the semiconductor characteristics, these holes in the vb can be significantly oxidized (+1-3.5V vs. typical hydrogen electrode (NHE)) and subsequently react with molecules of water or hydroxide ions (OH) for generating OH•. As shown in Eqs., has a powerful oxidising capacity that is involved for the mineralization of contaminants and organic molecules to produce $RX^+$ (Equations (2–4)).

$$TiO_2(h^+) + H_2O \rightarrow OH^\bullet + H^+ + TiO_2 \quad (2)$$

$$TiO_2(h^+) + OH^- \rightarrow OH^\bullet + TiO_2 \quad (3)$$

$$TiO_2(h^+) + RX \rightarrow RX^+ + TiO_2 \quad (4)$$

According to Equations. (5–9), the electron conduction band is highly lowering (+0.5 to 1.5V versus NHE) and can decrease dissolved oxygen species for the generation of $HO_2$ and superoxide ions •. (9).

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{(\bullet-)} \quad (5)$$

$$O_2^{(\bullet-)} + H^+ \rightarrow HO_2^\bullet \quad (6)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (7)$$

$$TiO_2(e^-) + H_2O_2 \rightarrow OH^\bullet + OH^- + TiO_2 \quad (8)$$

$$H_2O_2 + O_2^{(\bullet-)} \rightarrow O_2 + HO_2^{\bullet} + OH^- \quad (9)$$

At last, they reach the photocatalyst's surface, where they interact with adsorbed species. As a result, the oxidizing power of the holes is employed by heterogeneous photocatalytic processes to either directly or indirectly destroy medicinal substances [24-26].

*2.2.1. Oxidation processes*

Heterogeneous photocatalysis, a kind of AOP, is a very successful approach that generates a hydroxyl radical (OH•) that readily decomposes pharmaceutical compounds into $CO_2$, inorganic acids, and $H_2O$ [27]. The oxidation procedure has three steps [8]: (1) contaminants diffusion to the semiconductor's surface. (2) the same pollutants are diffused onto the surface of the catalyst on which they were degraded by OH radicals produced by the water oxidation or positive holes OH formed in the valence band (2 and 3 Eqs.). Adsorbed contaminants can interact with positive holes directly, although interactions with water happen more often and lead to oxidative breakdown. The results of pollutant oxidation are then desorbed and dispersed from the semiconductor's surface. Moreover, in the use of wastewater and water, the oxidation process primarily aids in the destruction of various pharmaceutical chemicals [28-31].

*2.2.2. Reduction processes*

A series of complex reactions of heterogeneous photocatalytic decomposition of the remaining pharmaceutical substances causes the conversion of photon energy into chemical energy through a redox reaction [23]. Along with the oxidation carried on by the holes, according to Eq. (5), the reduction process happens on the surface of the catalyst, where $O_2$ combines with the electron in the conduction band, in order to generate superoxide ion ($O^{2\bullet}$). According to equation (6), $O^{2-}$ can react with hydrogen ions and produce $HO_2$ [25]. The formation of $H_2O_2$ from $HO_2$• via Eq. (7) and subsequent cleavage of OH• (Eq. 8) by an electron in the cocb on the surface of catalyst is what causes certain leftover medicines to break down into intermediate compounds [32].

## 3. Carbon-based Materials for Removal Pharmaceutical

Up to date, numerous adsorbents have been created and due to carbon-based adsorbents have large specific surface areas, plentiful pore structures, and strong interactions theyhave been recognized as useful adsorbent for pollutant removal. Carbon based materials include AC, graphene, CNTs, and their composites which are promising materials for removal of antibiotic [33-35].

Up to date, Researchers have developed various absorbents among which carbon-based absorbents show excellent properties such as high specific strong interactions, surface areas, and abundant pore structures. In next section we introduce these materials and review their properties.

