Enhanced photocatalytic degradation of Bisphenol-A using TiO_2/gC_3N_4 materials

POSTER

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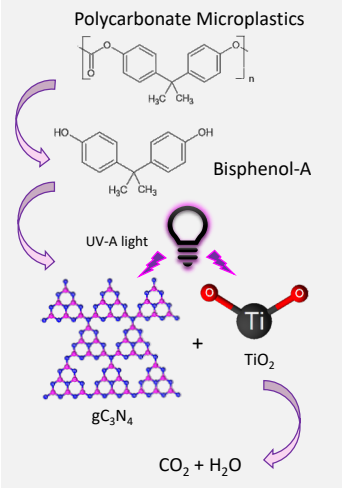

Microplastics (MPs) are contaminants of growing concern that are ubiquitous in almost all types of environmental matrices. Water is one of the most important reservoirs of MPs and is becoming a public health problem that requires attention. Photocatalysis is a promising and sustainable technology to enable the degradation of these pollutants from aqueous media. The degradation route of polycarbonate MPs involves the formation of intermediate compounds, among which Bisphenol A is commonly found. In this work, the photocatalytic properties of TiO_2 are improved by supporting it on gC_3N_4 with the aim of degrading BPA solutions. The composites with different ratio of both materials were synthesized following a wet impregnation method and characterized by FT-IR spectroscopy, UV-Vis spectroscopy and SEM-EDX microscopy. The activity of the synthesized composites is experimentally tested for the photodegradation of BPA under UV-A light achieving a complete degradation of BPA after 90 min. The performance of the photocatalysts is analyzed in terms of degradation kinetics concluding that the the fastest degradation was achieved with TiO_2/gC_3N_4 10:1 under UV-A light.

Introduction

Microplastics are increasingly present in land, water and air. It is well known that they produce harmful effects on the environment and concerns arise as they potentially may also have negative effects on human health and they can act as vectors for persistent organic pollutants. Furthermore, it has been confirmed the presence of different microplastic particles of polyethylene, polystyrene and polycarbonate, in real water matrices [1]. Some of them are deliberately manufactured and added to products such as exfoliating beads in facial or body scrubs. Moreover, they can also form unintentionally when large pieces of plastic, such as car tires or synthetic textiles, wear and tear.

As a solution to this environmental issue, photocatalytic degradation has been selected to degrade this contaminants. This work proposes the synthesis and validation of different composite materials based on TiO_2 and gC_3N_4 to enhance the photocatalytic degradation of microplastics. TiO_2 is a widespread used semiconductor for wastewater treatment. However, TiO_2 possesses certain limitations such as poor absorption of visible radiation and the rapid electron-hole pair recombination. With the aim of enhancing its properties, gC_3N_4, which is a carbon based, visible light responsive, conjugated polymer with attractive electronic band structure is tested. As a case of study, degradation of bisphenol A (BPA) as intermediate product in the degradation of of polycarbonate microplastics [2] is selected.

Material and Methods

Urea was calcined at 450°C for 5 hours to synthesize gC_3N_4. The TiO_2/gC_3N_4 composites were synthesized via wet impregnation method [2] with different ratios between both materials, 10:1, 1:1 and 1:10. Several experiments were carried out using 30 mg L^{-1} of BPA (Sigma Aldrich) as initial concentration and 0.5 g L^{-1} of the composite photocatalysts Experiments were performed in a 0.5 L Pyrex glass photoreactor provided with UV-A light technology from APRIA SYSTEMS. with an irradiation of 200 W m^{-2}. The assesment of the BPA degradation was performed with a High-Performance Liquid Chromathograph (HPLC) acquired from Agilent with a Zorbax C18 column of 3 x 150 mm. The properties of the synthesized materials were carried out using Fourier Transform Infrarred spectroscopy (Perkin Elmer Spectrum 65), UV-Vis spectroscopy (Shimadzu UV1800), SEM-EDX microscopy (Carl Zeiss, model EVO MA15).

