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Electrochemical efficacy of a carboxylated multiwalled carbon nanotube filter for the removal of ibuprofen from aqueous solutions under acidic conditions

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HIGHLIGHTS

- Electrochemical filtration was used for the first time for the removal of ibuprofen.
- MWNTs-COOH performed better than pristine MWNTs under acidic conditions.
- Complete removal of ibuprofen can be achieved at 2–3 V applied DC potential.
- MWNTs-COOH filter has great potential for being used as a polishing step.

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ABSTRACT

This study provides insight into the efficiency of a functionalized multiwalled carbon nanotube filter for the removal of an anti-inflammatory drug, ibuprofen, through conventional filtration and electrochemical filtration processes. A comparison was made between carboxylated multiwalled carbon nanotubes (MWNTs-COOH) and pristine multiwalled carbon nanotubes (MWNTs) in order to emphasize the enhanced performance of MWNTs-COOH for the removal of ibuprofen using an electrochemical filtration process under acidic conditions. Ibuprofen-removal trials were evaluated based on absorbance values obtained using a UV/Vis spectrophotometer, and possible degradation products were identified using liquid chromatography mass spectrometry (LC-MS). The results exhibited near complete removal of ibuprofen by MWNTs-COOH at lower applied potentials (2 V), at lower flow rates, and under acidic conditions, which can be attributed to the generation of superoxides and their active participation in simultaneous degradation of ibuprofen, and its by-products, under these conditions. At higher applied potential (3 V), the possible participation of both bulk indirect oxidation reactions, and direct electron transfer were hypothesized for the removal behavior over time (breakthrough). At 3 V under acidic conditions, near 100% removal of the target molecule was achieved and was attributed to the enhanced generation of electroactive species toward bulk chemical reactions and a possible contribution from direct electron transfer under these conditions. The degradation by-products of ibuprofen were effectively removed by allowing longer residence time during the filtration process. Moreover, the effect of temperature was studied, yet showed a non-significant effect on the overall removal process.

1. Introduction

Carbon nanotubes (CNTs) have been shown to be uniquely successful in their ability to remove organic contaminants and pathogenic microorganisms through filtration and electrochemical filtration (Gao and Vecitis, 2011; Liu and Vecitis, 2011; Vecitis et al., 2011a; Rahaman et al., 2012; Gao et al., 2014). A comprehensive study of the aqueous dye oxidation reactive transport mechanism during electrochemical filtration was conducted by Liu and Vecitis (2011). In this study, a six-fold enhancement of mass transfer was observed during electrochemical filtration as compared to that during batch electrolysis. This improvement was related to the convection mass transport of organic molecules to the electrode surface under hydrodynamic flow (Liu and Vecitis, 2011). In another work, it was reported that multilayer CNTs supported on a

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polyvinylidene fluoride substrate, to provide more stability and flexibility for the filter, can be efficiently employed for the mineralization of nitrobenzene by sequential reduction/oxidation processes, using CNTs as both the anode and cathode material (Gao et al., 2014). Moreover, Rahaman et al. (2012)reported on the efficiency of a CNT filter for the removal and inactivation of viruses through electrodisinfection.

The adsorptive ability of CNTs for the removal of various organic contaminants from aqueous solutions has also been previously investigated. Shao et al. (2011) discussed the efficacy of MWNTs grafted with methyl methacrylate in the removal of 4,4′-dichlorinated biphenyl. They reported that such surface modifications could enhance the ability of MWNTs in the removal of the target molecule with an increased thermal stability due to strong adsorption of the model contaminant on the modified surface. The surface structure and the nature of CNTs related to the adsorption of organic molecules was also investigated by molecular dynamics (MD) simulations in a study investigating the adsorption of perfluorooctane sulfonate on single-walled carbon nanotubes (SWNTs). Factors such as the size of the CNTs and electrostatic interactions were observed to have significant influences on the affinity of adsorption. It was concluded that adsorption of perfluorooctane sulfonate on SWNTs was controlled by hydrophobic interactions (Li et al., 2013). Moreover, the beneficial application of CNTs as a substrate for the growth of boron-doped diamond (BDD), a widely used material for electrode fabrication in electrochemical wastewater treatment, was introduced, and a methodology was proposed to increase the double-layer capacitance, decrease impedance, and enhance the current collection of BDD (Hébert et al., 2014).

The presence of pharmaceuticals in surface and ground water is an emerging concern due to their persistence and harmful effects on human and aquatic ecology. Several pharmaceuticals (e.g., ibuprofen, naproxen, sulfamethoxazole and iopromide) have been reported to escape primary treatment and exhibit a resistance to total removal in a subsequent biological treatment (Li et al., 2014). Antibiotics have been shown to be resistant to conventional biological methods of wastewater treatment; therefore, an efficient methodology for the removal of antibiotics requires the application of other advanced treatment processes.

