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Review

Graphene-family nanomaterials in wastewater treatment plants

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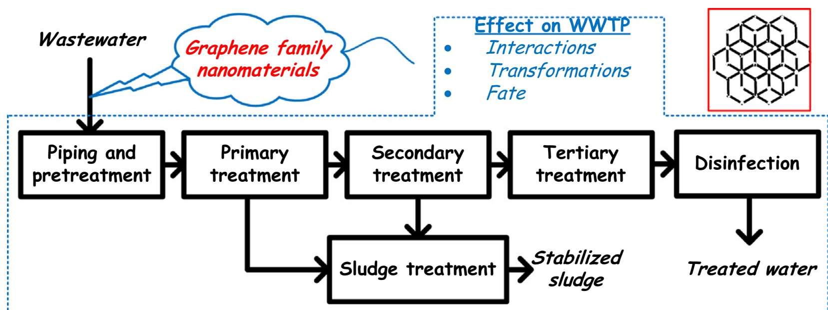
HIGHLIGHTS

- Graphene nanomaterials (pGr, GO, RGO, FLG and MLG) have a different fate in WWTPs.
- pGr, FLG and MLG settle down more easily than RGO in the primary clarifier.
- GO hinders the anaerobic denitrification, but improves the anaerobic NH_4^+ oxidation.
- Various minerals can adsorb GFNs and improve the pretreatment/primary sedimentation.
- GO and RGO favoured the formation of disinfection by-products (trihalomethanes).

GRAPHICAL ABSTRACT



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ABSTRACT

The release of graphene and its derivatives in soil, air and water seems an inevitable consequence of the massive future use of these carbonaceous allotropes. From an environmental engineering point of view, it should be noted that part of the aqueous streams containing these nanomaterials will end up in wastewater treatment plants, and there will be interactions between the nanomaterials, the other pollutants in the sewage and the microorganisms of the secondary treatment, which could affect the effectiveness of the depuration process. The present work reviews the available literature on the behaviour of these nanoallotropes in wastewater treatment plants (a literature which is almost exclusively focused on graphene oxide and reduced graphene oxide), and also includes research dealing with simpler systems: i) graphene in purified water, ii) graphene in purified water with salt, and iii) graphene in purified water with organic matter and salt. It is probable that the fate of most of the graphene-family nanomaterials will be the primary/secondary sludge, and that a small portion (mainly in the form of graphene oxide) will pass to the tertiary treatment. Besides, graphene oxide has a negative effect on the biological treatment.

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Nomenclature

anammox	Anaerobic ammonium oxidation
LDH-Cl	Chloridion intercalated nanocrystallined Mg/Al layered double hydroxides
CQDs	Colloidal quantum dots
NH_4^+	Dissolved ammonia
DO	Dissolved oxygen
P	Dissolved phosphorus
FLG (2–5 layers)	Few-layer graphene
FWNT	Few-walled nanotubes
BOD_5	Five-day biological oxygen demand
GO	Graphene oxide
GQDs	Graphene quantum dots
GFNs	Graphene-family nanomaterials
MLG (2–10 layers)	Multilayer graphene
MWNT	Multiwall nanotubes
$LDH\text{-}CO_3$	Nanocrystalline Mg/Al layered double hydroxides
NOM	Natural organic matter
PO_4^{3-}	Phosphates
pGr	Pristine graphene
ROS	Reactive oxygen species
RGO	Reduced graphene oxide
SWNT	Single-walled nanotubes
TOC	Total organic carbon
TSS	Total suspended solids
UV	Ultraviolet
VSS	Volatile suspended solids
WWTPs	Wastewater treatment plants

