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A review on nano-carbon materials for pollution remediation

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Abstract

In this review, carbon-based materials (CBMs) relied primarily on the use of technologies such as adsorption, filtration, and advanced oxidation processes (AOPs) to get rid of various pollutants from numerous climatic media; such as air and water, is discussed. The unique characteristics and effectiveness of CBMs obtained at nanostructures have made them potentially ideal for these types of operations because they have a large surface-to-volume ratio, predominately leading to a higher reactivity. An overview of carbon nanotubes, graphene and carbon dots-based as carbon nanostructures (CNSs) used for environmental treatment is given in this survey. For the therapy of diverse natural toxic heavy metals, dyes, chemical molecules, volatile organic components, and herbicides, the employment of these nanostructures mentioned above is reviewed. Moreover, the costs associated and how the effectiveness of technology used in environmental treatment could be optimized are also important factors to be considered.

Keywords: Carbon nanotubes; graphene-based materials; carbon dots; environmental pollution technologies

Introduction

The environmental problems that pollute the water, soil and air have affected each aspect of the mankind life. The shortage of safe and clean water has become an omnipresent issue throughout the world, on an increment addition to the growing population, industrialization, and urbanization. The pollution of groundwater and soil by toxic chemicals, for instance, represents a substantial technological and economic obstacle for remediation. "In the USA, the annual pollution charge is estimated to have been around $110 and $127 billion, which is considered as" intractable "in exchange for being able to assembly cleanup standards [1].In the meantime, more than half of the world's population, primarily in developing countries, faces serious deficiencies of clean water [2]. This is because the insufficient water supplies calls for effective wastewater refinement technologies as well as seawater desalination technologies. Environmental conservation has become a significant affair of main social concern, as numerous pollutants, such as dyes, heavy metals, pesticides, herbicides, fertilizers, oil spills, hazardous gases, industrial waste, sewage, and volatile organic chemicals, are discharged into the ecosystem. Therefore, in order to achieve a safe and clean climate, finding an effective strategy for new techniques and treatment methods and improving the effectiveness of current remediation for many environmental contaminants have become a vital necessity.

Due to the distinctive physical properties of nanostructured materials as, morphology, porosity, texture and chemical composition, nanotechnology has acquired great attention in the last decades. Because of their greater surface-to-volume ratio, nanomaterials offer improved reactivity and thus better performance relative to their bulky counterparts. In addition, nanomaterials provide the ability to exploit unique surface chemistry, so that can be designed and synthesized or grafted with functional groups that would react with pollutant molecules of interest. Further, the surface nature-rich chemistry modification together with the configurable physicochemical characteristics of the nanoparticles

provide advantages over the conventional materials , particularly; nanomaterials can be combined to produce composites / hybrids with other materials, obtaining unique desirable characteristics from each of its components , making them significantly effective in environmental treatment. In fact, the use of nanotechnology combined with either physical or chemical alteration of the surface of the materials creates engineered materials that can overcome a variety of challenges involved in pollutant remediation to avoid agglomeration, and improve dispersibility and stability [3-5].

Another obstacle that may place a constraint on their use is the potential toxicity of metallic nanoparticles collected during the treatment process, along with their by-products and the cost of recovery from the remediation medium. Therefore, in order to promote good nanomaterials capable of classify environmental problems, a keen understanding of the material structure, manufacturing process, and performance optimization is required. Accordingly, since (CBMs) can be able chemically mixed with other carbon-based materials and with a variety of various elements to form strong covalent bonds, they have shown great flexibility. As consequence, they display outstanding features such as elevated thermal and chemical stabilization, wide surface area, and supreme hardness. Therefore, one of the most important subjects in materials science is carbon-based nanostructures, such as fullerenes, carbon nanotubes, carbon dots and graphene. All of them are subject to extensive research and promise a wide variety towards nanotechnology applications, e.g. in the purification of the environment, photocatalysis, electronics, energy storage, medical science and chemical engineering. These substances have quite a significant impact on natural ecosystems. Figure 1 shows possible techniques in which a pollutant can be removed through the use of various materials [5].

1.2. Carbon nanostructures

Over the last two decades, carbon nanostructures (CNSs) have emerged as a field of novel molecular materials because of their remarkable structural, electrical, optical, thermal, mechanical and chemical properties. These materials have been developed tremendous interest worldwide, from both the point of view of fundamental research and their implementation in the areas of molecular electronics,
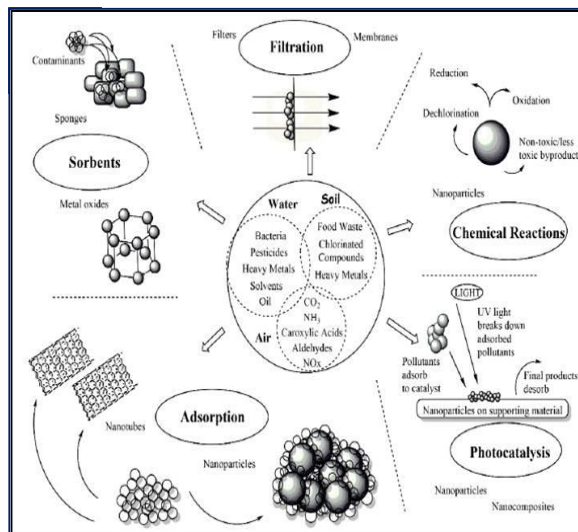

Fig. 1. Schematic diagram illustrates the techniques used in environmental pollution [5].

materials science, energy storage, climate purification and biotechnology. The electronic properties and optical, spectroscopic and electrochemical activity of CNSs are strongly dependent on their distinctive nanometric dimensions. Low-dimensional carbon nanomaterials are commonly divided into, depending on their nanoscale range, classes of zero-dimensional (0D) to one-dimensional (1D) and two-dimensional (2D). For example, the spectrum of dimensionality of sp2 bonded carbon materials such as zero-dimensional (0D) fullerenes, one-dimensional (1D) carbon nanotubes, two-dimensional (2D) graphene and three-dimensional (3D) graphite, as shown in Figure 2: (a/– d/) spectrum dimensions of sp2carbon materials of fullerenes, carbon nanotubes, graphene, and graphite, respectively. (a) Fullerene (inside red circle) trapped inside the cavity of multi-walled carbon nanotube (MWCNT), (b) STM images of single-walled carbon nanotube (SWNT), (c) Photograph (in normal white light) of a relatively large multilayer graphene flake with thickness ≈ 3nm on top of an oxidized Si wafer, and (d) A piece of natural graphite [6]. The real application potential of such CNSs lies when composited with other materials such as metals, metal oxides, and polymers. Depending upon the guest materials and functionality, these composite materials can find applications in various fields including energy, environment and bio-related fields.
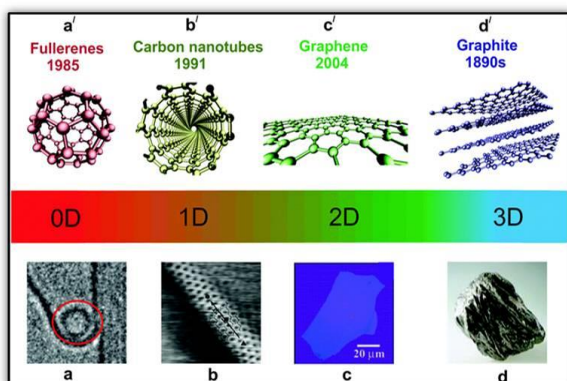
Fig.2. Spectrum dimensions of sp2carbon materials of fullerenes, carbon nanotubes, graphene, and graphite, respectively [6].

1.3. Achievements in Carbon nanostructures

By designing novel arrangement of ribbon, hybrid, polymerized, doped, and hetero-structures, the frontiers of carbon nanomaterials, frequently resulting in material science and engineering directions were moved by researches from varied disciplines. The considerable increase in the number of publications and patents on carbon nanotubes (CNTs) and graphene over the last decade is shown in Figure 3. It is evident from the figure that (CNTs) and graphene output capacity have been significantly increased since 2006, and the annual number of newspaper publications and patents release suggest that substantial advancement has been achieved in recent years [7, 8].

