

Immobilization of TiO₂ nanoparticles on sintered, crushed glass for the degradation of humic acid

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Abstract—Disinfection is a crucial process in water treatment that inactivates disease-causing organism, being chlorines the most widely-used disinfecting agent. However, chlorination has become a major challenge because it yields the formation of carcinogenic disinfecting by-products such as trihalomethanes (THMs). THMs are formed when natural organic matter (NOM) in water reacts with chlorine. This endeavor aims to develop and evaluate an advanced oxidation process to destroy NOM to avoid THMs formation after chlorination. The process consists in establishing a titanium dioxide (TiO₂)-based composite made out of crushed, sintered glass to promote a photocatalytic reaction to destroy organic compounds in water under the influence of UV light. The present study developed a protocol to immobilize TiO₂ nanoparticles in a sintered glass substrate and performed photodegradation studies to evaluate the effectiveness of the glass-TiO₂ composite in degrading humic acid, a major component in the NOM. Results show that a maximum of 92% destruction of HA can be achieved for an irradiation time of 8 hour at a solution pH =3.

Keywords—titanium dioxide, trihalomethanes, humic acid, sintered glass, degradation.

I. INTRODUCTION

The primary objective of a water treatment plant (WTP) is to ensure the quality of drinking water by eliminating or reducing pollutants that may have adverse effects in people's health. Disinfection is a crucial process that integrates a conventional water treatment to remove or inactivate disease-causing organism in water such as pathogens. The most commonly disinfection treatment method is chlorination in which the disinfecting agent is chlorine. This practice is very effective in reducing waterborne diseases; however, the process has become a major challenge for WTPs. Specifically, for processes where the water supply source comes from surface waters (e.g.; rivers, lakes and reservoirs). These water sources tend to have high naturally occurring organic matter (NOM) levels, which in turn may compromise drinking water quality [1] since the NOM can interact with chlorine to create hazardous disinfection by-products such as trihalomethanes (THMs). The formation of THMs has been of great concern because they are considered carcinogenic substances. Consequently, for a WTP, it is essential to pursue an optimal balance between the removal of pathogens (i.e. chlorination) and the potential formation of THMs.

A reasonable strategy to minimize the THM's formation potential is to reduce NOM concentration, which has been referred as THM's precursors. The major constituent of NOM

is humic substance (HS) [2] and comprises three fractions: humic acids (HAs), fulvic acids (FAs) and humin. HA is the most predominant type of NOM in aqueous systems and, hence, is considered one of the major THMs precursors [1], [3], [4]. This study aims to develop and evaluate a filter-like composite made out of sintered crushed glass bearing titanium dioxide (TiO₂) nanoparticles to promote a photocatalytic reaction under the influence of ultra violet (UV) light for the destruction of HA in water. The project has been divided in two main components: 1) the developing of a protocol for the controlled incorporation/adhesion of TiO₂ nanoparticles onto the glass matrix in such a way to increase the exposure of the TiO₂ to the UV light; and 2) validating the protocol effectiveness by monitoring the glass-TiO₂ composite (GTC) capacity in degrading HA by means of total organic carbon (TOC) levels in water before and after treatment.

II. ONGOING WORK AND MOST RELEVANT RESULTS

A. TiO₂ nanoparticles immobilization on the sintered glass substrate surface by gravitational deposition using ethanol and ethanol + nitric acid

The process consisted in the deposition of the TiO₂ nanoparticles by gravitational decanting from a TiO₂ liquid suspension. First, a TiO₂ suspension is prepared adding 3 g of TiO₂ nanoparticles in 40 mL of ethanol in a beaker. The suspension is stirred for 1 h and then a sintered glass substrate (SGS) is immersed in the well-mixed suspension. The system is left at rest until all the liquid phase has evaporated at room temperature (approximately for 24 hours). In the process, most of the TiO₂ nanoparticles settle out covering the immersed SGS producing a dense TiO₂ layer. The SGS + TiO₂ are then placed inside a muffle furnace to promote the attachment of the nanoparticles onto the glass surface by heat exposure at different temperatures and times. At the end, once the GTC has cooled down at room temperature, is washed with water to remove/detach those particles not stuck onto the glass. The quantity of TiO₂ been deposited and immobilized is obtained by mass difference. The temperatures applied to the GTC within the muffle furnace were 800 and 900 °C with exposure times of 45 and 75 minutes for each temperature.

It needs to be pointed out that two types of TiO₂ suspensions were prepared and evaluated: (1) TiO₂ + ethanol without altering their ordinary pH (pH = 5); and (2) TiO₂ +

ethanol with a reduced suspension pH (~ 1.7 – 1.8) by adding nitric acid to the mixture. The purpose of lowering the pH was to reduce and modify the isoelectric point of the TiO₂ to increase the zeta potential (ζ) and evaluate the effect in its deposition over the glass substrate. Table I shows the final TiO₂ mass attached and immobilized in the SGS obtained as function of suspension pH and furnace temperature.

TABLE I
TiO₂ IMMOBILIZED IN THE SGS BY SETTLING AND HEAT EXPOSURE

Temperature in muffle furnace (°C)	Time in muffle furnace (min)	TiO ₂ Immobilized at pH = 5 (g)	TiO ₂ Immobilized at pH = 1.75 (g)
800	45	0.6580	1.5447
	75	0.5808	1.0925
900	45	0.6098	1.4372
	75	0.5271	1.1420

According to the data shown in Table I, the TiO₂ immobilization is favored by reducing the suspension pH (or increasing the zeta potential). This suggests that by reducing the pH and increasing the zeta potential of the suspension, the nanoparticles tend not to easily agglomerate each other due to the predominance of repulsive forces, hence, they will end up producing flocs of smaller particle sizes and will settle out of the suspension at a slower rate allowing better distribution and accommodation of the TiO₂ within the glass substrate pores. Another observation is that the conditions in the muffle furnace that promote the higher TiO₂ immobilization were at 800 °C and 45 minutes for a final TiO₂ mass attached to the glass of 1.5447 g.

