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A Mini-review of Carbonaceous Nanomaterials for Removal of Contaminants from Wastewater

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Abstract: Recently, carbonaceous nanomaterials have been extensively studied for all sorts of contaminants removal from wastewater due to its extraordinary and tunable properties. The present and potential applications of these nanomaterials in wastewater treatment include adsorption, photocatalysis, disinfection, membranes process and other utilizations such as monitoring and desalination. In this paper, we concisely overview the current advances in carbonaceous nanomaterials, covering the basic information upon these nanomaterials (e.g., categories, structure, versatile properties) and their roles for removing diverse contaminants in different applications. Furthermore, the challenges and prospects for further utilizations are also outlined.

1. Introduction

With the rapid development of urbanization and industrialization, numerous contaminants were discharged from industrial production and households into aquatic environment. These contaminants include nutrients, toxic substances such as heavy metals, organic compounds, dyes, parasites and many other complex compounds, which have caused severe influence both on the health of ecological environment and human beings. Consequently, removal of toxic pollutants from wastewater is urgently needed. For this purpose, a number of conventional methods like precipitation, coagulation and other physicochemical technologies have been commonly employed. However, these approaches have been restricted by many factors, such as the increasing stringent water quality standards, the appearance of emerging contaminants, lower removal efficiency, complicated operating conditions, and expensive costs. For instance, chlorination could generate various disinfection by-products (DBPs) with a high mutagenic and carcinogenic risk as well as undesirable odors and tastes during the treatment process. Ion exchange, require complex condition actions and exhibit poor universality, which cannot meet the demands of rigorous water quality standards.

Recently, advance in nanoscience and nanotechnology have suggested that many environmental concerns involving wastewater decontamination could be solved or greatly diminished through the utilization of several promising nanomaterials. A variety of nanomaterials with unique functionalities such as nanoadsorbents, nanocatalysts, nanostructured membranes, have been considered as efficient, economical, and environmental-friendly substitutes to the current wastewater treatment agents.

Here, we provide a succinct review of recent advances in carbonaceous nanomaterials during waster decontamination. The utilizations of carbonaceous nanomaterials are strictly discussed on the basis of their functions in unit process and combined with other treatment approaches. The simple overview concerned the synthesis routes and brilliant properties of these exceptional nanomaterials are presented.

Furthermore, the gaps which limited their full-scale applications and the researches need to tackle it are also considered. The environmental fate along with other potential risks of these nanomaterials are beyond the scope of this article and thus would not be discussed at great length.

2. Carbonaceous nanomaterials

Carbonaceous nanomaterials integrate the distinctive properties of sp^2 hybridized carbon bonds with extraordinary physical-chemical properties at the nanoscale, generally exhibit excellent chemical, mechanical and electrical properties. They have attracted wide attentions in many applications, including environmental remediation, contaminants transformation, drug delivery, supercapacitors, catalysis, etc. With the booming developments of nanotechnologies, roles of carbonaceous nanomaterials would be more and more significant in future life. Nanoporous activated carbon (NAC) is quite common and will not describe in this section.

2.1. Fullerenes

Fullerenes are regarded as the third allotropic form of carbon materials since the discovery in 1985. They are enclosed cage-like structures comprising of 12 pentagonal rings and unspecific number(other than one) of 6-members rings, generally appear in the shape of 6-members rings in which carbon atoms placed. For example, C_{60} is composed of 32 faces with 12 pentagons and 20 hexagons, all carbon atoms are arranged at the 60 vertices of a truncated icosahedron, is highly symmetric[1]. Structures with fewer hexagons exhibit greater sp^3 bonding character, higher strain energies, and availability of more reactive carbon sites. Moreover, the chemical properties of fullerenes is abundant and various, which allow modifications of them for exploiting relevant environmental applications. Several measures such as covalent, supramolecular and Endohedral transformations have been taken to achieve the goal for practical use. Approaches that introducing -OH and -COOH groups could enhance the dispersion of pristine fullerenes, combination with polymers would alter its electrical and mechanical properties.

