



Graphene oxide-based degradation of metaldehyde: Effective oxidation through a modified Fenton's process



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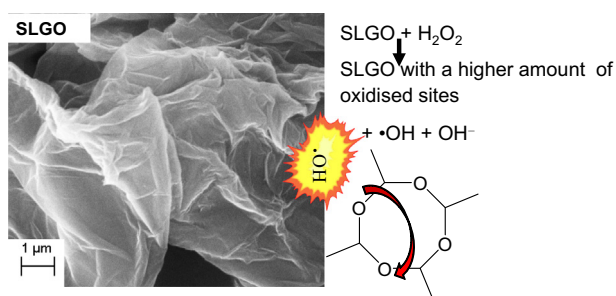
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HIGHLIGHTS

- SLGO and H₂O₂ can degrade metaldehyde-contaminated water.
- pH and total organic carbon are not critical in the modified Fenton's process.
- SLGO has been immobilized and can be re-used.
- Regeneration of SLGO is needed to improve cost-effectiveness.

GRAPHICAL ABSTRACT



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ABSTRACT

A modified graphene oxide-based Fenton's reaction has been investigated for the degradation of a challenging emerging contaminant which is not effectively removed in conventional water treatment. Metaldehyde, used as the challenge molecule in this study, is a common molluscicide that (like many highly soluble contaminants) has frequently breached European regulatory limits in surface waters. The new method involves graphene with higher hydrophilic characteristics (single-layer graphene oxide, SLGO) as a system that participates in a redox reaction with hydrogen peroxide and which can potentially stabilize the $\cdot\text{OH}$ generated, which subsequently breaks down organic contaminants. The modified Fenton's reaction has shown to be effective in degrading metaldehyde in natural waters (>92% removal), even at high contaminant concentrations (50 mg metaldehyde/L) and in the presence of high background organic matter and dissolved salts. The reaction is relatively pH insensitive. SLGO maintained its catalytic performance over 3 treatment cycles when immobilized. Its performance gradually decreased over time, reaching around 50% of starting performance on the 10th treatment cycle. X-ray photoelectron spectroscopy (XPS) analysis of modifications caused in SLGO by the oxidizing treatment indicated that the oxidation of C–C sp^2 to carbonyl groups may be the cause of the decrease in performance. The proposed modified Fenton's process has the potential to substitute traditional Fenton's treatment although regeneration of the nanocarbon is required for its prolonged use.

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1. Introduction

Conventional water treatment processes show limited efficiency for a number of increasingly utilised organic chemicals, which are then discharged to the environment after their

incomplete removal. As a consequence, a range of biologically-active micropollutants can be found at parts per billion level in surface and drinking waters (e.g. estrogens, personal care products, pharmaceuticals, pesticides, organic solvents, disinfection by-products) [1–3]. One example of these biologically-active micropollutants is metaldehyde, a molluscicide widely used in large-scale agriculture and in gardens, particularly in regions (such as NW Europe, South East Asia, parts of China and the USA) where long wet seasons require the control of molluscan pests. Metaldehyde has been observed frequently to breach European regulatory limits in surface and drinking waters (0.1 µg/l, based on the European Drinking Waters Directive 1998 and 2000) [4,5] in the UK and elsewhere due to its high solubility and frequent application [6]. This highly polar molecule is relatively resistant to conventional chlorination or ozonation treatment, and is one of a group of emerging contaminants such as acrylamide, geosimine, 1,1,1-trichloroethane, and methyl tert-butyl ether (MTBE) that (due to their small organic “skeleton”) show limited interaction with the conventional granular activated carbons (GAC) currently applied in tertiary water treatment [7,8]. It was reported in 2011 that water treatment works could achieve a removal of only up to 50% metaldehyde, and that the regulatory limit target was difficult to achieve for this contaminant [9].

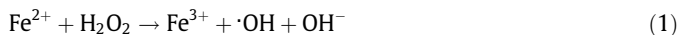
Recent research into metaldehyde and similar emerging or problem contaminants has focused on developing improved adsorptive or catalytic destruction methods for their removal from treated waters. For example, Busquets et al. noted the improved adsorption of metaldehyde using “tailored” activated carbon beads (i.e. with controlled surface chemistry and pore size distribution) synthesised from phenolic resin [10,11], while Autin et al. reported successful photodegradation of metaldehyde using UV/H₂O₂ and UV/TiO₂ (although the effectiveness of metaldehyde removal was significantly reduced by the presence of background organic matter) [12]. Bing and Fletcher report the destruction of metaldehyde using sulfonic acid functionalized mesoporous silica [13], and ion exchange resins with sulfonic acid groups in a system that can also adsorb any acetaldehyde generated [14], while Nabeerasool et al. report effective removal of metaldehyde using a coupled batch adsorption/electrochemical regeneration technique, based on low capacity graphitic material (the Arvia™ process) [8]. A slow but sustained oxidation of metaldehyde (31% degradation in 60 h) was also achieved using macrocyclic ligand catalysts based on Fe(III) and H₂O₂ (TALM/H₂O₂) [15].