Graphene has progressively become the core focus of study in various fields, such chemistry physics, material science, system engineering and nanotechnology, since its first exploration in 2004. After the discovery of Buckminster fullerene (C60) in 1985, both CNTs in 1991 and graphene in 2004 [9] materials have become of great importance in the development of science and technology. Whereby, they provide chemists, physicists, biologists, engineers, and material scientists with interesting opportunities. As shown in Figure 4, fullerenes have been attracted the primary attention of the scientific community, as evidenced by the growing number of related publications from 1993 to 2009. Recent times, referring to fullerene and graphene nanomaterials, the number of CNT publications is extremely greater [10]. Intensive attention has recently been given for producing (CDs) in the field of environmental pollution remediation [4]. As seen in figure 5, the

number of relevant CDs publications is increasing significantly annually.

Worldwide efforts attempts are being made to eliminate hazardous and toxic pollutants, both natural and industrial, that are harmful to the lives of all living organisms. The objective of this review is to provide an   overview about the use of low-dimensional nanostructures of CBMs such as carbon nanotubes CNTs, graphene-and carbon dots-based substances. Surface treatment, activation or functionalization of the pristine carbon material has been stated to be needed first in order to increase the efficiency of sorption process to allow it especially useful for eliminating organic and inorganic contaminants from the air and from massive amounts of aqueous soles. Investigate CDs as modern carbon-based nanomaterials and their importance towards ecological impacts applications.
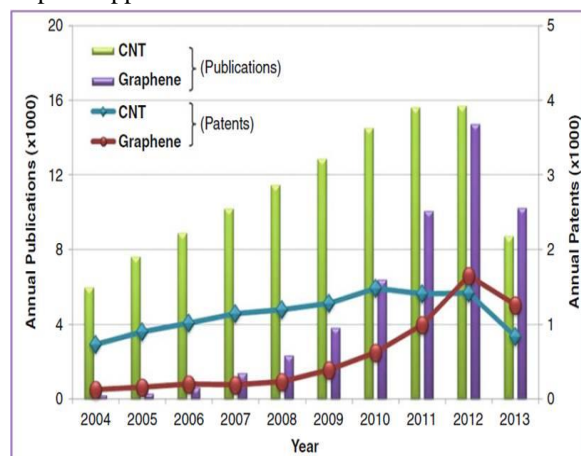

Fig. 3. Trend in the number of publications and patents based on CNTs and graphene [7, 8]
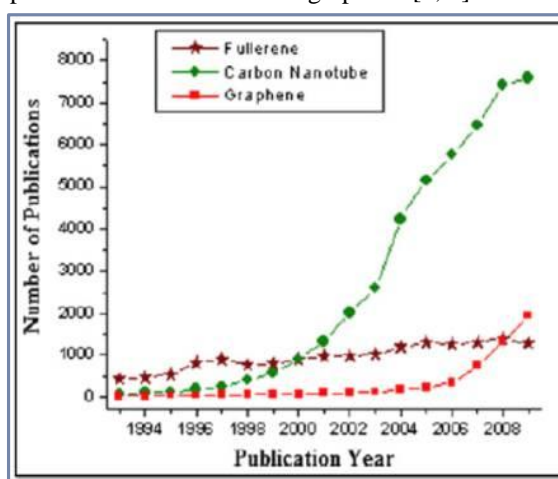

Fig. 4. Number of publications on CNTs, fullerene and graphene nanomaterials [10].

Fig. 5.   Number of publications on carbon dots (CDs) from 2010 to 2019 [4].

1.4. Synthesis and properties of CNTs and graphene-based materials

Synthesis proceedings had been used in the manufacture of CNTs and graphene-based substances are concise below in this context.

(I)- CNTs processing is currently carried out by methods including such arc discharge [7], laser ablation [11], and chemical vapor deposition [12]. Indeed, it is very essential that the surface and morphology of CNTs could be modified in order to be used in water treatment [13]. Factors including the form, length, diameter, surface area, functional groups of the surface, distribution of pore size and CNT purity have a significant impact on the adsorption properties of carbon nanotubes. CNTs are rolled graphene sheets in a cylindrical form and consist of sp^2 hybridization that are completely stronger than sp^3 bonds in alkanes that provide high-strength nanotubes [14]. There are two major kinds of nanotubes of carbon that can have high structural excellence. Single-walled nanotubes (SWCNT) composed of a single seamlessly wrapped graphite sheet in a cylindrical tube. As shown in Figure 6, double-walled (DWCNT) and multiwall nanotubes (MWCNT) comprise a range of nanotubes, one concentrically positioned inside another like tree trunk rings. In various applications such as adsorption process, catalysis, energy storage, and gas storage, CNTs exhibited excellent mechanical strength and chemical stability, allowing them to potency candidates for these implementations [14].

The surface of CNTs offers the opportunity of combining with other types of nanomaterials to form nanocomposites. This property is owing to its outstanding nanoscale structure and morphology that

provides the ability to create hydrogen bonds, stacking π-π, dispersion, and electrostatic forces, hydrophobic interactions, thereby enhancing their adsorptivity, durability, stability, and selectivity.

Figure 6 represents the schematic diagram showing the types and structure of CNTs [14].
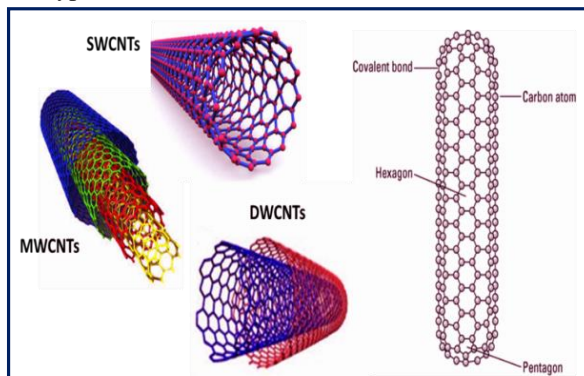

Fig. 6. Schematic diagram showing the types and structure of CNTs [14].

(II)- Since the first report by Novoselov et al. [8], graphene has attracted worldwide attention. Novoselov et al. [8] reported the first graphene preparation procedure by means of mechanical exfoliation (top-down approach). Highly-oriented pyrolysis process graphite has been injected into photo-resistant material, and adhesive tape has been used successively to peel- off graphene layers. Another way using chemical oxidation was done via oxidizing mixture ($KClO_4$ + fuming HNO_3) with graphite flakes which forms GO with graphitizable carbons [15, 16]. In 1958, Hummers and Offeman [17] reported the common method to prepare GO using H_2SO_4 and $KMnO_4$. Presently, most of GO is synthesized using the modified Hummers method via chemical oxidation and exfoliation of pristine graphite. This method based on the reaction of graphite, and condensed acid (HNO_3 and H_2SO_4), followed by the intercalation of metal oxides ($KClO_3$, $KMnO_4$ and $NaNO_3$) into the graphitic structures and fragmentation of the layers into smaller components. The intercalation of functional groups containing oxygen increases the lattice gap of the graphite, and thus promotes the weakness of van der Waal forces between the adjacent layers structure of graphite [18]. Exfoliation is usually employed using sonication in presence of organic solvents. Other approaches, such as thermal treatment, chemical vapor deposition,

plasma, and microwave, rather than exfoliation and chemical reduction of graphene oxides, have recently been developed for obtaining graphene [19]. Chemical reduction of GO to graphene nanosheets (GNs) was obtained after exfoliation using aqueous reducing agents such as hydrazine followed by sonication for minutes. The introduction of porosity or different functional groups to the graphene matrix is a crucial challenge in order to boost graphene-based materials' adsorption capability. Numerous techniques for the processing of single-layer graphene have been introduced to date, like, thermal-or plasma-enhanced CVD, sublimation of SiC, exfoliation of graphite, and other processes [20].
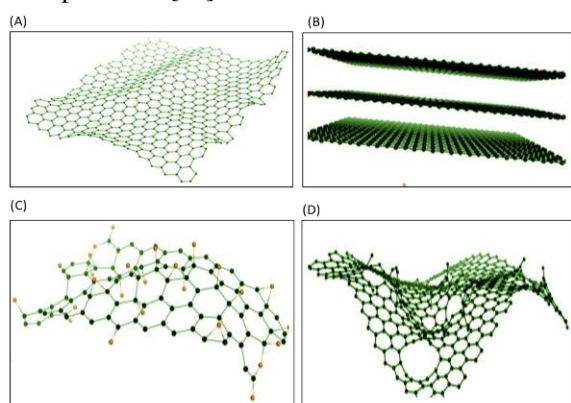

Fig. 7. Types of graphene derivatives: (A) graphene,

(B) few-layer graphene, (C) graphene oxide (oxygen atoms are in orange) and (D) reduced graphene oxide [15].