*3.1. Activated carbon*

AC is a solid substance containing active black carbon with good

**Table 1.**
Different activated carbon based composites and their removed capacity for removal of various pharmaceutical components.

| Material | Removed Pharmaceutical | Mechanism | Removed Capacity | Ref. |
|---|---|---|---|---|
| α-Fe/$Fe_3C$ | Tetracycline<br>hydrochloride | Adsorption | 156 mg/g<br>158 mg/g | [46] |
| $ZnFe_2O_4$/AC* | Gemifioxacin mesylate<br>Moxifloxacin hydrochloride | Adsorption | 433.4 mg/g<br>388.8 mg/g | [43] |
| Chitosan/40%NAC*/2%APTES* | Acetaminophen | Adsorption | 407.83 mg/g | [47] |
| MAC/$Fe_2O_3$ | Ibuprofen<br>Amoxicillin | Adsorption | 95%<br>90% | [48] |
| $NiFe_2O_4$/AC | Ibuprofen<br>ketoprofen | Adsorption | 261.35<br>97.75 mg/g | [49] |
| $Fe_2O_3$@bismuth carbonate/ AC fiber | Antipyrine | Photocatalysis | 60% | [50] |
| $TiO_2$/ 10 %AC | Benzodiazepine | Photocatalysis | 90% | [44] |
| MAC*/$TiO_2$ | Tetracycline | photocatalysis | 93% | [51] |
| AC/$TiO_2$-9% | Diclofenac<br>Carbamazepine<br>Sulfamethoxazole | Photocatalysis/Adsorption | 153.8%<br>105.3%<br>125% | [52] |
| AC/$TiO_2$ | Sulfamethazine | Photocatalysis/Adsorption | 90% | [53] |
| Oxygen-activated carbon fibre | Acetaminophen | Photocatalysis | 99.9% | [54] |
| Activated carbons from Brazil nutshells | Acetaminophen | Adsorption | 98.9% | [55] |
| CA*-OGR*-NPs*Ag/CuO | Cephalexin | Adsorption | 756.8 mg/g | [56] |
| AC/$TiO_2$ | Ceftriaxone | Photocatalysis | 99.6% | [57] |
| GAC/$TiO_2$ | Metronidazole | Photocatalysis | 97.4% | [58] |
| Ag/AgBr-Activated Carbon | Tetracycline | Photocatalysis | 925 | [59] |

* AC: Activated Carbon
* MAC: Magnetic Activated Carbon
* NAC: Nano Activated Carbon
* APTES: (3-Aminopropyl)Triethoxysilane
*CA: Activated Carbon
*OGR: Graphene
*NPs: Nanoparticles

pore size, high absorption, and a high surface area that is frequently utilized in the industry for purification of air and water. In general, any carbon-based materials may be used to make AC, but its characteristics and activation procedures determine its application [36-38].

Thermal activation and Chemical activation are the methods for production of activated carbon. Thermal activation is a physical process with two primary phases. In the first step, volatile compounds are removed from the raw materials by thermal carbonization at temperatures between 500 and 600 degrees Celsius. In the second stage, the surface and porosity are modified by means of gasification. Steam or Methane, CO2 are employed as an oxidizing gas in the gasification process at temperatures over 800-1000 °C [39]. Activation by chemicals: The surface area and microporosity of activated carbon can be enhanced by adding inorganic salts like metal chloride prior to the carbonization procedure [39]. ZnCl2, CaCl2, ZnCl2, $H_2O_2$[40] $K_2CO_3$, and other salts are among the most frequently employed activators [41, 42]. The composite of porous carbon formed from the metal-organic framework (MOF) is an effective adsorbent for the separation of antibiotics owing to its unique features. However, the use of a costly substance as an organic ligand, like terephthalic acid ($H_2$BDC), reduces the material's cost benefits and practical applicability. It has been reported that $H_2$BDC was recovered from discarded polyethylene terephthalate (PET) bottles by alkaline hydrolysis catalyzed by ultrasonication and phase transition under moderate circumstances. In the production of magnetic porous carbon composite (-Fe/$Fe_3C$) formed from iron-based MOF, high-purity $H_2$BDC was utilized and also it was examined as an adsorbent for the removal of TCH from an aqueous solution [42].