Results and Discussion

The characterization of the synthesized materials was performed to confirm the correct synthesis of the gC_3N_4 and TiO_2/gC_3N_4 composites and to evaluate the properties of the materials. Fourier Transform Infrarred spectra confirmed the correct calcination of gC_3N_4 and the presence of both TiO_2 and gC_3N_4 in the composites, with a higher intensity of the bands according to the ratio of the materials. UV-Vis spectra also showed increased light absorption when the amount of TiO_2 in the composite was increased.

According to the results shown in Figure 1, dark experiments depicted that BPA is not adsorbed on the synthesized photocatalysts. However, when the light was switched on, BPA was degraded under UV-A light. UV-A degradation experiments showed a complete degradation of BPA after 90 min of experiment for all the photocatalysts, highlighting that even gC_3N_4 is able to degrade BPA. Comparing the photocatalytic performance of the materials, TiO_2/gC_3N_4 10:1 composites achieved best results of BPA degradation in kinetic terms. The kinetic curves were fitted to first and second-order kinetic models. Table 1 collects the values of the corresponding kinetic constants that in the case of TiO_2/gC_3N_4 10:1 are 5.4 10^{-3} min^{-1} and 8.3 10^{-3} mM^{-1} min^{-1}, respectively.

Furthermore, according to the values of mean standar deviation collected in Table 1, it is possible to conclude that the degradation of BPA under UV-A light is better described with a first order kinetic model than with a second order one for all the synthesized composites.

Analyzing the BPA degradation results under UV-A light, TiO_2/gC_3N_4 10:1 is the photocatalyst that exhibits a noteworthy performance. This enhancement is attributed to the addition of gC_3N_4 as support of TiO_2. TiO_2 nanoparticles were deposited on gC_3N_4 sheets enabling a good interaction between them. Upon UV-A light irradiation, both TiO_2 and gC_3N_4 were excited and thus electrons (e^-) and holes (h^+) were formed in the conduction (CB) and valence bands (VB) of the two materials, respectively. In this way, the holes were able to oxidize water forming reactive oxygen species, which are able to degrade BPA [4].

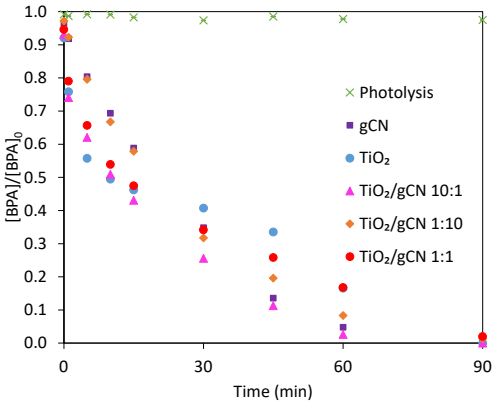

Figure 1. BPA degradation when using 0.5 g L^{-1} of catalyst and 30 mg L^{-1} of BPA as initial concentration under 200 W m^{-2} of UV-A light irradiation.

Table 1. Kinetic constants for the removal of BPA under UV-A light irradiation.

Catalyst	First order		Second order	
	k (min^{-1})	σ (mM)	k (mM^{-1} min^{-1})	σ (mM)
TiO_2	3.6 10^{-2}	6.7 10^{-3}	5.8 10^{-1}	6.8 10^{-3}
gC_3N_4	3.7 10^{-2}	2.0 10^{-3}	4.9 10^{-1}	7.7 10^{-3}
TiO_2/gC_3N_4 10:1	5.4 10^{-2}	2.9 10^{-3}	8.3 10^{-1}	5.1 10^{-3}
TiO_2/gC_3N_4 1:1	3.7 10^{-2}	8.9 10^{-4}	5.1 10^{-1}	6.3 10^{-3}
TiO_2/gC_3N_4 1:10	4.2 10^{-2}	4.2 10^{-3}	6.3 10^{-1}	4.8 10^{-3}

Conclusions

This study succesfully demonstrates the effectiveness of TiO_2-gC_3N_4 composite photocatalyst for the degration of BPA, intermediate compound formed in the degradation route of polycarbonate MPs using UV-A light. As future work, the composites which achieved higher performance will be tested in the photocatalytic degradation of polycarbonate microplastics. Moreover, experiments will be carried out under different types of light source such as visible light and solar light.

Acknowledgments

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