Graphene is very thin on its own with an atomic thickness and has a purely two-dimensional (2D) structure. Also, its morphology shows extraordinary properties because it has strong and flexible bonds bind the same kinds of carbon atoms. Different forms of graphene nanomaterials appear in Figure 7. As clearly seen, it can be formed as single-layer graphene, few-layer graphene (2-10 layers), ultrafine graphite (more than 10 sheets with thickness less than 100 nm), and graphene oxide."GO" with a single layer structure, typically involves several oxygen-containing functions groups, with less electrical conductivity. Reduced graphene oxide "rGO" usually includes a single layer structure with less oxygen-containing functions groups, with high electrical conductivity, as well as graphene ribbons, and graphene dots [15]. Because of the reduction of significant fractions of oxygen-containing moieties,

rGO is thermally more stable than GO. Furthermore, graphene has a high surface area (2630 m^2 g^{-1}), that qualifies its planar sheets for an effective adsorption process [16]. Additionally, strong π-stacking interactions with benzene ring can be developed by the strong delocalized π-electron on the graphene framework. This may make graphene a good source for aromatic rings compounds formation.

On the other hand, GO can be functionalized easily. Graphene and its derivatives have extraordinary properties, which make them function as superior sorbents. These materials have also attracted considerable interest in diverse fields such as engineering, medicine, electronics and energy storage.

2. Environmental applications of CNTs and graphene-based materials

Environmental pollution resulted from urbanization, industrialization, modernization of the transportation system, oil industries, and power sector has led to huge harms to humans and the environment. These processes introduce harmful pollutants into the environment such as greenhouse gas emissions, toxic heavy metals, pigments, drugs, pesticides, hazardous substances and volatile organic compounds. Such contaminants have a negative impact on the economic growth as well as environmental development which requires economic remediation to reduce them. The environmental remediation of different pollutants from water, air and soil using CNSs materials is found to be very effective and easier as compared to other traditional technologies. Because of their large surface area, well-developed porosity, strongly delocalized π-conjugated electron bonds, and hydrophobic properties. These substances have a tremendous ability, based on their high adsorption potential, to reduce many forms of pollutants [13, 14, 16, 19-23].

2.1. Remediation of air pollution by the studied CNSs

Sequestration of flue gases and by-product vapors such as carbon dioxide (CO$_2$) methane, nitrogen oxides (NOx) and sulfur dioxide (SO$_2$) gases has become of critical importance in reducing the impact of global warming on both the global climate and to the human environment [23-25]. For instance, Figure 8 illustrates the biochar technology for gas adsorption. Gases adsorption via carbon nanotubes and graphene-based materials has been revealed to be possible and cost-effective on biochar and activated

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carbon [23, 26, 27]. CO_2 capture over $CNTs$-SiO_2 reinforced hollow fibers impregnated with polyethylenimine has recently been tested, providing positive gas adsorption results [26]. The overall surface area of the CNTs could be increased from 203.6 m^2 g^{-1} to 283.2 m^2 g^{-1} and achieve a high CO_2 adsorption of 1.92 mmol g^{-1} at 0.15 bar CO_2 partial pressure through, the incorporation of silica particles with polyethylenimine [26]. In a recent study, thermally treated graphene nanosheets exhibit crystalline structure arrangement as shown in Figure 9, with significant-high surface area, pore size distribution in the range of large-micro pore / small-mesoporous, leading to highly effective, rapid, and selective CO2 capture [27]. Compared to pristine graphene (0.81 mmol g^{-1}) at 0oC and 1 bar, the thermally-treated graphene specimens displayed substantially greater CO_2 adsorption capacity (up to 2.89 mmol g^{-1}) [27].
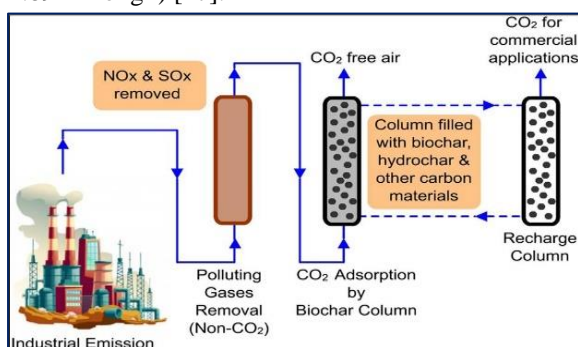

Fig. 8. Biochar-based sequestration technology for adsorption of CO_2 from atmosphere as solution toward air pollution [25].
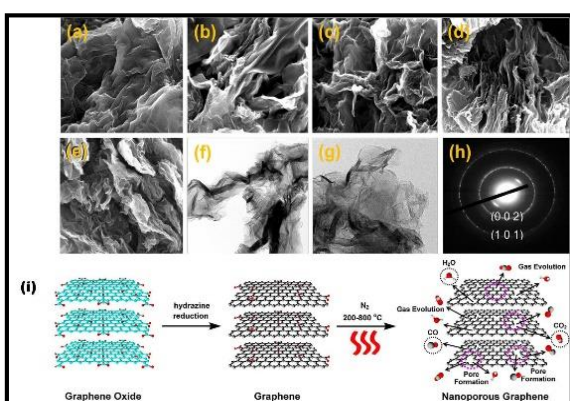

Fig. 9. FE-SEM images of graphene nanosheets(GPN) treated at different thermal temperatures as (a) GPN-200, (b) GPN-400, (c) GPN-600, (d) GPN-800, (e) TEM images (f, g) and (h) SAED pattern of GPN-800. (i) Schematic of pore formation on graphene

nanosheets through gas evolution during thermal treatment [27].

The incorporation of metal-organic-frameworks (MOFs) with carbon nanotubes (CNTs) and graphene oxides (GO) for environmental cleanup from Harmful gases for the environment and (VOCs) in the ecosystem have been studied by Zhu et al. [28] in a recent mini-review. The results indicated that the accommodation of nanocarbons into MOFs matrix can improve the physico-chemical properties of parent MOFs with enhancing its chemical robustness, mechanical and electronic thermal robustness as a result in synergistic effect of both. Li et al. [29] have prepared Cu-BTC@GO as a model of MOF/GO nanocomposite via solvent-free mechanochemical for water stability and toluene uptake (VOC) studies. The Cu-BTC@GO obtained had a better surface area of 1362.7 m^2 g^{-1} and a pore size of 0.87 cm^3 g^{-1} and its toluene absorption at 298 K up to 9.1 mmol g^{-1} and excellent water stabilization compared to the initial Cu-BTC MOF, as shown in Figure 10.

The coordination between the oxygen groups in the GO and Cu_2 + core in $[Cu_3(TMA)_2(H_2O)_3]n$ [29], exhibited the excellent water stability and high adsorption potential of toluene using Cu-BTC@GO. VOC adsorption on Cu-BTC@GO is, therefore, considered to be an effective technology for reducing the emission of VOCs that are often toxic, malodorous, and carcinogenic even at very low proportions for human and air ecosystem. Furthermore, Gangupomu et al. [30] reviewed the use of CNTs as optimal adsorbents for air remediation.

The elimination of hazardous air contaminants (HAP) using CNTs, in particular, showed promising results attributed to their high capacity for adsorption and accessible binding sites. Hybrid architectures developed by an arrangement of graphene with a range of metal oxides as sensors for toxic gases have been documented by Chatterjee et al. [31]. Various carbon substances furthermore, such as carbon nanotubes (CNTs), charcoal, graphene oxide (GO), etc., have already been shown to be efficient as gas sensors because of the flexibility in modifying their characteristics through easy chemical treatments [23-31].
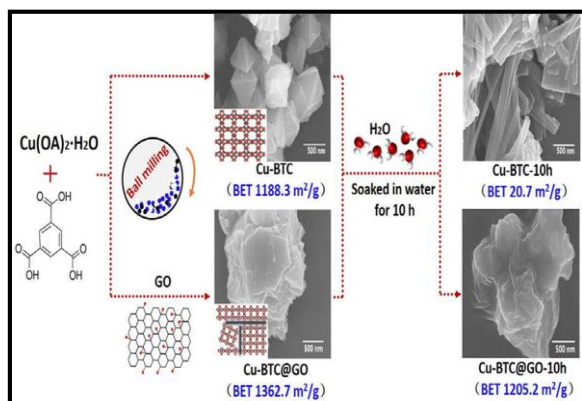
Fig. 10. Schematic diagram for synthesis of Cu-BTC@GO [29].