The use of nanocarbon-based materials in adsorptive and catalytic applications for removal or destruction of emerging (or problem) contaminants has also been widely discussed [16–20]. Graphene in particular has been the focus of much research due to its high specific surface area, tunable surface behavior, and extremely high electron mobility [21,22]. Graphene-based materials have been used as adsorbents or heterogeneous (photo)catalysts for effective removal or degradation of a range of heavy metal/metalloid and organic contaminants, including As, Cr, U, dyes, bisphenol A, perchlorate, bulk oil and gasoline [17,19,23–25]. Graphene can also be used as part of a modified Fenton's process to generate the highly reactive and oxidizing hydroxyl radical (2.8 V oxidation potential) from hydrogen peroxide, which in turn can effectively degrade a range of common organic contaminants. For example, Liu et al. used a graphene oxide-FeS₂ composite, in the presence of H₂O₂, to degrade 4-chlorophenol (97% removal within 60 min, pH 7, starting concentration of 4-chlorophenol: 128.6 mg/L) [26]. Given the hydrophobic nature of 4-chlorophenol, this contaminant could also be adsorbed in addition to being chemically degraded by the Fenton's reaction, although this mechanism was not explored in the aforementioned work. Further insights into the role of graphene oxide in Fenton's reaction processes have been given by a system where the nanomaterial was doped with

Fe₃O₄: here Csp² was oxidised and the electrons transferred to the Fe₃O₄, which enhanced the catalytic efficiency [27].

The standard Fenton's process whereby iron salts activate and catalyze the decomposition of H₂O₂ is shown in Eq. (1) (for which optimal conditions are at acid pH, i.e. pH 3). Eq. (2) shows an alternative, modified Fenton's process using single layer graphene oxide (SLGO) as a heterogeneous catalyst, which operates at neutral and alkaline pH [28].

“Standard” Fenton's process (Fe²⁺)



Modified Fenton's process using SLGO



In both reactions H₂O₂ can act as an ·OH scavenger as well as an initiator, as shown in Eq. (3).



Voitko et al. compared the H₂O₂ decomposition capability of various nanoscale and macroscale (activated) carbons, and observed that single layer graphene oxide (SLGO) exhibited greater reaction rate stability over repeated reaction cycles than bulk activated carbon, or N-doped, oxidised and as-supplied carbon nanotubes (CNTs) [21]. Thus, this work implied that SLGO may have potential for repeated use in water treatment applications. The potential benefits of graphene-based processes (shown in Eq. (2)) over conventional Fenton processes involving an addition of ferric ions (Eq. (1)) include effective catalytic performance with less need for strict pH control (as long as the pH is sufficiently stable to avoid folding and agglomeration of the graphene [29]) and easier separation of graphene (as compared to a homogenous catalyst such as cationic Fe²⁺) from the reaction mixture following application. In this study, we examine this modified Fenton's process in more detail, its effect on SLGO chemistry, and report for the first time the effective oxidative degradation of metaldehyde in environmental waters using a SLGO – peroxide treatment.

2. Materials and methods

2.1. Chemicals

Single-layer graphene oxide (SLGO) was obtained from Cheap tubes Inc. (USA). Metaldehyde (analytical grade), and 2-chloro-4-ethyl-d₅-amino-6-isopropylamino-1,3,5-triazine (d₅-atrazine, 99% purity, used as an internal standard) were purchased from Sigma Aldrich (UK). Metaldehyde stock solutions were prepared by dissolving the standard in 5% methanol in water and diluting further with ultrapure water, surface water or buffer solutions for the preparation of spiked aqueous samples. Some experiments used higher concentrations of metaldehyde than typical environmental levels to assess degradation processes and possible adsorption of metaldehyde onto SLGO under conditions of potential maximum adsorption. Levels of metaldehyde resembling environmental conditions (2 µg/L) were used in a kinetic study. The conditions assayed to test the stability of metaldehyde in systems where ·OH was generated are given in Table 1. These conditions include use of 0.3 M Fe²⁺, which was prepared by dilution of FeSO₄·7H₂O (from BDH Laboratory supplies, UK) (1 M) in aqueous solution at 50 °C, followed by cooling to 25 °C. All studies in this work were carried out at 25 °C. Ultrapure water, generated with an ELGA Purelab purification system (Veolia, UK) was used throughout the study, unless otherwise specified.

The SLGO structure (sheets of 300 nm × 800 nm and thickness of 0.7–1.2 nm approximately) was confirmed with Atomic Force

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