Li et al. reported the synthesize of $ZnFe_2O_4$/AC as a magnetic adsorbent via microwave method. 433.4 and 388.8 mg/g adsorption capacities for removing Gemifizacin Mesylate and Moxifloxacin Hydrochloride was achieved via $ZnFe_2$O4/AC composites respectively [43]. pH, scavenging agents, initial pollutant concentration, and chemical oxidation are such input which have an effect on the performance of carbon-based composites systems. Temperature is one of the parameters which affects removal efficiency of pharmaceuticals. Cunha and et al. reported the lower efficiency of $TiO_2$/AC10% calcined at 500°C than $TiO_2$/AC10% calcined at 400°C. This can attribute to $TiO_2$ nanoparticles aggregation into clusters on the surface of active carbon. So, at this temperature, the number of activation sites on the surface of $TiO_2$ particles and a specific surface area of $TiO_2$ will decrease [44].

Due to the rise of oxygen-containing functional groups on the AC surface after three cycles of adsorption-ozonation, the adsorption capacity of AC rose from 80 to 215 mg/g.

Ren and et al, increased Chlorobenzene removal efficiency of powdered activated carbon from 80 to 215 mg/g by Ozonation. This was because of rise of oxygen-containing functional groups on the activated carbon surface [45].

To eliminate acetaminophen from aqueous solutions, beads made of chitosan/nano-activated carbon composite (CS-NAC) were combined with (3-aminopropyl)triethoxysilane (APTES). A greater adsorption capacity (407.83 mg/g) was observed for the aminated adsorbent (CSNACAPTES beads) produced with 2% v/v APTES and 40% w/w NAC The CS-NAC-APTES beads surface area was found to be greater than that of the CSNAC beads using a Brunauer-Emmett-Teller (BET) study (1.16 times).

### *3.2. Carbon Nanotubes*

The use of carbon nanotubes (CNT) as adsorbents for cleaning water has shown promising results. CNTs are cylinder-shaped carbon allotropes that have an aromatic surface and are rolled into shape [38, 60, 61]. Carbon nanotubes' distinctive structure results in low electrical resistance, great thermal conductivity, and high mechanical strength [38, 62]. CNTs are divided into two main types based on cylindrical shells' number, which include multi-walled CNTs (MWCNT) and single-walled CNTs (SWCNT). Each end of a single-walled carbon nanotube (SWCNT) which has a cylindrical's diameter about 0.42nm, is capped with a ring of graphite [63, 64]. MWCNTs, on the other hand, take the form of concentrically arranged cylinders whose diameters range from 2 to 25 nm and whose layer-to-layer spacing is 0.34 nm [33]. Ranjbar et al. studied deference of single- and multi-walled carbon nanotubes adsorption of pharmaceutical components. The performance of multi-walled carbon

**Table 2.**
Carbon Nanotube based composites and their removed capacity for removal of various pharmaceutical components.

| Material | Removed Pharmaceutical | Mechanism | Removed Capacity | Ref. |
|---|---|---|---|---|
| CNT [a]/MOF-808 | Carbamazepine | Photocatalysis | 68% | [71] |
| $WO_3$/CNT | Tetracycline | Photocatalysis | 60 mg/L | [72] |
| MWCNT [b]–$TiO_2$–$SiO_2$ | bisphenol A | Photocatalysis | 95% | [73] |
| | Carbamazepine | | 98% | |
| N-CU@$TiO_2$/CNTs | sulfamethoxazole | Photocatalysis | 100% | [68] |
| CNTs/L-cys [c]@GO [d]/SA [e] | Ciprofloxacin | Adsorption | 200 mg/g | [14] |
| CDs*/CMNTs* | Carbamazepine | Adsorption | 65 mg/g | [74] |
| Single-walled CNTs | Aspirin | Adsorption | 83.72% | [75] |
| | Atrazine | | 84.08% | |
| Multi- walled CNTs | Aspirin | Adsorption | 86.38% | [75] |
| | Atrazine | | 86.88% | |
| Ceramic Membranes/MWCNTs | Tetracycline | Adsorption | 45.4% | [65] |
| MWCNTs/AC | Ciprofloxacin | Adsorption | 73% | [76] |
| Fe/N-CNT + PS [f] | Acetaminophen | Adsorption | 98.4% | [77] |
| Magnetic chitosan/ MWCNTs | Acetaminophen | Adsorption | 98.1% | [78] |
| CNT/Clay/$Fe_2O_3$ | Amoxicillin | Adsorption | 87.56% | [79] |
| Ti/Fe /CNT@Alg[g] | Tetracyline | Adsorption | 294.12 | [80] |
| CNT-COOH/$MnO_2$/$Fe_3O_4$ | Ibuprofen | Adsorption | 103.093 | [81] |
| | Paracetamol | | 80.645 | |
| $Bi_2WO_6$/CNT/$TiO_2$ | Cephalexin | Photocatalysis | 99.2% | [82] |