2.2. Remediation of wastewater by CNSs

Much attention has been paid to the handling of wastewater sources of urbanized and industrial fields. Clean water has become more difficult to maintain with a drastically growing population and multiple environmental pollutants, that making water scarcity a real problem that must be addressed. The presence of contaminants like, toxic heavy metals, solids dissolved or suspended, natural and/or synthetic waste dissolved, will have adverse impacts on mankind future and the aquatic ecosystem. Human health and social development are, in reality, highly related and dependent on the availability of fresh water. Therefore, processing the wastewater streams to be cleaned water and then flowing into recirculation has becoming an emergency [32-37]. For environmental treatment, various approaches are used which are categorized into physical, chemical, biological, and advanced oxidation processes. CNSs can serve as sufficient adsorbents for pollutant removal [33,35]. Adsorption system is commonly used among these technologies and has emerged as simple and easy operation as well as can effectively uptake of various contaminants from the aquatic environment.

The prospective utilization of CNTs and graphene-based compounds as adsorbent materials in wastewater treatment of a wide variety contaminants has also been published recently, [2-5, 13, 14, 16, 19-23]. Due to their large surface area and well-defined porous structure, activated carbons have long been commonly used for wastewater treatment and gases adsorption [38]. ACs sorbents, however, have a limited ability for sorption of conventional pollutants including pigments and oil molecules with high molecular size. This is owing to their low density of surface-active sites, small activation energy of sorption bonds, slow diffusion and non-equilibrium of sorption in solid-liquid systems. As a result, these drawbacks also limit their use in wastewater treatment and thus complicate efforts of researchers in surface-ground water remediation. In order to avoid these limitations, the distinctive characteristics of CNSs have been taken into account; high performance has been achieved in environmental and industrial applications like separation, purification, regeneration, photocatalysis and fuel storage process [33, 35]. Also, they are emerged as effective adsorbents due to they can exhibit short equilibrium time and easy regeneration and their surfaces can be easily functionalized with various functional surface groups for enhancing the adsorption capacity. An outlined report has been published on the contributions of carbon-based nanomaterials in many environmental applications such as adsorbents, filters, antimicrobials, high-flow membranes, environmental sensors and in technologies for renewable energy [39].

Except graphene oxide, CNTs and graphene showed some disadvantages in liquid-phase applications such as the hydrophobic surface, low dispersibility and lack of functional groups as well as the accumulation of their particles in the aqueous phase, owing to weak van der forces between the graphitic layers structure, making them have limited adsorption capacity toward the pollutants. These limitations can be avoided via chemical oxidation processes using oxidizing agents such as oxidized by gaseous oxygen, $NaOCl$, HNO_3, $KMnO_4$, H_2SO_4, ozone or plasma [40]. Thus, the functionalized carbon-based nanomaterials can exhibit excellent adsorption ability than that of comparable pristine ones. Due to the introduction of more active adsorption sites as increasing number of carboxyl, hydroxyl, and nitro-as polar oxygen-containing functional groups that, are formed over their interface through the chemical oxidization. Therefore, the rate of adsorption of heavy metals, dyes and organic anions pollutants on these nanocarbons could be improved.

2.2. A. Removal of heavy metals by CNSs

The consequences of rapid population growth, a rise in the negative impact of agricultural waste, the drawbacks of various modes of transport, and industrial progression are the main reason for the discharge of multiple toxic elements and materials within the environment and atmosphere [41, 42]. One

of the harmful environmental problems is the presence of toxic metals, including both heavy metal ions and radioactive metals. Heavy metal ions are usually categorized as metal cations, for example, Ni(II), Hg(II), Cu(II), Pb(II), Cd(II), etc., which characterized by an atomic weight in the range of 63.5–200.6 g/mol, and a specific gravity greater than 5.0. The toxic metals in wastewater, may present in either single or mixed form. The complexity of its disposal process is what raises their risk [42, 43]. The Environmental Protection Agency (EPA) and the World Health Organization (WHO) has determined the acceptable amount of discharge of harmful metals into the environment to minimize pollution. Nevertheless, there are more than acceptable limits for contamination of discharged effluent annually [23, 44]. Whereby discharging toxic metals into the water, that are converted to hydrated ions with higher toxicity more than their original form. Therefore, to reduce their risk influence the adsorption process has become very essential. The adsorption of heavy metals on CNTs has been documented by Ouni et al [45]. Ruparelia et al.[46] have reported comparative studies on sorption from aqueous solutions of several divalent heavy metals ions such as Cd^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}, over amorphous nanocarbons composed of multi-folded graphene layers and cylinders compared to industrial activated carbon (AC). It was found that the efficient rate of the adsorption process of the synthesized carbon-based nanomaterials was higher than that of AC. The explanation for this result was a return to their unique surface morphology, which is providing favorable sorption active sites more than that of AC [46]. They further noticed that CNT sorption of heavy metal ions was observed in ascending order, as follows, $Pb^{2+}> Ni^{2+}> Zn^{2+}> Cd^{2+}$. The adsorption of such metal ions to CNTs depends significantly on the aqueous medium's pH. The maximum adsorption ability of some CNTs and other adsorbents to eliminate some heavy metal ions is given in Table 1. As shown, under similar conditions, the adsorption efficiency of CNTs is the greatest compared with the other adsorbents [47-55]. Studies on the adsorption of cadmium, copper, nickel, lead, and zinc as divalent heavy metals from aqueous solutions using various types of CNTs as well as the factors affecting the performance of CNTs were reported also by Rao et al [56]. The extraction of divalent metal ions by the pure and oxidized CNTs

was informed in the consequence order: $Pb^{2+}>Ni^{2+}>Zn^{2+}>Cu^{2+}>Cd^{2+}$, taking into account the ionic radius is Cd^{2+} (0.97Å)>Zn^{2+} (0.74Å)> Cu^{2+} (0.72 Å)>Ni^{2+} (0.69Å).

Table 1. The maximum adsorption capacity (Q, mgg^{-1}) of several heavy metal ions on CNTs and other adsorbents.

Sorbates	Sorbents	Q (mgg^{-1})	Conditions	Refs.
Pb^{2+}	Pure CNTs	1.00	pH: 7.0, *T*: 298K	[47]
	Oxidized CNTs	49.9		
	Oxidized MWCNTs	97.1	pH: 5.0, *T*: 298K	[48]
	oxidized MWCNTs	49.7	pH: 5.0, T: 298K	[49]
	Cotton-stalk-activated carbons	25.0-50.0	pH: 5.0, T: 298K	[50]
	AC/ F-400	30.1	pH: 5.0, T: 298K	[51]
Cd^{2+}	Oxidized MWCNTs	10.9	pH: 5.0, *T*:298K	[48]
	AC/ F-400	8.00	pH: 5.0, T:298K	[51]
Cu^{2+}	Oxidized MWCNTs	24.5	pH: 5.0, *T*: 298K	[48]
	As-produced CNTs	8.25	pH 6, T: 300K	[52]
	NaOCl-modified CNTs	47.4	pH 6, T: 300K	[52]
	Activated carbon	19.5	pH: 6, T: 303K	[53]
Ni^{2+}	NaOCl-modified MWCNTs	38.5	pH: 5, T: 298K	[54]
	Granulated activated carbon	2.88	pH 4.5, T 298K	[55]

They deduced that the adsorption of metals on CNTs does not only depend on the ion radius of metal ions but also on the surface characteristics of CNTs. The heavy metal adsorption mechanism is likely to include adsorption-precipitation, electrostatic interactions, and binding energies on the surface of CNTs. The main mechanism is firmly believed to be the chemical interaction between metal ions and surface functional groups of CNTs. With regard to heavy metals adsorption on graphene-based materials, graphene nanosheets (GNs) was thought to have a lower rate of adsorption for certain metal ions due to the deficiency of oxygen functional groups after the reduction process of GO. However, the high surface of GNs may be enhanced the adsorption affinity to some extent. In comparison to GO, the adsorption on GNs occurs mainly via van der Waals forces on their plane surfaces.

Recent research has focused on the possible use of graphene and its derivatives via the adsorption process

in wastewater treatment. Yusuf et al. [57] examined the use of graphene-based materials for the removal of heavy metal ions as well as pigments in aqueous systems. In aquatic settings, the adsorption affinity of GNs is regulated by their pH at a point of zero charge (pHpzc).At pH >pHpzc, the negative surface charge is surrounded around the GNs surface due to the de-protonation of carboxyl and hydroxyl. Hence, electrostatic forces with positively charged adsorbates have occurred. In contrast, the net positive charge on the GNs surface happens at pH <pHpzc and thus electrostatic repulsion is obtained with positively charged adsorbate. Huang et al. [58] have studied the adsorption of Pb^{2+} ions from an aqueous solution using prepared GNs. Although there was a significant decrease in the oxygen complexes of GNs, it still had strong adsorption of Pb^{2+}ion. Interestingly, due to the Lewis basicity, the adsorption of Pb^{2+} ions was increased when heat treatment was increased. Liu et al. [59] discussed the extraction efficiency of toxic heavy metal ions using different graphene-based nanostructures from their aqueous medium. Quite recently, Xu et al. [60] outlined the elimination of harmful divalent metal ions from their aqueous systems by functionalized CNTs and graphene.