B. HA degradation treatability studies for the glass-TiO₂ composite (GTC)

For the treatability studies, first a HA stock solution is prepared by diluting 0.1 g of HA powder in 100 mL of distilled water. The stock solution is stirred for 24 h and is then vacuum filtered through a 0.45 micron membrane filter to remove all suspended solids not dissolved. From the stock solution different HA dilutions ranging from 0 to 20 mg/L are prepared to construct a calibration curve using a TOC analyzer to detect the organic content in the sample.

Subsequently, several degradation experiments were carried out by placing a HA solution in contact with the GTC in a closed-box reactor under the influence of UV light. Different conditions of HA concentrations and pH were considered in order to elucidate the influence of the solution's pH in the decomposition and mineralization of HA. Figs. 1 and 2 show the residual HA levels in function of UV light irradiation time by means of residual TOC fractions (i.e. TOC/TOC₀) at pH = 3 and pH = 6, respectively.

From both figures it is observed a decrease in the initial HA concentration (TOC₀) on each evaluated condition suggesting that the GTC has the capacity to degrade recalcitrant pollutants. However, it can be noticed that the GTC efficiency changes considerably according to the pH value. Results presented in Figs 1 and 2 show that the

decrease in the pH level considerably increase the rate of photocatalytic degradation.

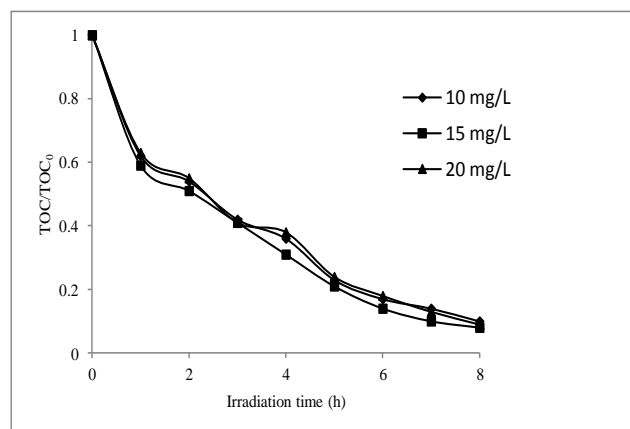


Fig 1. Photocatalytic degradation of different HA concentrations by the GTC in function of UV light irradiation time at pH 3

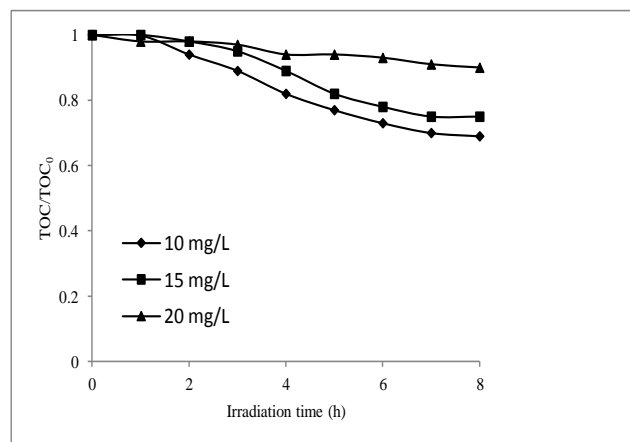


Fig 2. Photocatalytic degradation of different HA concentrations by the GTC in function of UV light irradiation time at pH 6

At the natural solution pH (pH = 6), as depicted in Fig. 2, less than 20% of the initial HA concentration was degraded within the first hour. In contrast, at pH = 3 (Fig. 1), up to 85% was decomposed in the first hour. Hence, one can see that removal efficiency significantly improves at pH = 3 for a maximum of 92% for 8 h of continuous UV light irradiation. This indicates that reducing the pH to acidic conditions increases the removal efficiency by a factor of almost 3.5.

The relationship between the degradation performance of the GTC and the solution pH can be explained considering the chemical characteristics developed in the system. Depending on the solution pH the TiO₂ particles as well as the HA macromolecule could be present as a negative, neutral or positive charges. This behavior is related to the protonation and deprotonation process of the catalyst and reactant surface. The natural pH of the solution is very similar to the pH of zero charge (PH_{pzc}) of the TiO₂, hence the TiO₂ is considered to possess negative or no charge, while the HAs molecules are deprotonated and tend to have negative charges causing an

increment in the electrostatic repulsion of HAs molecules and TiO₂ film. Consequently, promoting a colloidal suspension in the solution that affect the contact between the HA molecules and the GTC surface. For an efficient photocatalytic process and further degradation, it is necessary to evade the repulsion between the TiO₂ and the HA. The primary photochemical reactions towards the photomineralization of the HA occurs in the surface of the catalyst. A reduction in contact between the TiO₂ and the HA is produced under this neutral to alkaline media, in which the TiO₂ film is not able to adsorb the pollutant. As a result, the generated holes, electrons and hydroxyl radicals are not capable to completely decompose the HAs macromolecules. The opposite occurs in acidic conditions and the TiO₂ film in the GTC presents adsorptive characteristics since its surface develops an arrangement in which the positive charge particles are capable to attract the HAs.

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