Removal of contaminants from waste water using carbonaceous Nanomaterials: A Review

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Abstract: Extraordinary and tunable properties of carbonaceous nanomaterials in removal of contaminants from wastewater have been proved to be potential area of research in today's scientific world. This paper presents a brief review on current advances in carbonaceous nanomaterials including categories, structure, and versatile properties. The treatment of waste water includes basically adsorption, photocatalysis, disinfection, monitoring and desalination. In the present paper we have also discussed about the barriers or constraints for application of these nanomaterials in waste water treatment.

Keywords: Adsorption, Desalination, Versatile, waste water treatment, Pace, Disinfection

Introduction: In the present era, there is a rapid change in industrialization and urbanization or in other words it is increasing day by day at greater pace. This is major cause of release of numerous contaminants in aquatic environment. As we all know water has broad impact on all aspects of human life including but not limited to health, energy, economy, food. The social impact of this and need of fresh water can't be neglected. In the present scenario, more than 0.78 billion people around the world are lacking in access to safe water resources which is major cause of health problems. It is estimated that within couple of decades the current water supply will decrease by one-third.

This stable fresh water flow has been estimated at 12,500–15,000 km^3 per year from which 4000 km^3 per year is considered to be the total freshwater for irrigation, industry, and domestic purposes and which is estimated to increase to a range of 4300–5000 km^3 per year in 2025. Alternatively, only accessible fresh water is 0.5% of the world's 1.4 billion Km^3 of water which is furthermore poorly distributed across the globe. Consequently, removal of toxic substances from waste water is urgently needed. A no. of conventional methods has been already employed such as coagulation, precipitation, filteration, ion exchange method and other physio-chemical technology. However, these suffer from one or more constraints such low efficiency yields, complex operating conditions, expensive techniques and low removal efficiency. In some cases and methods there are carcinogenic and mutagenic risks as well as undesirable odors and tastes during the treatment process.

Hence, herein we provide a mini review of utilization of carbonaceous nanomaterial's for waste water treatment.

2.Result and discussion:

2.1 Carbonaceous Nanomaterials:

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.

2.1.1. Fullerenes:

A fullerene is an allotrope of carbon whose molecule consists of carbon atoms connected by single and double bonds so as to form a closed or partially closed mesh, with fused rings of five to seven atoms. The molecule may be a hollow sphere, ellipsoid, tube, or many other shapes and sizes. Graphene (isolated atomic layers of graphite), which is a flat mesh of regular hexagonal rings, can be seen as an extreme member of the family. Fullerenes with a closed mesh topology are informally denoted by their empirical formula C_n, often written C*n*, where *n* is the number of carbon atoms. However, for some values of *n* there may be more than one isomer. The family is named after buckminsterfullerene (C_{60}), the most famous member, which in turn is named after Buckminster Fuller. The closed fullerenes, especially C_{60}, are also informally called buckyballs for their resemblance to the standard ball of association football ("soccer"). Fullerenes had been predicted for some time, but only after their accidental synthesis in 1985 were they detected in nature and outer space. The discovery of fullerenes greatly expanded the number of known allotropes of carbon, which had previously been limited to graphite, diamond, and amorphous carbon such as soot and charcoal. They have been the subject of intense research, both for their chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology.

These are bucky balls having enclosed cage-like structures having pentagonal and hexagonal rings. For example C_{60} bucky ball consist of 32 faces with 20 hexagons and 12 pentagons, containing carbon atoms on 60 vertices of a truncated icosahedrons. It should be noted that greater the sp^3 bonding character, greater will be strain and greater will be carbon reactive sites.

2.2.1 Graphene based nanomaterials:

Graphene, the mother of all carbon atoms, is a single atomic thick, nanosized, two-dimensional structure and provides high surface area with adjustable surface chemistry to form hybrids. It was synthesized from graphite. In this review, we addressed the current state of the science and identified the knowledge gap for the future research development. The broad family of GBNs listed in this review includes graphene, graphene oxide (GO), reduced graphene oxide (RGO) and chemically modified graphene (that bears functional groups covalently bound to the surface of the individual layers of graphitic carbon).

2.2.2 *Graphene oxide and reduced graphene oxide:*

Graphene oxide is considered as the oxidized form of graphene. The discovery of graphene oxide goes way before the discovery of graphene. In 1859, GO was first synthesized by oxidation and exfoliation of graphite. However, until the discovery of graphene, graphene oxide remained rather insignificant. It was after the discovery of graphene that graphene oxide also attracted attention as a feasible way to obtain graphene. From that point on the studies on graphene oxide have picked up the pace and GO itself has found various different applications.

The synthesis of GO mainly achieved by the top-down approach which includes the treatment of graphite with strong oxidants or sulfuric acid and potassium permanganate, and the subsequent exfoliation step achieved by mechanical peeling methods such as sonication and shearing stress. However, is also possible to obtain GO through bottom-up synthesis methods such as chemical vapor deposition (CVD). Through the treatment process, the sp^2 structure of graphite layers is disrupted and acquires several different oxygen-containing functional groups such as carboxyl, hydroxyl, or epoxy groups. The oxidation of graphite layers increases the interplanar spacing of the graphite structure. The subsequent exfoliation step separates the layers of graphite oxide to obtain a solution of homogenous graphene oxide layers. Different parameters such as initial oxidation conditions, energetic input, source, and lateral size of graphite used as a starting material have strong impacts on the resulted GO structure and the level of oxidation. Through the manipulation of these parameters, it is possible to obtain a variability in the properties of GO. Especially the level of oxidation strongly affects the chemical variability of GO sheets.