Although excellent adsorption efficiency, however, many drawbacks hindered the use of graphene and GO in the adsorption process. Such drawbacks are concerning with the difficulty of separation, regeneration and high production costs of both from the liquid phase. Therefore, the need for carrying out further modifications on graphene and GO is very important [61]. Research works have been conducted to modify and/or shape graphene sheets with a three-dimensional (3D) framework to overcome these challenges [62, 63]. Today, the 3D structures of graphene have proved excellent adsorption capacity with easy regeneration and separation and have given superior sorption strength compared to commercially available sorbents.

Zhao *et al.* [64] have synthesized sulfur-doped graphene sponge to extract Cu^{2+} ions from its solutions. They found such material has a higher adsorption capacity of Cu^{2+} (228 mgg-1) which, has been 40 times better than the adsorbed ones by the surface of activated charcoal. Graphene (G) or graphene oxide (GO) can be assembled in situ with CNTs, or polymeric materials such as chitosan, polyvinyl alcohol, resulting in a variety of composites (G/CNTs, G/magnetic or G/Polymer) as thin films or membranes as 3D hybrids or being constructed into hollow 3D microspheres recently covered in a review [65-67]. As well, the magnetic carbon-based nanomaterials prepared with magnetic oxides have paid considerable attention due to its effective magnetic separation and recyclable benefits. In another work, the synthesis of cobalt ferrite supported by multiwall carbon nanotube magnetic hybrids via hydrothermal process was studied by Tan et al. [68], and compared their adsorption findings for uranium (VI) removal with those for MWCNTs and $CoFe_2O_4$ individually. It was found that $CoFe_2O_4$ / MWCNTs displayed a much higher U(VI) adsorption potential and could have been readily extracted from the solution by a magnet [68].

Chella et al. [69] manufactured nanocomposites of graphene manganese ferrite ($MnFe_2O_4$-G) via a modified Hummer technique and solvothermal removal process of Pb(II) and Cd(II). They found that the presence of nanoparticles of $MnFe_2O_4$ not only boosted the adsorption potential of graphene but also improved its antibacterial activity and separation process. Sun et al. [70] prepared GO-magnetic chitosan composite with ionic liquids (GO-MCS-ILs) for an efficient adsorption of lead ions as depicted in Figure 11. The results revealed that the integration of ionic liquids would not only increase the adsorbent's dispersivity, but also significantly improve the active sites of adsorption process. The distinctive results of FTIR, SEM, and XRD spectrum exhibit that the composite of GOMCS-ILs had a wide surface area and strong magnetic responsiveness. Adsorption by this composite was fit with adsorption data of Langmuir isotherm accompanied by monolayer capacity equal to 85 mgg^{-1} [70]. Chen *et al.* [71] cross-linked polyethylenimine (PEI) to the graphene oxide (GO), by means of an amidation reaction between both the amine groups on the polymer surface and the carboxyl groups at GO surface , which effectively prevented the agglomeration of GO nanosheets, to raise the rate of adsorption process of toxic metal ions. The prepared polymer composite with graphene oxide as an adsorbent showed a higher absorption ability for Cr (VI) removal, than many other traditional adsorbents, such as both ethylene-diamine-functionalized, Fe3O4 and PVP-modified activated carbon via the adsorption process.
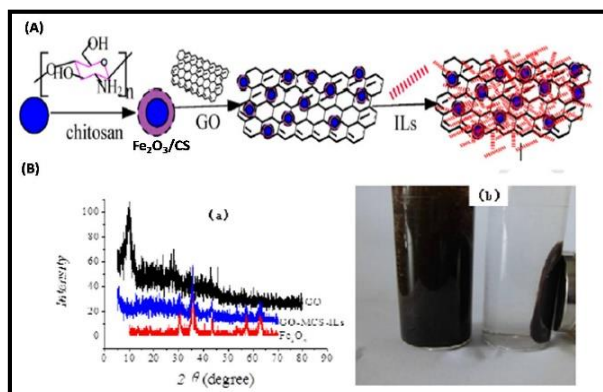
Fig. 11. (A) Synthesis route for preparation of GO–chitosan and GO–Chitosan Ionic liquid nanocomposites, (B): (a) XRD patterns of the Fe3O4, GO and the GOMCS-ILs, (b) Photo of GO-MCS-ILs in external magnetic field [70].

2.2. B. Removal of inorganics and organics by CNSs

Polluted water emanates from the pharmaceutical, leather, textile and domestic manufacturing companies and raw sewage sludge that releases many toxins, such as anions, fluoride, arsenic, cyanide, microorganisms, colorants, suspended solids, phenols, dissolved colored organic compounds, plankton and other microscopic organisms [5, 72-75]. Fresh water is essential for all living things, plants, animals, and humans all need it to survive. Therefore, water pollution is one of the major vital environmental problems, and getting rid of these pollutants has become an urgent issue for the survival of life.

For example, fluoride (F^{-1}) anion is one of the beneficial elements for the human body within the permissible limit; the ingestion of fluoride is beneficial for the calcification of dental-enamel and maintenance of healthy bones [72]. But if fluoride is present in excess of 1.5 mg/L, in water, it will affect the metabolism of elements such as calcium and phosphorus in the human body and causes molting of teeth and lesion of endocrine glands, thyroid, liver, and other organs [72-74]. Li et al. [73] found that the pristine graphene exhibited efficient fluoride elimination from the aqueous medium. The kinetic study measurements indicated that the adsorption of fluoride can be well described by the Langmuir isotherm model with monolayer capacity equal to 35.59 mg/g at 298 K and pH = 7.0. The adsorption reaction was a spontaneous and endothermic process

based on the thermodynamic studies. Hence, graphene adsorbent emerges as a promising fluoride adsorbent.

In another work, the adsorption of fluoride onto single-walled carbon nanotubes (SWCNTs) was examined for various aqueous medium [74]. The factors of contact time, dose, temperature, pH, agitation speed, and fluoride concentration in the solution have been studied. The study showed that the maximum adsorption fluoride capacity was ~ 60 mg / g at 298 K and 6.0. Additionally, adsorption of fluoride anions to SWCNTs was feasible, natural as well as an endothermic process. Compared to conventional sorbents such as clay, zeolite, and activated carbon, carbon-based nanomaterials have been considered beneficial for treating a wide variety of environmental toxins. This is due to their chemical compositions, the unique chemical characteristics of their adsorbent surface, effective electrostatic interactions, and rapid equilibrium of high sorbent capacity [5, 57, 75-80].Yang and Xing [75] presented a study of the degradation of certain organic contaminants by carbon-based nanomaterials with adsorption techniques. As an example, adsorption in CNTs depends mainly on the surface area, distribution of pores, surface functional groups, surface curvature and defects of CNTs.

The mechanisms of adsorption of organic substances to CNTs were also mentioned in previous studies [79]. Four mechanisms can be occurred at the same time including; hydrophobic surface interactions of carbon nanotubes, physical van der Waals forces, pi-stacking interactions, Hydrogen bonding attraction, and electrostatic interactions of ionic species. The efficiency of the sorption process is primarily controlled by structure and surface groups of both carbon nanotubes and adsorbed organic compounds. Also, the performance of CNTs as adsorbent is influenced by the available active sites and the defects within the structure of its walls.

Other crucial parameters affecting the adsorptive strength of such nanomaterials are dispersibility degree of active surface, pH and ionic strength. The surface of Pristine CNTs is hydrophobic and has a particular preference sorption for hydrocarbons like hexane, benzene, and cyclohexane, over many alcohols It was found that both the hydrophobic nature and surface region of CNTs has been reduced by rising the complexation of surface Functionalization, thus increasing the polar oxygen content, leading to reduce

the sorption rate of non-polar hydrocarbons. Accordingly, the oxidized CNTs showed low sorption of planar chemicals such as polymeric molecules due to insufficient interaction between CNTs and organics [5]. CNTs and functionalized CNTs have recently emerged as excellent adsorbents for organic dyes as compared to commercial activated carbons and clays [81, 82].