2.2. Graphene-based nanomaterials

2.2.1. Graphene. Graphene is an infinite two-dimensional (2D) monolayer consisting of sp^2-hybridized carbon atoms. It could be viewed as the fundamental building block for other carbon allotropes such as fullerenes and carbon nanotubes. It also exhibit intrinsic corrugations and some defects such as topological defects, vacancies, which would influence the reactivity of graphene with others. And the theoretical surface area of graphene could reach to 2630 m^2/g, is much higher than many materials. With these special structural properties, graphene has shown standout attributes and were studied in many applications. Various approaches were employed to synthesize graphene nanosheets and can be broadly categorized two sorts, “top-down” approach and “bottom up” approach, which include exfoliation of natural graphite and reduction from GO[2].

2.2.2. Graphene oxide (GO) and reduced graphene oxide (RGO). GO, can be made from chemical exfoliation of graphite by reactions, is a two-dimensional sheet with abundant oxygenated functional groups on their basal plane and edges. The fabrication process of GO breaks the π-conjugated network and thus make it highly water-dispersible[3], meanwhile, reduce the aggregation among individual GO sheets, display a wider potential in wastewater treatment. And GO itself has attracted significant attentions due to many intriguing properties and its role as a promising precursor for bulk production of graphene-based nanomaterials. Synthesis approaches of GO contains the Brodie, Staudenmaier, Hummers method, or modified methods based on them [2].

The structure of RGO is between graphene and GO, there are only a few functional groups embedding on the RGO surface, could be reduced from GO by solvothermal and hydrothermal methods [6]. The enhanced electronic and conductive properties make it a prospective candidate for pollutants removal in wastewater treatment process.

2.2.3. Graphene nanocomposites. In recent years, abundant polymers and metal oxides were incorporated to the graphene-based sheets, developed as nanocomposites. These nanocomposites exhibit standout structural performance and multifunctional properties by combing both components' characteristics. And it should be noted that integrated nanocomposites are not merely the sum of different components, but instead a new nanomaterials with entirely new properties [2]. The functionalization process could facilitate the dispersion and then prevent the aggregation of graphene sheet in the aqueous phase, and endow them with some superior chemical and physical attributes, which may contribute to many practical utilizations. For example, magnetic nanocomposites of graphene could be easily separated from treated water and thus reduce serious recontaminations, but it is difficult for separation of original graphene and GO. The incorporated nanocomposites could be more selective and bind the desired pollutants more tightly based on its structures.

2.3. Carbon nanotubes (CNTs)
CNTs, also called buckytubes, are cylindrical carbon molecules with unique properties. They can be divided into single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) on the basis of the tubes number in the CNTs, where SWCNTs are made of single layer carbon atoms while MWCNTs comprise of multilateral graphene sheet that rolled upon itself with dozens of concentric tubes [4]. As with graphene-based nanomaterials, CNTs exhibit unique properties such as large specific area, rich hollows and layered structure, which bring about a wide variety of remarkable applications in wastewater treatment, including the removal of organic contaminants and heavy metals. There are various methods could be employed to synthesize CNTs, for instance, chemical vapor deposition (CVD), the arc-discharge method, flame synthesis method and other modified methods[4]. Other nanocomposites incorporated with polymers and metal oxides could be prepared by hydrothermal method, microwave irradiation and other approaches.