[a] CNT: Carbon Nanotubes
[b] MWCNT: Multi Wall Carbon Nanotubes
[c] L-cyc: L-Cysteine
[d] GO: Graphene Oxide
[e] SA: Sodium Alginate
[f] PS: Persulfate
[g] Alg: alginate microbeads

nanotubes in absorbing atrazine has been reported to be superior than that of single-walled carbon nanotube. Polak et al. used GO, MWCNTs, and SWCNTs for modification of ceramic membranes for tetracycline removal from water. Results showed MWCNTs increased adsorption properties more than other modifier components [65]. Their adsorption properties is determined by factors like as purity, porosity, site density, functional groups, CNT type, and surface area [64, 66, 67].

Isari et al. modified single-walled carbon nano-tube with N-Cu doped $TiO_2$. The study showed that 60 mg/L sulfamethoxazole removed in 60 min and pH of 6. The adsorption capacity was significantly increased Because of the large SBET of CNT. N and Cu were introduced into the $TiO_2$ crystals, and as a consequence, above-valance bands and sub-conduction bands were formed above and under the $TiO_2$ vb and cb respectively. The rate of formation of e-/h+ couples was boosted by these sub-cb and above-vb. Furthermore, effective SMXZ mineralization was made feasible owing to the potential formation of π–π conjugated bonds between organic molecules and the CNT surface [68].Sheng et al. investigated the effect of polyethylene microplastic on the adsorption of carbamazepine MWCNTs. The adsorption capacity of carbamazepine by MWCNT decreased by entry of polyethylene microplastic [69].

Because of their special structure and functional groups, CNT surfaces interact with both organic and inorganic substances through a variety of intermolecular interactions [70].

### *3.3. Graphene*

Graphene is a two-dimensional carbonaceous nanomaterial formed from a layer of sp2 hybridized carbon atoms. The graphene nanomaterial has exceptional properties such as high specific surface area, high electrocatalytic activity, great thermal conductivity, high stiffness and strength and high speed electron mobility. one of the two-dimensional nanomaterial made of carbon is which graphene made of a layer of carbon atoms that have performed sp2 hybridization. high stiffness and strength, High great electrocatalytic activity, high-speed electron mobility superior thermal conductivity ,and specific area are only a few of the extraordinary qualities of graphene nanomaterials [83].

Because graphene is hydrophobic, it may interact with contaminants that are hydrophobic through van der Waals or π – π interactions. Hydrophobicity, nevertheless, could potentially restrict its use in aquatic conditions. Thus, graphene is often altered for generating redused graphene oxide (rGO) or graphene oxide (GO) [33]. The application of GO in aqueous environments becomes possible due to the presence of highly reactive functional groups which caused hydrophilicity improvement. Due to its unique physicochemical features, including as high mechanical strength, electroconductivity, thermal stability, and adsorption capacity, there has been increased interest in graphene-based nanomaterials in recent years [8, 84, 85].

Amali et al., reported 99.60% removal of sulfasalazine by Fe@$Fe_2O_3$/3D-GO composite. 3D graphene was synthesized by hydrothermal method and loaded with core-shell nanowires of Fe@$Fe_2O_3$. Khalil et al., synthesised porous graphene (PG) at low temperature for the removal of carbamazepine, diclofenac, ibuprofen, gemfibrozil, and ciprofloxacin. Removal efficiency PG and GO was compared and And it was suggested that rGO had a lower specific surface (98 m2/g) area than PG (670 m2/g). So, PG showed better performance [86]. In another study, Khalil et al., compared single and double layer of PG for filtration of carbamazepine and gemfibrozil and revealed that double layer PG had more outperformance [87]. Graphene can also be used as a solid electron mediator/acceptor. El-Fawal et al., constructed $AgFeO_2$-graphene/$Cu_3(BTC)_3$ nanocomposite for photocatalytic removal of amoxicillin and diclofenac. This tertiary heterojunction photocatalysts showed excellent act due to enhanced charge transfer mechanism via Z-scheme from CB of $Cu_2$(BTC)3 to VB of $AgFeO_2$ and graphene as a solid elec-