In most cases, the adsorptive mechanisms of dyes by CNTs are related to the type of dye whether such dyes are neutral, cationic or anionic. However, the interactions between CNTs and dyes may be followed by one of the four mechanisms have been mentioned earlier, which act simultaneously or individually [83]. Sorption of methylene blue dye onto three different sorbents (e.g., active carbon, graphene oxide and carbon nanotubes) has been compared. It was found that the highest removal occurred onto the ACs sample was due to its larger surface area [84]. Specifically, the sorption of organics and dyes on carbon nanomaterials is thus mainly governed by their surface areas and pore size distributions. Due to their attractive properties and good adsorption capabilities for the removal of different organic compounds [5, 80, 85-95], graphene-based adsorbents have attracted growing interest in water and wastewater treatment applications, as shown in the following studies.

Removal of various organic dyes such as malachite grey, rhodamine B, and acriflavine has been investigated by GO foam [91]. The GO foam obtained showed important sorption capacities of 460.0, 351.4, and 235.4 mgg-1 at 310 K, respectively. Tetracycline (TC), as a common antibiotic, is considered as an organic contaminant when exist in the water can be oxidized and formed harmful matters [93]. Very recently, the sorption of tetracycline on magnetic GO sponge (MGOS, Fe_3O_4/GO) was studied by Yu et al. [93]. Fe_3O_4 / GO sponge showed an enormous adsorption ability of tetracycline (473 mgg-1), and about 50 percent higher than those of graphene oxide. The rate of adsorption was relatively quick and could have been represented using a pseudo-second-order model as shown in Figure12. Up on incorporation of TiO_2 nanoparticles into GO sponge, (TiO_2-GO) composite, the adsorption of TC was reached to 1805 mg/g [94]. It was found that the adsorption process activity of organic pollutants at graphene, GO, CNTs and ACs to be very distinct, and relied on the physicochemical properties of these sorbents. Studies have been undertaken to compare the sorption

capacities of GNs, CNTs and ACs for removal of organic contaminants [95].

Pesticides are one of the most risky types of organic toxins that already available in the aqueous ecosystem because of their carcinogenic effects, on humans and animals. Graphene-based materials as effective adsorbents have an immense potential in decontaminating pesticide-bearing effluents [96, 97]. The advantages of the combination of graphene and TiO_2as a new magnetic photocatalyst showed good light absorption in the visible region and high organic pollutant adsorption ability, resulting in nearly 100% photocatalytic efficiency of the standard herbicide 2, 4-dichlorophenoxyacetic acid (2, 4-D) extracted from water under simulated solar light irradiation, far higher than the ratio 33% with commercial P25 [97]. Toxicity assessment indicates the total decomposition of the original substrate. Furthermore, the catalyst can be rapidly recovered with highly stable photocatalytic performance. After 8 successive cycles, the removal efficiency of 2, 4-D maintained 97.7%, and particularly, 99.1% 2, 4-D removal efficiency came back at the ninth recycle when the catalyst was re-treated by ultrasonication. The photocatalyst is a promising platform for removing herbicide pollutants from water.
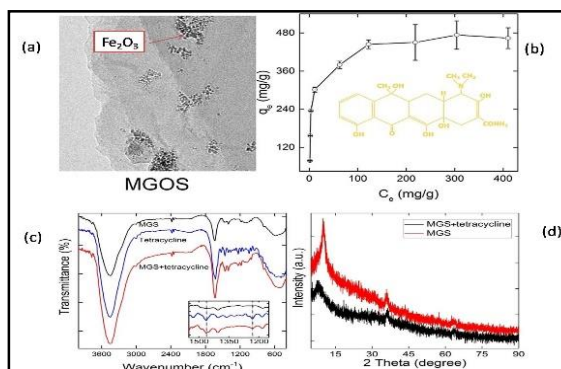

Fig. 12. (a) TEM image of MGOS, (b) Adsorption isotherm of TC onto MGOS, (c) FTIR spectra and (d) XRD of MGOS before and after TC adsorption [93].

2.2. C. Removal of organic pollutants by advanced oxidation processes (AOPs)

The destructive pollutants from wastewater can be easily eliminated via the adsorption mechanism, the process ends with presence of the secondary by-products that affect the quality of reused water from industrial sources (e.g., fine chemical, pulp and paper, textile and tannery, petrochemical, pharmaceutical and food industry) as well as drinking water, agro-industry

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and urban wastewater. Nowadays, considerable efforts have been carried out on improving the removal of organic pollutants through using carbon-based catalysts in advanced oxidation processes (AOPs) [98-104]. AOPs involve four categories; catalytic wet oxidation, catalytic air oxidation, Fenton-oxidation and photocatalytic oxidation processes, which depend on the generation of both the Hydroxyl radical (HO$^\bullet$) and superoxide radical($O_2^\bullet$) using oxidizing agents such as H_2O_2, O_3, sunlight, and UV in presence of the catalysts. Studies have been conducted that using carbon nanotubes individual and/or with titanium dioxide as catalysts for elimination of dyes, chemicals, oils, and pharmaceutical drugs [105-107].

Carbon nanostructures (CNSs) as carriers for semiconductors like TiO_2, ZnO, CdS, etc., provide excellent photocatalytic activity because they have wide specific surface area, unique electronic structure, commendable chemical stability, excellent absorbability, and nanoscale hollow tube property all of which can improve the quantum efficiency and light absorption region [108-110]. A large number of pollutants such as chromium [111], formaldehyde [112], bisphenol A [113], and tetracycline [114], methylene blue and methyl orange [115], and bromate [116] have been successfully degraded using CNSs and their composites. Table 2 summarizes the use of some selected CNSs as photocatalysts. Whereby, such materials and their composites showed the ability to give a greater transmittance for ultraviolet–visible light, excellent electrical and thermal conductivities and corrosion resistance [117]. In photo catalysis, TiO2, ZnO, CdS as semiconductors are incorporated into carbon nanostructures to promote their visible absorption, render the recombination of electrons-holes and boost their photocatalytic performance. Su et al. [104] reported that composition of porous photosynthetic ZnO/ rGO/carbon sponge-based nanocages extracted from MOF as shown in Figure 13 for an efficient breakdown of rhodamine B (RhB) in aqueous solution and hydrogen evolution. Figure 13 represents, {(a, b) Schematic illustration of the fabrication process and photocatalytic reaction in ZnO nanocages/rGO/carbon sponge (ZRCs), (c-f) ZRCs absorption and in-situ photocatalytic degradation of RhB/methanol aqueous solution, and (g) Schematic illustration to demonstrate the mechanism of simultaneous sunlight-driven photocatalytic degradation of RhB and H_2 production. The

combination of ZnO has shown to induce photoexcitation and subsequent charge transfer to the surface of the rGO / carbon sponge and to generate O_2-$^\bullet$ radical by interacting with oxygen. The superoxide radicals then interact with the H_2O molecule to develop HO$^\bullet$ radical that decompose the dye molecules into harmless compounds via the oxidative degradation process.

Table 2. CNSs and their composites used as photocatalysts

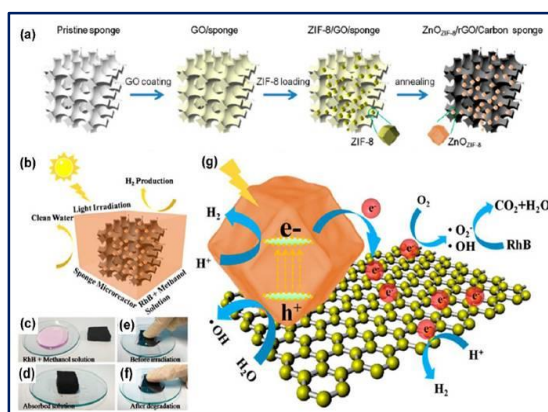| Catalyst/catalyst support material	Surface area (m²/g)	Pollutant compound	Catalytic removal %	Refs
Carbon nanotubes sponge	50–500	Tetracycline	88.00%	[105]
TiO$_2$ @Multi-walled carbon nanotubes	85.3–103.2	Rhodamine (RhB) Methylene blue (MB)	99% 99 %	[107]
Graphene hydrogel–silver bromide–graphene oxide	220	Bisphenol A	91.40%	[113]
Reduced graphene oxide/titanate nanotube composites	127.7-239.3	Methylene blue (MB) Methyl orange (MO)	95-100% 99.10%	[115]
Dopamine-bridged melamine–graphene/titanium dioxide nanocapsules	184	Formaldehyde	92.00%	[112]
Graphene oxide- and cobalt-doped titanium dioxide	–	Bromate	99.90%	[116]
Copper sulfide/graphene oxide	–	Chromium(VI)	95.00%	[111]

