



Kinetic evaluation of graphene oxide based heterogenous catalytic ozonation for the removal of ibuprofen

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ABSTRACT

In this study, the performance of graphene oxide (GO) in ozonation process was kinetically evaluated using the modified R_{ct} concept since GO may act as initiator, promoter and inhibitor in ozone radical chain reaction. The applicability of the modified R_{ct} concept was demonstrated using different GO suspensions (GO alone, GO/TiO₂, GO/Fe₃O₄, GO/TiO₂/Fe₃O₄) in ozonation process. Results showed that ozone exposure and •OH exposure were found to be higher for GO/Fe₃O₄ and GO/TiO₂/Fe₃O₄ compared to other GO suspensions, which was almost equivalent to O₃/H₂O₂ process. The determined initiation and inhibition rate constants of GO alone, were 1 fold higher than GO/Fe₃O₄ and GO/TiO₂/Fe₃O₄, since the GO alone suspension possesses higher O₃ decomposition but lower organic degradation because that GO does not yield •OH. Moreover, GO/Fe₃O₄ suspension, along with natural organic matter (NOM), was proven to be helpful in degrading ibuprofen in ozonation process, but the effect was minimal when compared to O₃/H₂O₂ process. These results exhibited that the surface modified GO suspensions could be utilized as future alternative AOPs.

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1. Introduction

Presence of pharmaceuticals and personal care products (PPCPs) particularly in natural water and ineffectiveness of conventional methods to remove these compounds has been a major concern in water treatment. The occurrence of PPCPs in trace concentrations in both groundwater and surface waters could have a negative impact on the purity of drinking water and can cause adverse health effects that are not clearly understood (Stackelberg et al., 2004; Halling-Sørensen et al., 1998; Heberer, 2002; Kümmerer, 2001; Ternes et al., 2004). Ibuprofen (IBP), an emerging low persistent organic pollutant (DT50 3.1–7 days), is a widely used as non-steroidal anti-inflammatory drug (NSAID) for pain relief, reducing fever and swelling (Ebele et al., 2017). The detected concentration of IBP ranges from ng/L to µg/L and varies considerably across different locations. Wastewater treatment can remove only 60–80% of this drug, and even very small concentrations in the environment can affect the way in which fish spawn (Andini et al., 2012; Fent et al., 2006; Stumpf et al., 1998; Winkler et al., 2001). The removal of IBP has been studied in different stages of drinking water

treatment. It has been found that microbial biodegradation and activated carbon adsorption do not eliminate pharmaceuticals due to the presence of organic matter, which competes in the removal processes. Therefore, advanced treatment technology is required in order to enhance IBP removal from water.

Ozonation based advanced oxidation processes (AOPs) have been widely applied for water treatment in which ozone molecules break down recalcitrant and toxic organic compounds into smaller molecules (Andreozzi et al., 1999; Rosal et al., 2009; Gottschalk et al., 2009). Huber et al. (2003) reported that IBP was highly reactive towards •OH but was unreactive with O₃ ($k_{\bullet OH} = 7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{O_3/P} = 9.6 \text{ M}^{-1} \text{ s}^{-1}$). So, it is important to enhance the •OH formation to improve the IBP degradation (Yang et al., 2009). Recently, several studies have explored activated carbon (AC) and carbon nanotubes (CNTs) as efficient catalysts for ozonation, demonstrating that they can, in fact, initiate and promote the •OH formation (Li et al., 2015; Yang et al., 2009). Relative to AC and CNTs, graphene oxide (GO) also possesses significantly high external surface area, and their surfaces can be chemically functionalized to potentially optimize the density of surface sites responsible for •OH formation. Graphene oxide (GO) is an oxidized form of graphene with carboxyl, hydroxyl, carbonyl and epoxy functional groups on its carbon lattice. Until recently, most researches based on GO have used O₃ as the oxidizing agent, to

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enhance the degree of organic oxidation; however little works have been carried out to detail the behavior of ozone and the kinetics of ozone-graphene (Perreault et al., 2015; Lee et al., 2009). Gao et al. (2014) used ozone to chemically modify GO to ozonized graphene oxide as the proton exchange membrane. Yang et al. (2014) proposed the mechanism of a GO surface when reacting with O₃, suggesting that GO undergoes two stages of reaction, including ozone oxidation (to introduce the ozone-containing group to the surface) and ozone decomposition (to release CO₂/CO). A recent study conducted by Liu et al. (2016) demonstrated that the degradation of DEET increased in the presence of O₃/GO due to the abundant generation of •OH. The above literature reviews evidenced O₃/GO process as a potential AOP for the degradation of micropollutants. Nevertheless, there are questions challenging the viability of graphene in combination with O₃ as a next-generation AOP. Aside from isolated comparisons to AC and CNTs, it is not yet understood how ozonation of graphene compares to more traditional AOPs, such as the O₃/H₂O₂ process. It is therefore important to address these knowledge gaps in relation to the use of graphene to enhance •OH exposure during ozonation.