**Table 3.**
Graphene based composites and their removed capacity for removal of various pharmaceutical components.

| Material | Removed Pharmaceutical | Mechanism | Removed Capacity | Ref. |
|---|---|---|---|---|
| MGO [a] | Amoxicillin | Adsorption | 98.41 mg/g | [89] |
| Nanostructured porous graphene | Carbamazepine | Adsorption | 154.25 mg/g | [86] |
| | Gemfibrozil | | 40 mg/g | |
| | Diclofenac | | 76 mg/g | |
| Graphene Nanoplatelets | Sulfamethoxazole | Adsorption | 210.08mg/g | [90] |
| | Acetaminophen | | 56.21mg/g | |
| $MnO_2$/Graphene | Tetracycline | Adsorption | 99.4% | [91] |
| Carbon xerogel/graphene | metronidazole | Adsorption | 110-166 mg/g | [92] |
| GO-PFB [b] | Sulfadiazine | Adsorption | 10020.21 | [93] |
| GO-PFBS [c] | | | 567.17 | |
| Fe@$Fe_2O_3$/3D-GO | sulfasalazine | Photocatalysis | 99.60% | [94] |
| $TiO_2$-ZnO/CS-Gr | Tetracycline | Photocatalysis | 20 mg/L | [95] |
| MgO/ZnO/G | Sulfamethoxazole | Photocatalysis | 55 mg/L | [96] |
| Porous Amine-Modified Green-Graphene | Metronidazole | Adsorption | 74% | [97] |
| TiO2-graphitized | Tetracycline | Photocatalysis | 94.64% | [98] |
| rGO/ $HoVO_4$-$TiO_2$ | ibuprofen | Photocatalysis | 96% | [99] |
| Graphene/Ni@$TiO_2$/W | Acetaminophen | Photocatalysis | 100 | [100] |
| graphene quantum dots(Spinel like) | doxycycline | Photocatalysis | 796 mg/g | [101] |
| | tetracycline | | 672 mg/g | |
| $AgFeO_2$-graphene/$Cu_3(BTC)_3$ | Amoxicillin | Photocatalysis | 87.4% | [88] |
| | Diclofenac | | 95.5% | |

[a] MGO: Magnetic Graphene Oxide
[b] PFB: Pentafluorobenzene
[c] PFBS: Pentafluorobenzaoate

tron mediator/acceptor [88].

*3.4. Carbon quantum dots (CQD)*

Because of their unique characteristics like simplicity/low cost, photoluminescence, water-solubility, easy surface modification, optical stability,and biocompatibility, scientific studies pertaining to carbon dots, an carbon nanomaterial unique type with a quasi-spherical shape and size below 10 nm, have been growingly released [102]. CDs are broken down into subcategories such carbon nanodots (CNDs), carbon quantum dots (CQDs), and graphene quantum dots (GQDs), based on whether or not their central carbon core is nanocrystalline, amorphous, or a mixture of the two[103]. With an average crystal lattice size of 0.24 nm, GQDs are single- or multi-layer structure nanoparticles that display quantum confinement thanks to their conjugated π -electron graphene layers. CQDs are restricted by quantum mechanics, despite having a crystal structure with an interlayer spacing of 0.34 nm, the same as that found in graphite [104]. Furthermore, CNDs are nanoparticles that lack quantum confinement due to their amorphous structure, which is made up of stacked or networked monomers or linear polymers. As a result of their complicated structure and the wide range of changes that might result from different precursors and different synthesis processes, carbon dots fall into a number of different categories [105]. CQDs, being nanosized materials with a high surface area to volume ratio, might offer up more active surface area for the interface's adherence of contaminants [105, 106]. [2]. Adsorption mechanisms are generally divided into two categories: chemical and physical absorption, which differ in terms of interaction with various reactive species (ions, atoms, molecules) [107]. CQDs' sp2 conjugated carbon structure may enhance molecular interactions in aqueous solution with the aromatic rings of organic contaminants via π–π stacking interaction. However, the functional groups' high concentration (e.g. epoxy, amino, carboxyl, carboxyl, and hydroxyl groups) on the surface of CQDs would improve their ability for interacting with a wide variety of molecules and heavy metal ions, resulting in greater adsorption performance [108].