Fig. 13 Schematic illustration of the fabrication process and photocatalytic   reaction in ZnO nanocages/rGO/carbon sponge (ZRCs) [104].
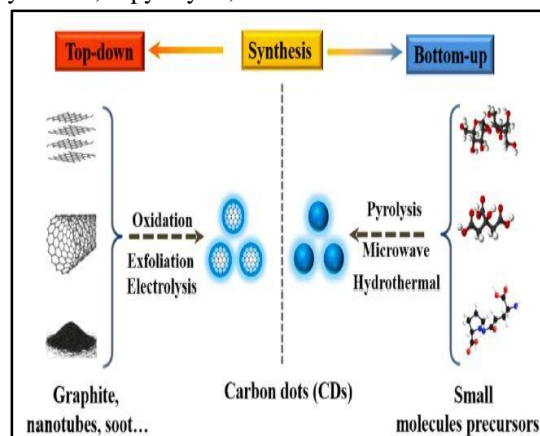
3. Properties, synthesis and environmental applications of carbon dots

3.1. Properties and Synthesis of Carbon Dots

Carbon dots or carbon quantum dots (CDs) have versatile properties and uses in environmental decontamination as newly CNSs. The production of such compounds has also recently attracted enormous attention as a remarkable form of carbon nanoparticles having a particle size of about 10 nm [118-121]. CDs demonstrate considerable characteristics as follows: (1) CDs have such a range of specific optical properties, such as continuous and wide absorption spectra, strong fluorescent behavior, excellent photo stability, highly tunable photoluminescence, and superb optoelectronic performance, (2) CDs have a wide variety of important physicochemical properties due to the variety of raw materials, synthetic methods such as extensive charged functional groups, ultra-small particle sizes, broad surface interfaces, and (3) CDs are inexpensive, extremely biocompatible, and environment benign. These peculiarities have allowed CDs to be used for pollutant monitoring and elimination [122,123]. Their surface structures and particle sizes are modifying by the oxygenated functional groups on its surface. Such categories of nanomaterials have a superior capacity to transfer charges, which can efficiently prevent the recombination of photo-generated active sites [124,127]. CDs exhibit excellent absorption ability in the UV-Vis region via the contribution of the chemical groups its surface.

It is possible to classify the synthesis of carbon dots into two techniques: (i) top-down and (ii) bottom-up, that could be represented in Figure 14. In the first route (i(, large carbon structures are converted into small molecules by anyone of the following methods: laser ablation, arc discharge, and chemical or electrochemical oxidation into quantum-sized and fluorescent carbon quantum dots [128]. The synthesis of carbon dots through arc discharge has been commonly used due to the extreme ease of control of the morphology of the produced nanoparticles during this process. For example, Ming et al. [129] produced a pure high-quality of CDs via a one-step electrochemical method which is reported as a high manufacturing quality approach that can make the synthesis of CDs is economical and environmentally friendly process. For the second technology (ii),

bottom-up synthesis of CDs can be obtained via hydrothermal processes, microwave-assisted synthesis, pyrolysis, or carbonization through

carbonizing the tiny-molecule precursors [130-133].

Fig. 14. Different synthesis methods of CDs [128].

Due to many features like abundant, inexpensive precursors, smooth synthesis, large influential instruments, and non-toxic pathway, hydrothermal carbonization is a common and environmentally friendly technique for CDs synthesis. Because of their minimal cost production, natural carbon products such as organic acids, carbohydrates, juice, or waste peels have increased the prevalence of carbon dot preparation compared to traditional sources in recent years [131-133].

3.2. Application of CDs for adsorption of contaminants

As an alternative to conventional adsorbent materials, carbon-based nanocomposites such as carbon dots attain several benefits as compared to CNTs and graphene materials [122]. This is owing to their small size and wide particular surface region, several adsorption active centers as resulting in abundance of surface functional groups, and easily synthesized from low-cost precursors. More significantly, there is a massive of hydrophilic functional groups in CDs, which could be the reason why CDs are capable of eliminating toxins from heavy metal ions and organic compounds [122,134]. Numerous variables such as pH value and ionic strength were found to influence the adsorption potential of CDs. The pH value greatly affects the adsorption process of metal ions on a surface of CDs material as adsorbent. The high concentration of hydrogen ions in the acidic solution would impede the

adsorption of metal ions to the adsorbent as they repel each other [135]. While the adsorption of organic pollutants is strongly influenced by ionic strength, due to the competition between the different charges within the electrolyte solutions [136].

3.2. A. Adsorption of heavy metal ions onto CDs

In heavy metal adsorption, the ability for adsorption is primarily dependent on the chemical composition of the CDs nanoparticles as adsorbents, broad surface extent, pore characteristics, and the nature of existed functional groups [137-141]. Sabet et al. have recorded that the metal ions (e.g., Cd2+ and Pb2+ ions) have been extracted from wastewater through the adsorption process onto nitrogen-doped CDs composite as result of its high total surface area [142].

A persistent mesoporous organ silicate (MS) substrate implanted with CDs as adsorbent for elimination of metal ions such as Hg^{2+}, Cu^{2+}, and Pb^{2+} was reported by Wang $et\ al.$ [137]. The combination of substrate MS with CDs led to presence of multiple functional groups and various polar moieties compared with pristine mesoporous silica alone, resulting in increased adsorption potential of the different heavy metal ions. CD-MS showed the adsorption percentages of $\approx 56\%$, 53, and 43 % toward Hg^{2+}, Cu^{2+} Pb^{2+}, respectively, with an initial concentration of $10-3$ M.

As seen in Figure 15, CDs modified with mesoporous organosilica as an adsorbent for the removal of 2, 4-dichlorophenol is covered with multiple groups of sialons, amides, aromatic rings and amine groups. Electrostatic and n-π stacking interactions (e.g., n-π electron donor-acceptor interaction between O- and N-containing groups) will give negatively charged nitrogen ions and oxygenated-functional groups as active sites that promote the relevant adsorption mechanism along the CDs-based absorbents and metal ions interface [143,144].

3.2. B. Adsorption of organic pollutants onto CDs

Elimination of organic contaminants by carbon dots nanocomposite via adsorption technique depends on various factors mentioned earlier. For both the adsorption of cationic and anionic dyes, the CDs-based adsorbent materials have used by means of a mechanism of potential electrostatic interactions. 2, 4-DCP is considered one of the most toxic organic contaminants as chlorophenol derivatives due to its high toxicity and difficult biodegradability [137]. Extraction of such organic compound has been well-done with the modified mesoporous organosilica / CDs as an adsorbent, with a 99.7 mg g^{-1} removal capacity. It was found that n-π electron donor-acceptor interaction between O- and N-containing groups is responsible for promoting the adsorption mechanism in the mesoporous organosilica and benzene ring in 2, 4-dichlorophenol [137].

The nanocomposite of CDs with $ZnFe_2O_4$ (CDs/$ZnFe_2O_4$), has found to have a high adsorption potential that could be efficiently used to remove methyl orange (MO) [145]. A series of experimental data showed that the MO adsorption mechanism using CDs /$ZnFe_2O_4$ is owing to the electrostatic attraction and van der Waals force at the interface of the adsorbent/dye. $NiFe_2O_4$/CDs nanocomposite was developed by a solvothermal one-pot process [136] to remove tetracycline (TC). It was found that the maximum adsorption capacity of 591.72 mgg^{-1} was significantly improved using the $NiFe_2O_4$/CDs nanocomposites. The adsorption potential is assigned to the groups of hydroxyl and carboxyl derived from the surface of CDs, and cation exchange between TC and $NiFe_2O_4$/CDs interface.

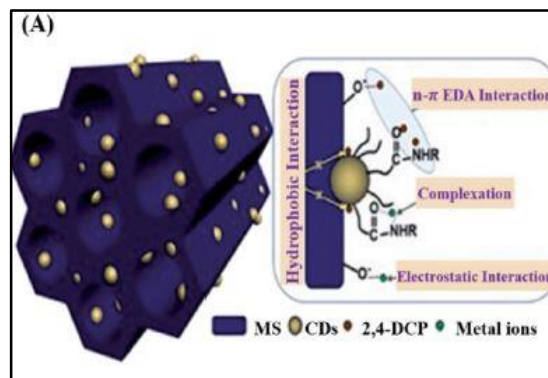Fig. 15. Carbon dots modified mesoporous organosilica as an adsorbent for the removal of 2, 4-dichlorophenol [137].

