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Solar activation of TiO_2 intensified with graphene for degradation of Bisphenol-A in water

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ABSTRACT

Photocatalytic degradation of a Bisphenol-A (BPA) aqueous solution was achieved using titanium dioxide (TiO_2) and graphene-based TiO_2 photocatalysts activated by solar light. First, a comparative study of the adsorption kinetics of BPA, in the presence of both catalysts, as a function of pH was performed. Then, the effect of the initial BPA concentration and catalyst loading was assessed and the optimal conditions for BPA degradation by means of heterogeneous solar photocatalysis were determined. It was observed that TiO_2 modified with 2 wt% graphene improved the photocatalytic efficiency in terms of BPA mineralization. The TiO_2/graphene photocatalytic composite achieved a 16% increase in the photocatalytic mineralization of the BPA solution under solar light compared to un-doped TiO_2. This enhancement of photocatalytic efficiency is a result of the increase of active sites for BPA adsorption, the more efficient harvesting of solar light, and the inhibition of electron-hole recombination. The dynamic behavior of hydroxyl radicals and dissolved oxygen in these systems was also discussed. Finally, the roles played by hydroxyl radical, $HO^{\cdot}$, superoxide radical anion, $O_2^{\cdot-}$, and singlet molecular oxygen, $^1O_2$, were studied in both TiO_2 and TiO_2/graphene systems. It was found that $O_2^{\cdot-}$ were the main oxidative species in both systems.

1. Introduction

Bisphenol-A (BPA) is a well-known endocrine disrupting chemical (EDC) that has been extensively detected in the environment. BPA can cause adverse health effects due to its interference with the human and animal hormones (Schafer et al., 1999; Gultekin et al., 2009; Rubin, 2011; Rogers et al., 2013). Due to its xenobiotic nature, this molecule cannot be completely degraded by the biological treatment processes used in wastewater treatment plants (WWTPs) and it is therefore discharged intact into the environment (Hu et al., 2007; Crain et al., 2007). Hence, an efficient treatment system for removing BPA or its oxidation reaction intermediates from the aquatic environment remains a pressing need for water industry and decision makers.

It is well-known that Advanced Oxidation Processes (AOPs) are effective methods for treating organic pollutants in water. The efficacy of AOPs is based on the generation of highly reactive free radicals, especially hydroxyl radicals ($HO^{\cdot}$) or sulfate radicals ($SO_4^{\cdot-}$), which are capable of transforming bio-recalcitrant molecules into biodegradable products. Among AOPs, heterogeneous photocatalytic degradation reactions using semiconductor metallic oxides, such as TiO_2, as photocatalysts to destruct persistent organic pollutants such as EDCs have been well studied (Esplugas et al., 2007; Durán et al., 2009; Xekoukoulotakis et al., 2011). Reactive oxygen species, mainly hydroxyl radical, superoxide radical anion, $O_2^{\cdot-}$, and singlet molecular oxygen, $^1O_2$, which can degrade a wide range of chemical contaminants in water, are generated during photocatalytic processes. However, the production of photons by means of artificial light sources requires a substantial amount of electrical energy (Pérez et al., 2002). Solar energy can be used, alternatively to UV lamps, as a more sustainable option in order to reduce the energy and costs of the water treatment process. TiO_2-assisted photocatalytic degradation of several organic contaminants by solar light has been successfully used. This was found to be an economically viable process since solar energy is an abundant natural energy source and can be used instead of artificial light sources which are costly and hazardous (Konstantinou and Albanis, 2003; Robert et al., 2004). TiO_2 has a wide band gap (anatase E_{bg} = 3.2 eV or $\lambda < 387$ nm) and requires UV excitation (energy equal to or greater than the band-gap) to form electron-hole pairs. The conduction band electrons are able to reduce dissolved oxygen to generate superoxide radical, $O_2^{\cdot-}$, hydroperoxyl radicals, $HO_2^{\cdot}$, and through subsequent