Koe et al., fabricated and deposited N.S-CQDs/$TiO_2$ nanocomposite on polysulfone (PSF) membrane for photodegradation of diclofenac. According to the results, an increase in degradation performance from 3.33% to 62.3% was observed by the use of N,S-CQDs [109]. Yuam et al. used N-CQDs on $BiVO_4$ for photodegradation of tetracycline. The formation of surface defects on N-CQDs is advantageous for the photocatalytic performance. The photodegradation efficiency for pure $BiVO_4$ was only 50.9% while it was increased to 75.7% for N-CQDs/$BiVO_4$

**Table 4.**
Carbon quantum dots based composites and their removed capacity for removal of various pharmaceutical components.

| Material | Removed Pharmaceutical | Mechanism | Removed Capacity | Ref. |
|---|---|---|---|---|
| N,S-CQDs/$TiO_2$ | Diclofenac | Photocatalysis | 62.3% | [109] |
| CQDs/rGO/S@g-$C_3N_4$/B@g-$C_3N_4$ | Chloramphenicol | Photocatalysis | 99.1% | [112] |
| CQD- g-$C_3N_4$-PANI [a] | Ciprofloxacin | Photocatalysis | 87.6% | [111] |
| $BiVO_4$/N-CQDs/$Cu_2O$ | Tetracycline | Photocatalysis | 99.1% | [110] |
| Si-CQDs/$TiO_2$ | Acetaminophen | Photocatalysis | 100% | [113] |
| N-CQDs/$InNbO_4$ | Ipronidazole | Photocatalysis | 97.2% | [114] |
| CQDs@CoO/$La_2O_3$/NiO | Ofloxacin | Photocatalysis | 93.8% | [115] |
| CQD/C-$TiO_2$ | Sulfamethoxazole | Photocatalysis | 100% | [116] |
| Cu-$TiO_2$/CQD4 wt% | Sulfamethoxazole | Photocatalysis | 100% | [116] |
| CUS/CQD | Panadol | Photocatalysis | 96.5% | [117] |
| N-SCQDs | Sulfadiazine | Photocatalysis | 100% | [118] |
| CQDs/g-C3N4 | Diclofenac | Photocatalysis | 99.9% | [103] |
| CQDs/g-C3N4 | Tetracycline | Photocatalysis | ~100% | [119] |

[a] PANI: Polyaniline

**Table 5.**
Removal efficiency of carbon-based composites and other materials.

| Removed Pharmaceutical | Carbon based composite | | | Other material | | |
|---|---|---|---|---|---|---|
| | Material | RE% | Ref. | Material | RE% | Ref. |
| Sulfamethazine | CQD/C-$TiO_2$ | 100% | [116] | Ferroxane | 80% | [127] |
| Diclofenac | N,S-CQDs/$TiO_2$ | 62.3% | [109] | Crystalline MnO | 21% | [129] |
| Diclofenac | $AgFeO_2$-graphene/$Cu_3(BTC)_3$ | 95.5% | [88] | Moringaoleifera adsorpant | 87.4% | [130] |
| Tetracycline | $WO_3$/CNT | 60 mg/g | [72] | Nonn-activated sludge-based | 10 mg/g | [131] |
| Tetracycline | $BiVO_4$/N-CQDs/$Cu_2O$ | 99.1% | [110] | HA/Fe-$Al_2O_3$/$O_3$ | 75% | [132] |
| Tetracycline | $MnO_2$/Graphene | 99.4% | [91] | Mn(2.62%)-$MoS_2$@ AABs* | 80% | [122] |
| Acetaminophen | Fe/N-CNT + PS* | 98.4% | [77] | CoS/S(IV) | 83.1% | [133] |
| Acetaminophen | Magnetic chitosan/ MWCNTs | 98.1% | [78] | $Fe^{2+}$/persulfate | 70% | [121] |
| Acetaminophen | Si-CQDs/TiO2 | 100% | [113] | Fe-$TiO_2$/Ag-ZnO | 85% | [134] |