Elovitz and von Gunten (1999), proposed the experimental R_{ct} concept (Eq (1)) using a probe compound, *p*-chlorobenzoic acid (pCBA), to indirectly determine the •OH concentration (Elovitz and von Gunten, 1999).

$$R_{ct} = \frac{\int [\bullet\text{OH}]dt}{\int [\text{O}_3]dt} \quad (1)$$

pCBA is highly reactive towards •OH ($k_{\bullet\text{OH}/\text{pCBA}} = 5 \times 10^9 \text{ M}^{-1}\text{S}^{-1}$) and non-reactive with ozone ($k_{\text{O}_3/\text{pCBA}} \leq 0.15 \text{ M}^{-1}\text{S}^{-1}$) (Buffle et al., 2006; Hoigne and Bader, 1979). Several studies based on heterogeneous catalyst had adapted the R_{ct} concept to evaluate the effectiveness of catalyst to form •OH using ozone exposure (ozone decomposition) and •OH exposure (pCBA decay) (Yoon et al., 2014; Rosal et al., 2011; Qi et al., 2014; Oulton et al., 2015). Oulton et al. (2015) studied the O₃/multi-walled carbon nanotubes (MWCNT) for pCBA and pharmaceutical degradation. Their study utilized the R_{ct} concept to understand the role of MWCNT as promoter and inhibitor in the ozonation process. Likewise, (Yoon et al., 2014) evaluated the catalytic effect of the ozone/carbon nanotube using pCBA decay. They found the •OH exposure was higher in the presence of carbon nanotubes. Therefore, the effect of heterogeneous catalyst on the production of hydroxyl radicals from ozone can be investigated based on the R_{ct} concept.

The experimental R_{ct} model is completely empirical and individual effect of initiators, promoters and inhibitors cannot be determined. Recently, Yong and Lin (2012) developed a simulated model of R_{ct} concept to determine the effects and rate constants of initiators, promoters and inhibitors of NOM, which is defined as the ratio between total initiation capacities to total inhibition capacity as shown in Eq. (2) (Yong and Lin, 2012).

$$R_{ct} = \frac{2k_1[\text{OH}^-] + \sum k_{i,i}[\text{M}_{i,i}]}{\sum k_{s,i}[\text{M}_{s,i}]} \quad (2)$$

where k_1 represents the adjusted rate constant between O₃ and OH⁻ to account for a lower inhibition capacity ($k_{\text{O}_3/\text{OH}^-} = 160 \text{ M}^{-1}\text{s}^{-1}$); $k_{i,i}$ and $k_{s,i}$ represents the rate constant of initiator and inhibitor; $\text{M}_{i,i}$ and $\text{M}_{s,i}$ represent the of initiator and inhibitor concentrations. Nonetheless, the applicability of this model on the catalytic ozonation process is still lacking. This

modified R_{ct} model can be adapted for the catalytic ozonation process in order to understand the influence of catalyst as initiator, promoter and inhibitor in ozonation process.

Thus, the main objective of the present study was to evaluate the kinetic performance of surface modified GO catalyst using the new R_{ct} modelling concept and to analyze the catalytic activity of GO on degradation of IBP. In addition, the influence of NOM along with GO on the degradation of IBP was evaluated and compared with the traditional O₃/H₂O₂ process.

2. Materials and methods

2.1. Chemicals/sample preparation

All the reagents used for the experiments were of analytical or reagent grade. Potassium Indigo trisulfonate, pCBA, *tert*-butanol, IBP, FeCl₃·6H₂O, FeCl₂·4H₂O, TiO₂ and sodium thiosulfate were purchased from Sigma-Aldrich. Graphene oxide (GO) (C: 54.9%, H: 2.32%, N: 0.04%, S: 0.8%, Mn: 0.05%) was purchased from Nano-Innova Technologies, Spain. High purity Millipore Milli-Q water (>18 MΩ cm at 25 °C) was used to prepare all stock solutions. The Suwannee river fulvic acids (SRFA) stock solution of 5 mg/L was prepared without any pH adjustments. The stock solutions were refrigerated for use in subsequent experiments. Gaseous ozone was generated using the Triogen ozone generator (model Lab 2B, Scotland) with oxygen gas feed. Ozone-saturated water (~60 mg/L) was prepared by sparging gaseous ozone through a gas washing bottle cooled in an ice-bath.

2.2. Preparation of catalyst

GO/Fe₃O₄ nanocomposites were prepared following the procedure in the literature (Zubir et al., 2014). Approximately 50 mg of GO was added to 100 ml of distilled water and then ultrasonicated for two hours. Ultrasonication was used to exfoliate the GO and to transform the carboxylic acid groups to carboxylate anions. 0.05 M of FeCl₃·6H₂O and 0.025 M of FeCl₂·4H₂O was dissolved in 250 ml of distilled water. The dissolved iron solution was then slowly added to the exfoliated GO mixture. The initial pH of the suspended mixture of exfoliated GO and iron was in a range of 1.5–1.6, and 2 M of NaOH was added dropwise until the pH reached a level of 10. The final mixture was matured by continuous stirring, followed by filtering and washing with dissolved water, and was then dried at 60 °C for a period of 48 h.

GO/TiO₂ nanocomposites catalyst were prepared using a microwave-hydrothermal synthesis method (MHS) (Appavoo et al., 2014). In the synthesis process, 5 mg of GO was dissolved in 50% of ethanol (30 ml) by ultrasonication for one hour. 0.2 g of TiO₂ was added to this suspended mixture and continuously stirred for another one hour. The final homogenous mixture of GO-TiO₂ catalyst was then transferred to the autoclave and placed in the MHS system. The GO reduction (rGO) and TiO₂ deposition onto the carbon substrate was obtained by maintaining the MHS system at 180 °C for another one hour. The resulting GO/TiO₂ composite was washed thoroughly with distilled water and ethanol. Finally, the nanocomposites were oven dried at 80 °C for a period of six hours. The GO/TiO₂/Fe₃O₄ catalyst was prepared by combining the preparation procedures of GO/TiO₂ and GO/Fe₃O₄. 1 g of GO-TiO₂ nanocomposites were mixed with the 250 ml of solution containing 0.05 M of FeCl₃·6H₂O and 0.025 M of FeCl₂·4H₂O. The resulting solution was then aged by constant stirring, filtered, washed with distilled water and oven dried at 60 °C for 2 days.

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