3.2. C. Photocatalytic degradation using CDs-based composites

Various studies have been shown that the Merging between CDs with other compounds to obtain a photocatalytic composite catalyst is a safer and more reliable way to develop the process of photocatalytic degradation [146,147].

Through light irradiation, CDs can also produce electron-hole pairs, and can act directly as a photocatalyst independently, comparable to a TiO2 semiconductor photocatalyst in the removal process of environmental contaminants [147]. The functional groups containing surface oxygen within the interface of the CDs help minimize the recombination of electron-hole-pairs and contribute to the absorption in the ultraviolet–visible regions, boosting the activity of photocatalytic degradation of organic pollutants [148]. For example the photocatalyst was first dispersed into a solution of Rhodamine B (RhB) (10 mgL^{-1}) and blended in the dark for 40 min [149] followed by xenon lamp irradiation for 200 min. Using a UV-Vis spectrophotometer, the solution samples were measured every 20 minutes. The results showed that about 100% of RhB reduction within 120 min was occurred due to the degradation of CDs in the presence of a Xenon lamp.

Application of conventional semiconductor photocatalyst with a wide-band gap (e.g. TiO_2, ZnO, Fe_2O_3, and Cu_2O) that, only be used under ultraviolet light irradiation. Since UV light accounts for only 4% of solar energy, these characteristics greatly limit their range of possible applications [150]. To enhance their photocatalytic operations, CDs-based materials have been combined with common semiconductors which could essentially enlarge the photocatalyst activity and optical response range under sunlight irradiation. The absorption of light will significantly extend into the visible spectrum region and it can even extend to the near-infrared spectrum region, with the semiconductors of broad band gap.

CDs-semiconductors photocatalysts are acted as an extraordinary electron acceptor and donor by improving photo-response, contributing to separate charges through essentially separating electrons and holes and displaying a remarkable and tunable up-conversion photoluminescent and optoeluminescent [120, 123, 128]. Ke et al. [151] in order to expand the absorption of light, they incorporated TiO_2 with CDs. They reported that the effective visible spectrum of solar light will be realized by CDs / TiO_2 photocatalyst due to its superior ability of CDs to extend the visible absorption and producing more electrons and electron–hole pairs for the degradation of pollutants. As a result, the composite photocatalyst was able to break down methylene blue dye under visible light rays within 120 minutes, achieving an adsorption capacity of about 90 % for MB, which was 3.6 times

higher than the unreinforced TiO_2. Huang et al. [152] prepared CDs/$ZnFe_2O_4$ composite as photocatalyst through hydrothermal process [152]. The obtained composite enhanced catalytic efficiency for NOx gases elimination and exhibited good selectivity for nitrate production through visible irradiation, which was approximately 8 times higher than that of the pristine photocatalyst $ZnFe_2O_4$ as illustrated in Figure.16. During the photocatalysis degradation processes of composites, CDs operate as carriers and electron reserves, as well as energy-efficient transfer components.
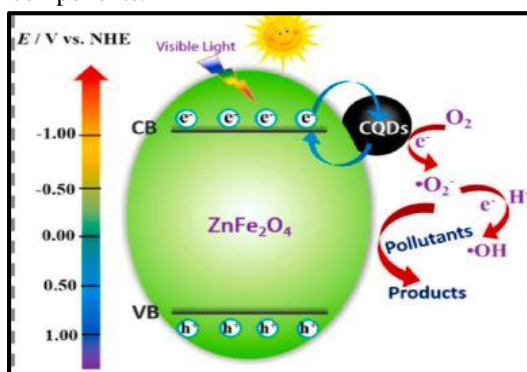

Fig.16. Reaction mechanism of CDs /ZnFe2O4 composite photocatalyst [152].

4.4 Egyptian Researcher's Contributions

In Egypt the adsorption efficiency of various carbon nanomaterials in individual or composite forms has been researched   in order to eliminate dyes and organic substances utilizing adsorption and catalytic processes. In recent years, however, few studies on water remediation using CNTs and graphene-based nanomaterials have been published.

Fathy and others reported the efficiency of MWCNTs to as promoter to MnO_2, Fe_2O_3-Ag_2O, TiO_2-Ag nanoparticles in dye remediation of polluted water [98-100] and studied the adsorption capability of reduced graphene oxide by removing p-nitrophenol from aqueous solutions [19]. CNTs-polymer composites have also been synthesized in NRC by Attia and coworkers for the adsorption of methylene blue dye and Pb (II) ions from aqueous solution [153]. Abdel Salam et al. [154] compared the adsorption efficiency of MWCNT unmodified and the modified one with 5,7-dinitro-8-quinolinolunder different conditions (shaking time, pH, ionic strength, metal ion concentration, and adsorbent dosage) for the disposal of Cu, Zn, Pb and Fe divalent ions. Nesma A. Fekry

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and colleague's [155] have focused on sorption performance of either free or modified resultant CDs. CDs have been successfully synthesized via green development from the starch-water method with a fast microwave-assisted heating approach for only 10 minutes, which produced a novel nanobiosorbent by supporting the PAFP polymer matrix to develop CQDs@PAFP as an effective nanobiosorbent for the adsorptive removal of U (VI) from aqueous solution. El-Shamy and Zayied [156] prepared a new PVA/CDs nano-composites films were made-up via solution casting approach for the methylene blue dye removal from wastewater. PVA/CDs nano-composite films were achieved by the combination of PVA and the CDs nano-particles, by microwave heating process. El-Shafiee et al. [157] have utilized the oxidized MWCNTs under variables such as pH, agitation intensity, contact time and adsorbent concentration, for the removal of phenol discharged from industrial wastewater was investigated. Khedr and others have recently been involved in the synthesis of CNTs as adsorbents by chemical vapor deposition route (CVD) of acetylene over various catalysts and supports and applied for methyl green adsorption [158]. Mohamed's group [159,160] reported the synthesis of CNT /TiO2 composites with Pt or Ag nanoparticles as photocatalyst for methylene blue dye degradation under visible light.

5. Conclusions and future perspectives

This review has been proposed to illustrate the function of CNTs, graphene-based and carbon dots-based materials either in individual or in hybrid forms, via diverse environmental remediation techniques. However, in environmental remediation using nanotechnology, researchers may face some challenges concerning processing expense, adsorption and catalytic performance of nanoparticles used and difficulties of separation / regeneration.

In brief, substantially carbon-based nanomaterials achieved promising elect environmental requirements in the separation, filtering phase and adsorption process, due to of their lightweight, high porosity and wide surface region. A few techniques are employed in order to boost the adsorption and regeneration performance of CNT, graphene- and CDs-based compounds in liquid-phase applications. Such technologies include the formation of CNT, GO, rGO or CDs, hybrid structures, transition metal oxide, C-C hybrids, MOFs, porous inorganic materials such as

zeolite or silica, polymers and magnetic materials. For the removal of hazardous substances from waste water, the integration of CNTs and graphene-based materials with magnetic nanomaterials including Fe, Ni, and Co and their alloys is considered the most critical purification advanced technologies.

Technology expense for wastewater treatment by carbon nanostructures as adsorbents depends on several factors, along with the cost /difficulty of CNT functionalization, the need for solid / liquid segregation, the nature of wastewater treatment, the cost and efficiency of recycling. Research is needed to improve the cost-effective development upon large-scale CNTs and graphene to reduce the cost of water treatment. The better the dispersion of an adsorbent is the difficult isolation from liquid media. It is also easier for adsorbent particles with a smaller size to form a homogeneous solution than those with a bigger size, but they are typically harder to distinguish by processes such as filtration, centrifugation and gravity of sedimentation.

An efficient way to solve the problem mentioned above is magnetic separation. It is a process which is physical, simple to operate, economical, and environmentally friendly. The adsorbents can be easily isolated by applying an external magnetic field after inserting some magnetic materials into their crystal lattice. These magnetic carbon-based nanomaterials are not only promoting the retrieval of adsorbents, but also enhance their adsorption ability. Through many recent papers, CDs have indeed revealed their concern for future environmental applications as modern carbon-based nanomaterials.

CNSs should be constructed with the regeneration and disposal of the substance adsorbed by the pollutants in mind. Before the introduction of CNSs as adsorbents, the life and reuse cycle should also be evaluated. The concept of safe disposal of contaminants needs to be taken into consideration in environmental purification techniques. However, large-scale production of such materials could get a huge effect in the future on growing their merits in terms of price as well as performance.

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