



Graphene oxide as electron shuttle for increased redox conversion of contaminants under methanogenic and sulfate-reducing conditions



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HIGHLIGHTS

- GO has the proper characteristics to promote the reduction of contaminants.
- GO increased up to 10-fold the abiotic reduction of contaminants with sulfide.
- GO increased up to 3.6-fold the microbial reduction of contaminants.
- Biogenic sulfide plays a major role on the GO-mediated reduction of reactive red 2.
- Effective electron shuttle under methanogenic and sulfate-reducing conditions.

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ABSTRACT

Graphene oxide (GO) is reported for the first time as electron shuttle to increase the redox conversion of the azo compound, reactive red 2 (RR2, 0.5 mM), and the nitroaromatic, 3-chloronitrobenzene (3CNB, 0.5 mM). GO (5 mg L⁻¹) increased 10-fold and 7.6-fold the reduction rate of RR2 and 3CNB, respectively, in abiotic incubations with sulfide (2.6 mM) as electron donor. GO also increased by 2-fold and 3.6-fold, the microbial reduction rate of RR2 by anaerobic sludge under methanogenic and sulfate-reducing conditions, respectively. Deep characterization of GO showed that it has a proper size distribution (predominantly between 450 and 700 nm) and redox potential (+50.8 mV) to promote the reduction of RR2 and 3CNB. Further analysis revealed that biogenic sulfide plays a major role on the GO-mediated reduction of RR2. GO is proposed as an electron shuttle to accelerate the redox conversion of recalcitrant pollutants, such as nitro-benzenes and azo dyes.

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1. Introduction

Nitrogenous organic chemicals, such as nitro-benzenes and azo compounds, are extensively used in several industrial sectors for the production of insecticides, herbicides, pharmaceuticals, dyes, rubber chemicals, among many other chemical intermediates. The intensive application and improper disposal of these compounds have resulted in serious environmental pollution. Nitro-benzenes and azo dyes are classified as priority environmental pollutants because they are potential human carcinogens, mutagens or toxics for humans or aquatic organisms (Stolz, 2001; Cervantes and Dos Santos, 2011; Zhu et al., 2014).

Conventional biological treatment systems, such as aerobic activated sludge processes, are ineffective for removing these contaminants since the electron-accepting groups present in their chemical structure compete with oxygen for the reducing equivalents available in the treatment system. In contrast, anaerobic bioreactors have achieved the successful reductive transformation of nitro-benzenes and azo dyes to the corresponding aromatic amines, although long hydraulic retention times (HRT, up to several days) are required to achieve complete conversion of these contaminants (Huang et al., 2012; Martinez et al., 2013).

Different redox mediators (RMs) have been applied in wastewater treatment systems to accelerate the reductive biotransformation of electron-accepting pollutants, including nitro-benzenes and azo dyes (Van der Zee and Cervantes, 2009). Moreover, several attempts to immobilize RM have lately been explored to develop engineered systems, integrating the redox mediating capacity of

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immobilized RM, to promote enhanced conversion rates of contaminants. RM have been immobilized by entrapment in calcium alginate, polyvinyl alcohol- H_3BO_3 and agar (Guo et al., 2007), by covalent binding on ceramic material (Yuan et al., 2012) and polyurethane foam (Zhou et al., 2014), by adsorption on metal oxides nanoparticles (Alvarez et al., 2010), by electrostatic attraction on the surface of anion exchange resins (Cervantes et al., 2011), and by electro-polymerization on activated carbon felt (Li et al., 2008). Furthermore, humic-mineral complexes have also been demonstrated as effective solid-phase RM during the reductive transformation of poly-halogenated contaminants (Alvarez et al., 2012; Zhang et al., 2014).

Lately, carbon based materials, such as granular activated carbon (Van der Zee et al., 2003), black carbon (Xu et al., 2013; Gong et al., 2014), biochar (Oh et al., 2013), activated carbon fibers (Amezquita-García et al., 2013; Rios-del Toro et al., 2013), carbon nano-tubes and carbon xerogels (Pereira et al., 2014), have also been applied as RM to increase the redox conversion of different contaminants.

In the present study, graphene oxide (GO) that is the newest member of the nanocarbon family and of great interest in many research areas nowadays, is evaluated as RM for the reductive biotransformation of 3-chloro-nitro-benzene (3CNB) and the azo dye, reactive red 2 (RR2) under two relevant environmental conditions: methanogenic and sulfate-reducing conditions. RR2 was selected as an azo model pollutant since it is a very recalcitrant azo dye, which has been used to represent reductive decolorization processes for textile wastewater (Pavlostathis and Beydilli, 2005; Cervantes et al., 2011); 3CNB was selected because it is a highly toxic nitro-benzene, which is extensively used as an intermediate in the production of pesticides, pharmaceuticals and industrial chemicals (Zhu et al., 2014).