[110]. Balakumar et al., decorated porous g-C3N4 / polyaniline with CQDs using ultra-sonication approach. The 5.0% g-$C_3N_4$ / polyaniline decorated CQDs composite showed 87.6% photocatalytic degradation of ciprofloxacin. This photocatalytic degradation is because of its higher charge separation and surface area, which lowered the recombination rate [111]. In another study, the modification of S@g-$C_3N_4$/B@g-$C_3N_4$ with CQDs and rGO was reported. The S@g-$C_3N_4$/B@g-$C_3N_4$/CQDs/rGO composite resulted in 99.1% photo-degradation of chloramphenicol [112].

## 4. Removal efficiency of carbon-based composites and other materials

Other than carbon based composites, Metal oxides, Sulfides, and Natural Coagulants are also used for removal of pharmaceutical components from water [120-122]. Nurhasanah et al. studied the potential of cerium oxide as an adsorbent for the tetracycline removal from a water/alcohol environment with the removal efficiency of 80-97% in 60 min reported for cerium oxide [123]. $TiO_2$ has been used in a wide variety of studies for the removal of pharmaceutical components. However, because of the wide band gap of $TiO_2$, and fast electron-hole recombination, it has low removal efficiency. To improve its removal efficiency, many researches have attempted to decorate it with other materials [124]. YaluWuYinyinXu et al. reported the synthestize of $TiO_2$/polypyrrole decorated NiCoP nanocomposites. The absorbance capacity for NiCoP/$TiO_2$/polypyrrole was reported to be 83% [125]. Leong et al, synthesized $Ni(OH)_2$ modified $TiO_2$ nanorods via hydrolysis process. $Ni(OH)_2$-modified $TiO_2$ showed 76% removal efficiency after 30 min adsorption process; whereas commercial $TiO_2$ showed only 57% removal efficiency [126]. This is while $TiO_2$ modification by carbon based materials results in a higher efficiency. For example, nano-$TiO_2$/Carbon and Magnetic Activated Carbon/$TiO_2$ possess removal efficiency of 100% and 93%, respectively. The study of iron oxide (ferroxane) semiconductors as catalysts for heterogeneous Fenton reactions for removal of Sulfamethazine showed 80% removal after 2 hour reaction period [127]. While, carbon modified composites such as CQD/C-$TiO_2$, MgO/ZnO/G, N-CU@$TiO_2$/CNTs, Fe@$Fe_2O_3$/3D-GO showed removal efficiency of more than 90% for Sulfamethazine. Gómez-Pacheco et al. studied the effectiveness of technologies based on the simultaneous use of $O_3$ on the Tetracycline (TC) removal from water and reported that TC removal rate has been increased in presence of activated carbon. This increase is due to the the generation of HO• radicals, which have greater oxidizing power over $O_3$ [128].

*AABs: Activated Alumina Bead

## 5. Conclusions and future insights

These days, due to the increase in use of pharmaceutical components in veterinary medicines and human life, releasing of these substances into aquatic environments is continuously increasing. Direct toxicity to environmental media, endocrine disorders, antibiotic resistance spread in microorganisms, genetic toxicity, and potential risks for human health are the effects of the contamination of these medicinal substances for the aquatic environment. Therefore, it is essential to remove pharmaceutical components from aquatic environments. Several materials such as polymeric materials, carbonaceous materials, silica-based adsorbents, clay and other materials have been used to achieve this aim. However, carbon-based materials show high removal efficiency and good performance. In this review, Carbon-based composites for removal of pharmaceutical components from water are summarized. Activated carbon, Carbon nanotubes, Graphene, Carbon quantum dots and their composites are the most studied materials which have been reviewed thoroughly in this work. Also, we discussed adsorption and photocatalysis as two main removal mechanisms. In addition, few researches have surveyed possible decomposition mechanisms for pharmaceutical components which can be an important topic for other studies in future.

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