1. Introduction

Pristine graphene (pGr) is a two-dimensional structure, formed by hexagonal rings of sp^2-hybridised carbon atoms, which is considered the precursor of the graphene-family nanomaterials (GFNs) and other families of carbon nanoallotropes [1,2]. Regarding to the first group, GFNs, a monolayer graphene sheet can be oxidised to form graphene oxide (GO) or packed in parallel with other sheets to form few-layer graphene (FLG, 2–5 layers), multilayer graphene (MLG, 2–10 layers) and graphite nanoflakes (uncountable number of layers, but with a thickness and/or lateral dimension less than 100 nm). The packing of an "infinite number" of layers generates graphite, which is a carbon nanoallotrope but is not a member of the GFNs. Regarding this second group (materials which do not belong to the GFNs), one graphene sheet can be cut following certain pattern and folded to build regular polyhedrons, called fullerenes; or rolled up to form single-walled nanotubes (SWNT). Additionally, FLG and MLG can be cut and wrapped up to build few-walled and multiwalled fullerenes (called onion-like carbon nanoparticles), or rolled up to form few-walled and multiwalled nanotubes (FWNT and MWNT, respectively). Fig. 1 represents some of these allotropes.

Due to its exceptional electrical and physical properties, pGr is suitable for applications in high-speed electronics, data storage devices, flexible touch screens, supercapacitors, solar cells and electrochemical sensors [3,4]. Research on GFNs had been done since the XIX century, but the interest for them started to grow in 2004–2005, when Novoselov and coworkers isolated pGr and reported its unique behaviour [5,6]. pGr can be obtained from graphite by dry mechanical exfoliation with an adhesive tape, by exfoliation in solvents with ultrasounds or by chemical intercalation of alkali metals between the sheets [7]. Graphene is also produced by deposition of the vapour generated after the thermal decomposition of carbon-containing substances on a metal surface (that catalyses the rearrangement of the vapour to form sp^2 carbon species), by heating of silicon carbide and by sonication in water of graphite oxide followed by reduction [7,8], being this last one the most popular. Graphite oxide is usually generated from graphite by the so-called Hummers' process (oxidation using potassium permanganate, sodium nitrate, and sulfuric acid), and is a material which displays a structure similar to that of graphite, but contains hydroxyl and epoxy groups in the basal planes and carboxyl groups in the edges of the sheets. The single layers obtained after this exfoliation are not of pGr, but of GO, and it has to be subjected to chemical reduction to eliminate the oxygen-bearing functionalities [6,9,10]. Nonetheless, the product of this reduction commonly presents several defects in the honeycomb lattice, besides some functional groups resist the reduction, and therefore, it is named reduced graphene oxide (RGO) instead of pGr [9,11]. GFNs, especially GO and RGO, have proved to be effective for water remediation and adsorption of noxious gases [12–14]. A schematised picture of RGO is also shown in Fig. 1.

The increasing production of GFNs raised concerns about their potential health and ecological risks in the early 2010s [15,16]. Furthermore, the higher the commercialised amounts of graphene, the higher the amount of GFN-containing wastes that will be released into sewages, and therefore, greater concentrations of these materials can be expected in the influent to wastewater treatment plants (WWTPs), since these facilities are the final destination of most of the residual liquid effluents from industrial and urban areas. Unfortunately, quantifications of the aforesaid concentrations are not available yet, unlike those of metallic nanoparticles, nanotubes or fullerenes [17]. A flow diagram of the different stages of a WWTP is shown in Fig. 2.

Initially, screens composed of gratings, wire meshes, perforated plates or parallel bars, rods or wires separate the coarser solids, whereas grit chambers remove sand, gravel, cinders and particles with sedimentation velocities considerably higher than those settling in the primary clarifier [18]. In order to facilitate the aggregation/flocculation of the remaining suspended solids, a coagulant can be added (such as iron or aluminium or salts, or long-chain polyelectrolytes). After the separation of the primary sludge, which is mostly formed by highly putrescible matter, a biological step removes the dissolved organic compounds that are easily biodegradable. This biological process, also called secondary treatment, is usually carried out by means of activated sludge, a