2. Methods

2.1. Materials and chemicals

The single-layer graphene oxide used in the present study was purchased from Graphene Supermarket[®], with the following characteristics: high density, concentration 6.2 g L^{-1} in aqueous solution, mono-layer >80%, nominal particle size between 0.5 and $5 \mu\text{m}$, C/O ratio 3.95. RR2 (Procion[®] Red MX-5B, 40% purity), 3CNB (purity 98%), 3-chloro-aniline (3CA, purity 99%), and aniline (purity 99.5%) were purchased from Sigma–Aldrich and used without further purification. All other chemicals used were of analytical grade and obtained from either Sigma–Aldrich or Merck.

2.2. Solutions

The basal medium used during abiotic and sludge incubations was composed of (mg L^{-1}) NH_4Cl (280), K_2HPO_4 (250), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (100), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (10), NaHCO_3 (5000) and 1 mL of trace elements solution with the following composition (mg L^{-1}): $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2000), H_3BO_3 (50), ZnCl_2 (50), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (38), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (500), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (50), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (90), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2000), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (92), $\text{Na}_2\text{SeO}_3 \cdot 6\text{H}_2\text{O}$ (162), EDTA (1000) and 1 mL HCl (36%).

A phosphate buffer was used during determination of aniline and 3CA to avoid their oxidation during quantification. The composition of the phosphate buffer was (g L^{-1}) $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (10.86), $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (5.38) and ascorbic acid (0.2) freshly added.

2.3. Inoculum

An anaerobic granular sludge originated from a full-scale upflow anaerobic sludge blanket (UASB) reactor treating brewery

wastewater (Cd. Obregón, Sonora, Mexico) was used as inoculum for biological incubations. The sludge was acclimated for 5 months in lab-scale UASB reactors (1.5 L) operated under methanogenic and sulfate-reducing conditions at a HRT of 1 day and with an organic loading rate of $1 \text{ g chemical oxygen demand (COD) L}^{-1} \text{ d}^{-1}$ at 25°C . A mixture of lactate/ethanol (0.5/0.5 in terms of COD) was used as energy source for the UASB reactors, which showed stable efficiencies in terms of COD removal (>90%) during steady state conditions. For the sulfate-reducing bioreactor a concentration of $1 \text{ g sulfate L}^{-1}$ was applied. Sulfate removal achieved in the sulfate-reducing UASB reactor was >80% in steady state conditions.

2.4. Characterization of GO

2.4.1. Identification of functional groups by FTIR

To identify functional groups of interest on the surface of GO, a portion of $500 \mu\text{L}$ of GO solution at 6.2 mg L^{-1} was dried at 60°C for 24 h. A pellet of KBr/GO at a ratio of 99%/1% (w/w) was then made and placed into a disk for FTIR analysis. The spectra (32 scans) were recorded on a Thermo-Scientific FTIR (Nicolet 6700 model) spectrophotometer under ambient conditions and with a resolution of 4 cm^{-1} .

2.4.2. Quantification of oxidized functional groups by Boehm titration

The carbonyl, phenolic, lactonic and carboxylic groups were quantified by Boehm's acid-base titrations with an automatic titrator (Mettler-Toledo T70): 0.05 g L^{-1} of GO were contacted with 25 mL of neutralizing solution in a polypropylene tube of 50 mL. The experiments were stirred at 150 rpm for 5 days, and then the solutions were filtrated and titrated with 0.1 N HCl.

2.4.3. Size distribution and zeta potential of GO

Size distribution and zeta potential of GO was determined in a solution containing 30 mg L^{-1} of GO in deionized water. Samples of 1.5 mL with a pH previously adjusted with HCl and NaOH 0.1 N were processed in a MICROTRAC Zetatrac NPA152-31A equipment for analysis.

2.4.4. Oxidation reduction potential (ORP)

The ORP of GO and of the two contaminants studied in the present work (RR2 and 3CNB) was assessed under the experimental conditions established during the reduction of these pollutants using an Thermo Scientific electrode with a reference solution of Ag/AgCl Orion 900011 (+415 mV at 30°C). All redox determinations were conducted in an anaerobic chamber with a N_2/H_2 (95%/5%, v/v) atmosphere.

2.5. Role of GO on the reduction of RR2 and 3CNB under abiotic and biological conditions

The potential role of GO as electron shuttle during the reductive transformation of RR2 and 3CNB was evaluated in batch incubations. Abiotic conditions evaluated the redox conversion of these contaminants using sulfide as electron donor. Furthermore, the biological reduction of RR2 and 3CNB was also studied in the presence and in the absence of GO under two different environmentally relevant conditions: methanogenic and sulfate-reducing conditions.

2.5.1. Role of GO on the chemical reduction of RR2 and 3CNB with sulfide as electron donor

To assess the contribution of GO on the abiotic redox conversion of RR2 and 3CNB with sulfide as electron donor, batch incubations were prepared in 60-mL glass bottles provided with 50 mL of bicarbonate buffered basal medium (10 mL as a headspace, N_2/CO_2 80%/20%). Sulfide was provided from a stock solution to obtain a final

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