Electrochemical degradation is a subject of ongoing interest for researchers working in the field of environmental science and engineering. The complete removal of the antibiotic sulfachloropyridazine by electrooxidation was investigated on both BDD and platinum anodes, and it was shown that complete removal of the antibiotic could be achieved on both types of electrode materials under the conditions of Fenton chemistry with sufficient residence time (Dirany et al., 2012). Electrochemical degradation of nitrobenzene was also successfully achieved using fabricated titanium dioxide nanotubes/antimony-doped tin dioxide/lead dioxide electrodes with enhanced electrochemical stability, increased potential for oxygen evolution, and enriched formation of hydroxyl radicals for electrooxidation of the carcinogenic molecule (Chen et al., 2014). Motoc et al. (2013) investigated the electrochemical degradation of ibuprofen (2-[4-(2-methylpropyl)phenyl]propanoic acid) on multiwalled carbon nanotube/epoxy (MWCNT) and silver-modified zeolite/multiwalled carbon nanotube-epoxy (AgZMWCNT) composites and found that AgZMWCNT provided better electrical conductivity, larger active surface areas, and better electrooxidative removal performance of ibuprofen than MWCNT. However, studies on the efficiency of CNTs for the removal of persistent organic molecules such as ibuprofen by electrochemical filtration are notably absent in the literature. Electrochemical filtration offers the removal of contaminants though adsorptive filtration, as well as electrochemical degradation of the target molecules under applied voltage. Moreover, this process overcomes solute transfer limitations faced by the conventional batch electrochemical process, in which the contaminants are degraded through direct electron transfer onto the electrode surface. Therefore, this process is advantageous over conventional batch electrolysis, in regards to time requirements and overall energy efficiency.

The current study aimed to investigate and provide suitable conditions for the removal of ibuprofen from aqueous solutions via an electrochemical filtration process with CNTs. This removal of ibuprofen through electrochemical filtration has not previously been tested, even though electrochemical filtration has been shown to be an innovative technology with simple installation requirements and promising outcomes (Vecitis et al., 2011a; Gao et al., 2014).

The goals of this research were twofold. The first was to establish appropriate pH conditions and filter type, and therefore accommodate suitable surface interactions between the ibuprofen molecules and the CNTs, such that filtration capacity is increased. Secondly, applied voltage was tested for the removal of the target molecule, observing the contributions of both direct electron transfer from ibuprofen molecules to CNTs under the applied positive potential, and bulk oxidation by the generation of electroactive species. In order to investigate the effect of residence time on effective ibuprofen removal, the residence time of ibuprofen molecules within the filter body was increased (low flow rate) at these conditions of applied potential (2 V) to allow conditions for optimal and complete removal of the target molecule. A comparison was also made between pristine MWNTs and MWNTs-COOH to gauge the difference in complete removal of ibuprofen from aqueous solutions. Throughout the course of the study, MWNTs-COOH consistently exhibited better performance for ibuprofen removal under acidic conditions; these conditions led to the almost complete elimination of ibuprofen at 2 and 3 V of applied DC potentials.

2. Materials and methods

2.1. Materials

Multiwalled carbon nanotube filters were prepared using both pristine MWNTs (99.8% purity) and carboxylated MWNTs (MWNTs-COOH) (>95% purity and 1.8% COOH groups by weight), purchased from Cheap Tubes Inc., Cambridgeport, VT, USA. The actual purity was found to be ≥98% for both MWNTs types, as determined by TGA. Both MWNTs types have specifications of an outer diameter (OD) of 10–20 nm, inner diameter (ID) of 3–5 nm, length of 10–30 μm (as specified by manufacturer). As observed by SEM, the OD ranges from 10 to 35 nm. The electrical conductivity of >100 S/cm was reported by the manufacturer and the specific surface area was determined to be 125.04 m^2/g for MWNTs and 133.03 m^2/g for MWNTs-COOH. Ibuprofen ($C_{13}H_{18}O_2$) with ≥98% purity and a molecular weight of 206.29 g/mole was purchased from Sigma-Aldrich (Oakville, ON, Canada). Sodium chloride and hydrochloric acid were both ≥99% trace pure, purchased from Sigma-Aldrich (Oakville, ON, Canada) and were used in preparing background solutions. Nitro blue tetrazolium (NBT) chloride of assay 98%, taurine of assay≥ 99% and hydrogen peroxide were purchased from Sigma-Aldrich (Oakville, ON, Canada) and was used for superoxide and hypochlorous acid assays. MWNTs and MWNTs-COOH suspensions were prepared in ≥99% purity dimethyl sulfoxide (DMSO), purchased from Fisher Scientific (Ottawa, ON, Canada). Magnesium sulfate, sodium bicarbonate, calcium chloride, potassium dihydrogen phosphate, ammonium chloride, and trisodium citrate were purchased from Fisher Scientific (Ottawa, ON, Canada) and were used for synthetic secondary wastewater effluent preparation. 5-μm