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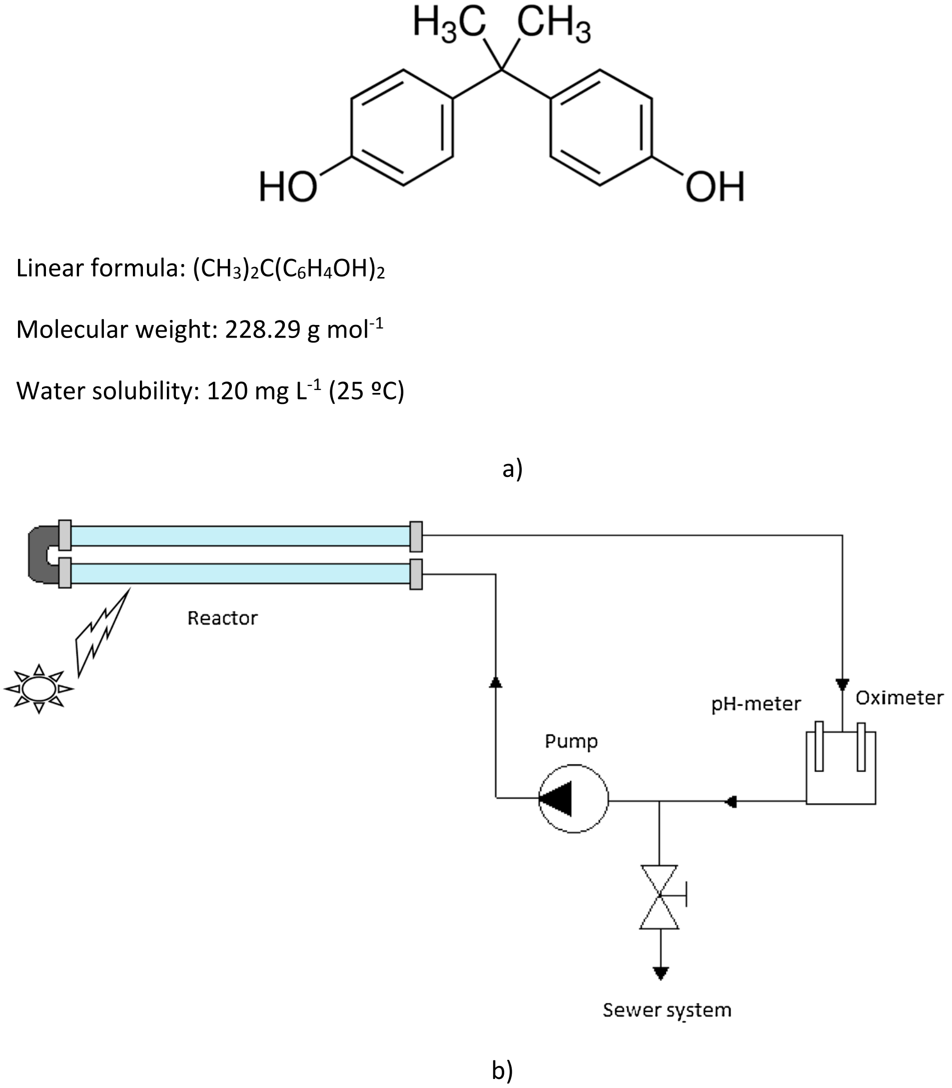
reduction reactions, hydrogen peroxide, H_2O_2, and hydroxyl radical, $HO^{\cdot}$. The valence band holes, h^+, are able to oxidize water to form $HO^{\cdot}$. The drawbacks of solar photocatalysis are that the UV radiation received by the earth is only around 5% of the entire solar energy spectrum and the photogenerated electron-hole pairs have fast recombination rates. In this sense, the efficiency of solar photocatalysis can be improved by doping TiO_2 composites with materials, such as graphene (Kumordzi et al., 2016), in order to expand the catalyst band-gap to the visible light region of the solar spectrum ($\lambda > 400$ nm) and prevent electron-hole pair recombination (Fukahori et al., 2003; Bellobono et al., 2005; Ni et al., 2007; Fujishima et al., 2008). The use of graphene is of great scientific interest due to its excellent properties such as chemical inertness, stability in both acidic and basic mediums, its abundance and large surface area (2630 m^2/g) (Upadhyay et al., 2014).

BPA degradation has been previously investigated in many oxidative treatment processes, such as UV/H_2O_2 and UV/persulfate (Yoon et al., 2012). A comparative study on the oxidative degradation of BPA by Fenton reagent, UV, UV/H_2O_2 and Ultrasound has been also reported (Young et al., 2013). The removal of BPA by means of UV, UV/H_2O_2, UV/$K_2S_2O_8$ and UV/Na_2CO_3 processes was also studied (Sanchez-Polo et al., 2013). F–TiO_2–RGO nanocomposites were examined for BPA degradation under UV light illumination (Luoa et al., 2015). TiO_2/graphene/Cu_2O was applied in the photoelectrocatalytic oxidation of BPA under artificial visible light irradiation (Yanga et al., 2016). The catalytic ability of TiO_2–reduced graphene oxide hybrid (TiO_2 – RGO) in photocatalysis using an artificial 365 nm light and ozonation combined system to degrade BPA was also investigated (Liao et al., 2016).

However, to the best of our knowledge, the application of graphene-TiO_2 composites irradiated by natural solar light for BPA degradation has not been studied yet. Therefore, further studies are required in this area to develop a more sustainable and cost efficient treatment technology. The aim of this work is to investigate BPA mineralization reactions by using solar photocatalytic oxidation in the presence of TiO_2 and TiO_2/graphene composites. First, the influence of pH on BPA adsorption kinetics for both TiO_2 and TiO_2/graphene composites was investigated. Then, the effects of various process parameters, such as initial concentrations of BPA and suspended photocatalysts as well as the type of the catalyst on mineralization reactions were evaluated. Afterwards, the dynamic behavior of $HO^{\cdot}$ radicals and the profile of dissolved oxygen in both catalytic systems were determined. Finally, the roles played by different reactive oxidative species such as $HO^{\cdot}$, $O_2^{\cdot -}$ and $^1O_2$, in both TiO_2 and TiO_2/graphene systems were evaluated using appropriate scavengers.



Linear formula: $(CH_3)_2C(C_6H_4OH)_2$

Molecular weight: 228.29 g mol^{-1}

Water solubility: 120 mg L^{-1} (25 ºC)

Fig. 1. (a) Structure and properties of Bisphenol-A; (b) Schematic illustration of the experimental set-up.