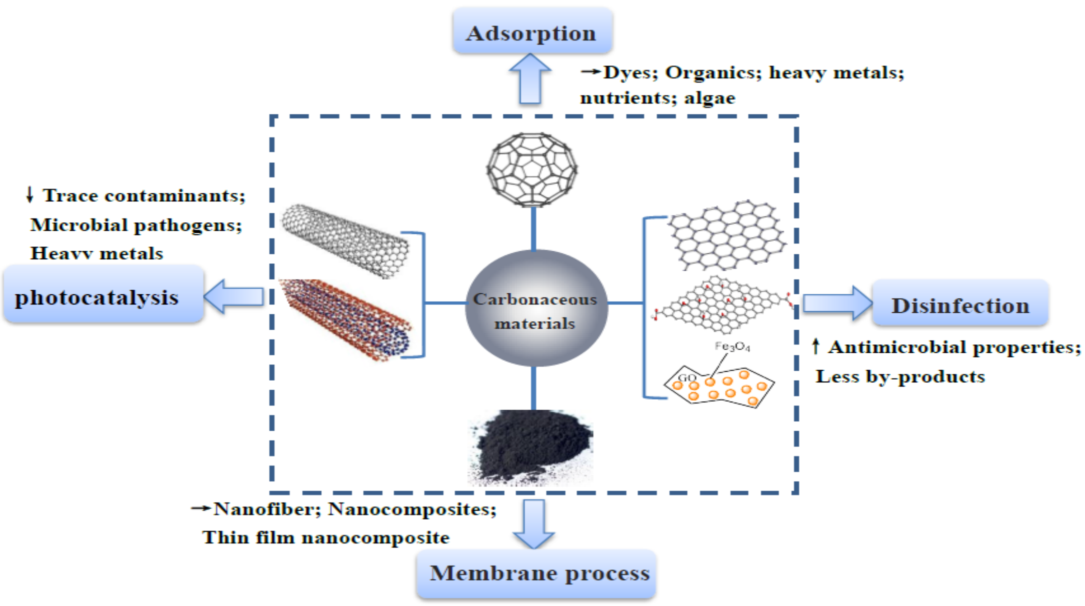

Figure 1. The potential applications of carbonaceous nanomaterials in wastewater treatment. Carbonaceous nanomaterial could be divided into four categories: fullerenes, graphene-based nanomaterials, CNTs and NAC. All these nanomaterials exhibited great potential in many aspects of wastewater treatment such as adsorption, photocatalysis, disinfection and membrane process, etc.

3. Applications of carbonaceous nanomaterials in wastewater treatment
Carbonaceous nanomaterials showed great potential in wastewater treatment (see **Figure 1.**), would be discussed concisely in this part.

3.1. Adsorption

Adsorption has been considered as the most promising method for contaminants removal from aqueous phase due to its low cost, simple operation and no by-products. Nevertheless, the efficiency of conventional adsorbents is always limited and thus inhibit the pollutants removal process. Compared to traditional adsorbents, nanostructured materials possess a higher specific area and associated sorption sites along with tunable surface characteristics, which give them some strengths such as higher efficiencies and rapid adsorption rates over a broad pH range.

3.1.1. Removal of organic contaminants. Graphene-based nanomaterials have displayed exceptional adsorption capacity toward various organic compounds, covering dyes[5], antibiotics[6], polycyclic aromatic hydrocarbons (PAHs)[7], phenolic compounds[8], pesticides[9], and so forth. In aqueous phase, adsorption capacities of chlorpyrifos, endosulfan, malathion on RGO could reach to 1200, 1100, 800mg/g, respectively [9]. Other carbonaceous nanomaterials such as CNTs, fullerenes and nanocomposites are also effective to remove organics from wastewater and have been widely studied and extensively reviewed. Their strong adsorption capacity are mainly attributed to the incredibly specific surface area, abundant pore size distribution, and feasible surface properties, which make them interact vigorously with organic compounds, via hydrophobic effects and EDA interactions, hydrogen bonding interactions, etc.
Additionally, studies pointed out that environmental conditions and surface characteristics of different type adsorbents would affect the adsorption capability, and thus a little departures could be found among adsorption performance. The aggregation of CNTs in aqueous phase create a lot of interstitial spaces and grooves, which belong to high-energy adsorption sites and could contribute to organic contaminants removal. For GO, enormous oxygen-containing functional groups (e.g.,–COOH and–OH) on the edge would weaken the hydrophobic effect with nonpolar organics, and suppress the adsorption on it. For NAC, large-sized molecules (e.g., algal toxins) are inaccessible due to its micro-porous structures, but can be benefit for the relatively small molecules.

3.1.2. Removal of heavy metals. Many researchers have launched extensive studies concerning the adsorption characteristics of heavy metals onto GO and oxidized CNTs, indicating that both GO and oxidized CNTs showed great adsorption performances and rapid adsorption rates for metals removal[10, 11]. The ability of carbonaceous nanomaterials to adsorb different heavy metals (e.g. Cd^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}) have been reviewed critically[12, 13]. The maximum adsorption capacities of Cd^{2+} and Co^{2+} on GO are 106.3, 68.2mg/g, respectively, which higher than other nanoadsorbents such as NAC[13]. The electrostatic attraction and chemical bonding such as ion exchange dominated the adsorption process where the surface functional groups of GO and oxidized CNTs provide the major adsorption sites to heavy metals. Fast adsorption kinetics could be attributed to the highly accessible adsorption sites and the short intraparticle diffusion distance. Other nanomaterials and nanocomposites also have attracted increasing attentions for heavy metals removal.