The disruption of the sp^2 bonding network leads to distinctive properties. Graphene oxide shows low electrical conductivity causing an insulating or semi-conductive behavior depending on the degree of oxidation. The specific surface area of GO sheets is around 890 m^2g^{-1}. GO shows high mechanical strength with Young's modulus of 207.6 ±23.4 GPa and fracture strength of ~120 MPa. The epoxy and hydroxy groups of GO sheets are located at the carbon basal plane while carboxy groups are located at the edges. The varying amounts of carbonyl, phenol, lactone, and quinine are also observed in the GO structure. The abundance of functional groups results in a hydrophilic behavior which is strongly dependant on the level of oxidation. GO sheets show good dispersibility as a result of their strongly charged nature and hydrophilicity. They form stable aqueous dispersions in a wide range of concentrations. Additionally, they are dispersible in organic solvents such as ethylene glycol, dimethylformamide (DMF), n-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) due to the hydrogen bonding between the surface and solvent interface. Graphene oxide shows optical transparencies stemming from the oxidized components while the graphene domains of GO show broadband fluorescence.

Reduced Graphene Oxide

The reduction of graphene oxide is considered to be an attractive route to obtain graphene-like behavior. Chemical, thermal, or photo-thermal reduction methods are used to obtain reduced graphene oxide structures. However, rGO cannot reach the pristine graphene structure. Even after severe reduction rGO still contains residual oxygen and structural defects originated in the chemical oxidation synthesis of GO.Chemical reducing agents used for rGO synthesis are often inorganic agents such as NaB or organics, such as phenyl hydrazine hydrate or hydroxylamine. Thermal reduction occurs in an inert or reducing atmosphere at temperatures between 300°C-2000°C.Finally, the photothermal-reduction of GO can be done with a direct laser beam at wavelengths under 390 nm (energy > 3.2 eV). The studies show that thermal reduction methods are advantageous compared to chemical reduction methods. Not only a lower level of reduction is achieved by chemical reduction methods but also the reducing agents used in methods are highly toxic. The thermal reduction methods have the upper hand due to their high level of reduction and relatively environmentally friendly process. The carbon to oxygen ratio of the resulting product is an important feature. The higher the C/O ratio, closer the properties of rGO to the properties of pristine graphene.

The reduction process causes drastic changes in the structural properties, mechanical strength, stability, dispersibility, and reactivity of GO. These changes are directly related to the elimination of the oxygen containing compounds in the GO structure and restoration of the sp2 structure after the reduction process. One of the most important effects of GO reduction process is the increase of electric conductivity up to 6300 S $cm^{-1}$and high mobility of 320 cm2 V^{-1} s^{-1}. The surface area of rGO also increases during the reduction process. rGO sheets show strong mechanical strength, with Young's modulus of ~1.0 TPa and breaking strength of ~130 GPa which is similar to the graphene. As opposed to GO, reduced graphene oxide acquires a hydrophobic behavior due to the increased C/O ratio of the structure. Stemming from the hydrophobicity of rGO, the dispersibility of this material also decreases after reduction. In addition to the dispersibility, the colloidal behavior of rGO is also affected by the reduction process decreasing the critical coagulation concentration. Even though the graphene structure is not fully recovered by the reduction of GO. Reduced graphene oxide still holds useful properties such as controllable functionality, high electric and thermal conductance the availability of initial material, cheap and scalable preparation process.

Both graphene oxide and reduced graphene oxide have developed to be valuable derivatives of graphene. However, they show critical differences in both their structural and chemical properties. As it was mentioned in the above sections, the main difference between GO and rGO is the C/O ratio in their structure. While the C/O ratio is very low in GO structures, it is significantly higher in rGO structures approaching to almost zero oxygen content. The rest of the differences between GO and rGO materials mainly stem from this difference between C/O ratios. The most important difference is considered to be the electrical conductivity of these two materials. While GO show insulating or semi-conducting behavior, rGO shows high electrical conductivity 6300 S cm^{-1}. The difference in the conductivities of GO and rGO opens up different application possibilities for these materials. Another significant difference between GO and rGO structures is the specific surface area. GO shows relatively lower surface area (890 m^2g^{-1}) in comparison to rGO structure which almost restores the extremely high surface area of pristine graphene (~2600 m^2 g^{-1}). The mechanical strength of GO is also found to be lower than the mechanical strength of the rGO structure. The Young's modulus of GO is found to be almost half of rGO and graphene. Another important effect of the oxygen containing compounds is the hydrophilic behavior induced by the increased surface charge. Hence, GO structures show hydrophilic behavior while rGO shows hydrophobic behavior due to the loss of oxygen containing compounds. The differences between hydrophilic/hydrophobic behavior also induce a difference in the dispersibility of GO and rGO. Graphene oxide shows high dispersibility in aqueous media while rGO shows significantly lower dispersibility. For example, as the oxygen content of rGO is reduced from 31% to 9% the dispersibility of the material after sonication decreased from 8 to 2.5µg/ml.

Additionally, the colloidal behavior of the rGO follows the same trend as dispersibility. The different properties of GO and rGO have both found various applications in the scientific community and the industry.

CONCLUSION:

Graphene and carbon-based sponges are 3D aerogel networks with high surface area, high chemical/electrochemical stability, and extremely high surface hydrophobicity. Thus, these materials are used to demonstrate the feasibility for bridging the nanoscale properties of carbon-based materials to practical macroscale applications in oil and organic solvent spills.

The development of graphene and carbon-based adsorbents not only focuses on the enhancement of adsorption capacities and lowering cost but also on the smart control of adsorption and desorption behaviors of adsorbents. A combination with functional materials, such as magnetic nanoparticles, is a possibility.

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