3.2. Photocatalysis
Photocatalytic technique is an advanced oxidation process for removal of trace contaminants and pathogens from wastewater, which have been considered as an useful pretreatment approaches for toxic substance and non-biodegradable pollutants to enhance its biodegradability [14]. Currently, many researches focused the photocatalysis enhancement by carbonaceous nanomaterials have been rigorously examined. One hot topic is the utilization of carbonaceous nanomaterials (e.g., CNTs, fullerenes, RGO) in synergy with catalyst particles (TiO_2, etc.). By incorporating TiO_2 onto individual graphene nanosheets with even distribution could gain desirable properties from their fabrication process, reinforce the photocatalysis performance for target contaminants. Yang et al synthesized a series of TiO_2-graphene, -CNTs, -fullerenes nanocomposites photocatalysts to oxidize benzyl alcohol to benzaldehyde, indicating that integrated nanocomposite could broaden the adsorption edge to the visible light region. Apart from TiO_2/carbonaceous nanocomposites, several other hybrid photocatalysts have been investigated for the detoxification of organic contaminants, such as ZnS-RGO [15], ZnO/graphene, etc. Indeed, CNTs and graphene would not only provide high-surface area support and immobilization for photocatalysts particles (e.g., TiO_2). And the presence of

carbonaceous nanomaterials could enhance the photocatalysis performance through three primary mechanisms: (1) providing high quality adsorption active sites; (2) improving the migration efficiency of photo-induced electrons and delaying electron-hole recombination; (3) tuning the band gap or photosensitization.

3.3. Disinfections

Disinfection is an effective method to remove organic contaminants and biological pollutants such as pathogens from wastewater sources. While conventional technologies (e.g., chlorination, ozonation) could form hazardous DBPs in the decontamination process and pose a threat to human health. Advance in nanotechnology provide a new perspective to overcome weakness of these old methods.

Carbonaceous nanomaterials exhibit strong antibacterial activity and lower oxidation ability, could effectively inactivate pathogens under visible-light irradiation or direct contact, have low tendency to form DBPs. Graphene-based nanocomposites were widely investigated as disinfectants in the last few years. The magnetic graphene developed by Ganesh et al[16] exhibited disinfection activity (40ug/L) toward *E.col* with 100% killing efficiency as well as desirable low toxicity toward zebrafish. The magnetic RGO functionalized with glutaraldehyde nanocomposite (MRGOGA) synthesized by Wu et al.[17] also showed the brilliant disinfection ability towards *S. aureus* and *E.col*, up to 99% of gram-positive and gram-negative bacteria were killed effectively in 10 minutes upon near-infrared laser irradiation. The antibacterial activity, large specific surface area and strong conductivity of graphene-based nanomaterials enabled their use in disinfection applications. And the antibacterial mechanism of these carbonaceous nanomaterials was reported to involve two aspects: (1) destroying the integrity of cell membranes upon direct contact; (2) disturbing the particular microbial progress via oxidative stress. Furthermore, additional researches associated with maximizing disinfection performance and environmental effects of nanomaterials should be paid more attention.

3.4. Membrane process

Membrane technique is considered an effective and economical approach in many fields of wastewater treatment, its performance significantly depends on the selectivity and permeability of the membrane materials. High energy consumption caused by membrane fouling and other problems limited the wide application of this technique. Considerable studies have reported that incorporation of carbonaceous nanomaterials into membranes make it possible to improve the selectivity, permeability and fouling resistance of membranes.

CNTs could be incorporated with other polymers or nanomaterials to develop multifunctional membranes. Song et al. [18] infused CNTs into a double-skinned thin film nanocomposite (TFN) membranes and characterized the morphology, structure, permeation performance and antifouling ability of the integrated membranes. It was found that TFN membranes exhibited higher water flux and remarkable antifouling capacity by incorporating CNTs. This result was consistent with research of Ho et al. [19], incorporation of GO and oxidized CNTs have significant effect on membrane characterization including surface charge, porosity, pore size structure, mechanical strength, toughness and other indicators. Hence, the mixed-matrix membranes increased the membrane hydrophilicity and antifouling properties, meanwhile, improved the rejection rate of both organic pollutants and inorganic matters. Free-standing carbonaceous nanofiber membranes are the another type of carbonaceous filters, which possess huge specific surface areas, high degree of uniformity and massive active sites. They combined the excellent performance of carbonaceous nanofiber and the advantage of membranes blocking with strong permeability and antifouling capacity, beyond the traditional adsorption technique. Carbonaceous nanofiber membranes could remove dyes (MB) quickly at a very high flux of 1580 L m^{-2} h^{-1}, which is much higher than many commercial ultrafiltration membranes with similar behaviors [20]. Besides, other catalysts also could be doped into carbonaceous membranes to remove contaminants through various mechanisms simultaneously.

3.5. Other applications

Apart from the above-mentioned applications, there are still several utilizations of carbonaceous nanomaterials in wastewater treatment, which include sensing, monitoring and desalination. Nurul et al. [21] incorporated MWCNTs and single layer graphene (SLG) nanoparticles into cellulose triacetate (CTA) polymer matrix and developed a MWCNTs-MMM and SLG-MMM nanocomposites, respectively. It illustrated that both nanomaterials were successfully applied for PAHs detection in wastewater samples with a detection limit of 0.02-0.09 ng/mL, were comparable or even better than standard SPE technique. The adsorption behavior that occurred on the active sites of nanomaterials' surface took charge of the microextraction process. Researches involving detection of other trace contaminants and pathogens along with other potential utilizations are growing rapidly, and we believe that more comprehensive and full-scale applications of carbonaceous nanomaterials would be found in the future treatment process.

4. Challenges and prospects for further application

Carbonaceous nanomaterials possess high specific surface areas, outstanding electrical, optical, thermal and chemical activity; have been considered one of the most prospective candidates to remove chemical and biological contaminants from wastewater. Previous studies have already concerned the potential application of these nanomaterials for wastewater treatment in lab scale. However, the future developments and full-scale applications of these nanomaterials still face a wide variety of challenges and more thorough studies are certainly needed.

1) The current synthesis methods for carbonaceous nanomaterials (e.g., RGO) is still complicated and low-efficient, although numerous studies have been conducted to tackle it. More simple, robust and efficient fabrication methods are urgently needed. Meanwhile, commercial large-scale production of carbonaceous nanomaterials is challenging and need to be addressed for broad range applications.

2) The agglomeration of CNTs and graphene-based nanomaterials in aqueous phase is another weakness in water decontamination. Aggregated nanomaterials would decline the surface area as well as active sites and hence affect the accessibility to them, resulting in decreased efficiency on pollutants removal. Nanomaterials modified with various functional groups and metal oxides have been employed to overcome them, and further researches should focus more on the targeted modification and enhance the removal efficiency as well as selectivity and affinity toward specific contaminants.

3) Almost all the studies were conducted under laboratorial conditions, the performances of carbonaceous nanomaterials in treating real natural and wastewater from industries need to be tested. Further researches should be launched under more realistic conditions to evaluate the efficiency and applicability of diverse carbonaceous nanomaterials in wastewater treatment. Besides, the long-term performance of carbonaceous nanomaterials should also be taken into consideration.

4) The cytotoxicity of carbonaceous nanomaterials for human beings, living things and ecosystem have not been investigated intensively, the gap between potential environmental effects and carbonaceous nanomaterials' properties should be filled as soon as possible. In order to guarantee the environmental and public health, risk assessment for carbonaceous nanomaterials is urgently needed with the increasing emission of these nanomaterials.

Carbonaceous nanomaterials have many advantages as well as limitations in wastewater treatment, it is indeed potential nanomaterials for solving diverse environmental problems.

5. Conclusions

Water decontamination is one of the most essential tasks for both environmental protection and wastewater reuse. Among various wastewater treatment techniques, using carbonaceous nanomaterials to remove diverse pollutants have attracted wide attentions in many sectors and momentum. The unique properties of carbonaceous nanomaterials bring about great chance to revolutionize wastewater treatment. Although most of highlighted applications of carbonaceous nanomaterials are still in the laboratory stage, some have proved marvelous properties in the real wastewater treatment process. Further work concentrated on the modification of these nanomaterials is a helpful approach to accelerate the potential applications by improving intrinsic properties and economic benefits of carbonaceous nanomaterials, display a brighter future in wastewater treatment.

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7. Reference

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