DEGRADATION OF A MIXTURE OF PAHs IN AQUEOUS SOLUTION USING THE UV-A/H_2O_2/Fe^{2+} PROCESS DIRECTLY POWERED BY PHOTOVOLTAIC ENERGY

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Abstract

Due to the high electrical costs associated with the implementation of AOPs during water pollution treatment, alternative sources of energy to power the systems are required. In this work, the feasibility of the use of a photovoltaic array to supply the electrical power needs of the UV-A/Fe^{2+}/H_2O_2 system for degrading a natural water with 12 and 3 µg/L of anthracene and benzo[a]pyrene, respectively, was studied. It was found that more than 99% and 30% of the studied compounds and the organic matter were converted, demonstrating the performance of the oxidation system from photovoltaic energy.

Key words: *water treatment, micropollutants, advanced oxidation processes (AOPs), Photo-Fenton process, solar light*

1. INTRODUCTION

As the development of humankind increases, the number of contaminants in the environment rises. In the case of aquatic compartments, traditionally, water decontamination has been carried out by using conventional techniques (Rubio Clemente et al. 2013). However, with the development of more sensitive analytical methods, a wide range of micropollutants have been detected in natural, wastewater and even drinking water (Busetti et al. 2006; Felix-Cañedo et al. 2013; Martinez et al. 2013; Luo et al. 2014; Machado et al. 2016; Zahn et al. 2016). One class of compounds contained in water at trace and ultra-trace levels are polycyclic aromatic hydrocarbons (PAHs) (Busetti et al. 2006; Shemer & Linden 2007). PAHs constitute a large group of organic substances with fused aromatic rings that occur natural and artificially mainly from the incomplete combustion or pyrolysis of wood, gas, oil and coal (Sakulthaew et al. 2014; Rubio-Clemente et al. 2014b). They are lipophilic chemicals, being consequently, absorbed onto fatty tissues and bioaccumulating through the food chain.

Growing evidence suggests that PAHs, such as benzo[a]pyrene (BaP), have carcinogenic, mutagenic and teratogenic potential (Mastandrea et al. 2005; Rubio-Clemente et al. 2014b). Additionally, they can produce more toxic compounds when irradiated. This is the case of anthracene (AN), whose photoinduced toxicity has been widely reported (El-Alawi et al. 2002; Sanches et al. 2011; Fu et al. 2012), not only because of the formation of more dangerous phototransformation products, such as anthraquinone, but also because of the generation of reactive oxygen species which are responsible for the oxidative damage in biological systems. Moreover, PAHs are suspected to be potential endocrine disruptors and can suppress the immune system (Vela et al. 2012; Rubio-Clemente et al. 2014b), increasing the chances of suffering from diseases. Therefore, the presence of PAHs in the environment, especially in aquatic systems, raised human health concern.

In order to overcome the problem of water pollution with PAHs, advanced oxidation processes (AOPs) have been shown to be effective methods for organic pollutants conversion (Matilainen & Sillanpää 2010; Homem & Santos 2011; Rubio-Clemente et al. 2014b; Ribeiro et al. 2015). Particularly, the combination of Fenton's reagents, consisting of iron and hydrogen peroxide (H_2O_2),

and the action of ultraviolet (UV) radiation has demonstrated to be highly efficient for the degradation of organic pollutants that cannot be degraded by means of conventional water treatments.

In photo-Fenton process the production of HO^o is produced from the reaction of iron ions with H_2O_2, as represented by Eq. 1 and 2 (Rubio-Clemente et al. 2014a, 2015).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^o \quad \text{Eq. 1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^o \quad \text{Eq. 2}$$

During this process, iron is regenerated according to Eq. 2. However, the recycle of iron is limited since Eq. 2 reaction rate kinetic constant is lower than that of Eq. 1 (Neyens & Baeyens 2003; Rubio-Clemente et al. 2015). By introducing radiation in the system, photons impacting the solution can interact with ferric ions (Fe^{3+}), accelerating iron regeneration, as indicated in Eq. 3 (Rubio-Clemente et al. 2014a, 2014b, 2015). Additionally, when irradiating the system, the number of hydroxyl radicals (HO^o) generated is increased and, subsequently, the oxidation capacity of the treatment system, as oxidative degradation by-products are formed according to Eq. 4.

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + H^+ + HO^o \quad \text{Eq. 3}$$

$$PAHs + HO^o \rightarrow Intermediates \quad \text{Eq. 4}$$

In spite of the reported efficiency of photo-Fenton process to tackle with pollutants refractory to conventional treatment, this process, as other advanced oxidation technologies, have associated high operating costs, especially attributed to the electrical costs in the case of those advanced oxidation treatment system using electromagnetic radiation.

Generally, the applicability of a process at large scale is highly dependent on its total costs (i.e., capital, operational and maintenance). Among the capital costs, the reactor design and construction costs, the used devices costs and all the costs involved during the operation of a specific AOP must be included. In turn, the operating and maintenance costs consist of the replacement of parts, the labor, analytical, chemical and electrical costs. In general, total costs depend on the nature and concentration of the specific pollutant, used process, water quality and matrix, flow rate of the effluent, duration of the required treatment, pollutant removal percentage requirements, reactor design and power consumption, where the power consumption depends on the equipment used in a given AOP (Ortiz et al. 2007, 2008; Hernandez-Sancho et al. 2011).

On the other hand, it is important to note that electricity generated by coal, oil, natural gas and nuclear power has a negative environmental impact, since CO_2 emissions are increased, which are the major cause of global warming. In this sense, the use of alternative sources of energy is required in order to avoid the burning of fossil fuels. Among these renewable sources of energy, wind, solar, biomass, tidal and hydropower can be named (McEvoy et al. 2003; Drouiche et al. 2013; Solanki 2013). Therefore, the use of renewable energy technologies and their hybrid ones can be an attractive option for fulfilling the energy needs of water treatment systems that would result in significant energy security and economic and environmental benefits.

In turn, Colombia, due to its geographical location and climatological conditions, is a country with a great potential in terms of renewable energy generation; especially, from biomass, water, wind and solar resources. Hydropower is a Colombia´s major source of electricity generation, making up over 60% of its total electricity production. In this sense, hydropower develops an important role in the country. As estimated, a total of 118 GW can be produced including small and large hydropower plants (ECLAC 2004) In addition, as agricultural region par excellence, Colombia has a high potential in the transformation of agricultural residues, including cane bagasse and rice husks, in power. Nevertheless, the power potential estimated is less than 0.1% of the total energy produced. Biofuels are another promising energy production, particularly palm-oil based biodiesel. However, there is still an internal confrontation in agricultural areas about if land is intended to be cultivated for food production or energy generation (ECLAC 2004). On the other hand, with one of the best wind regime among the South American regions, Colombia has a theoretical large energy production potential from wind of 21 GW in La Guajira region (ESMAP 2010). Nonetheless, these renewable sources of energy

have been regarded as sources of significant negative environmental impacts, particularly concerning to wild life and ecosystems. Therefore, solar energy could be one of the best sources of energy alternative to conventional ones. In Colombia, thanks to its location in the equatorial zone, solar irradiation hits almost parallel to the terrestrial surface, with the subsequent high amount of energy per area with regard to other areas where the sun rays stroke more obliquely (ECLAC 2004; ESMAP 2010). Thus, solar energy can be an attractive renewable energy source for the countries having tropical and subtropical climate with a relative constant temperature and seasonal pattern, due to solar energy is abundant, freely available, sustainable, free from greenhouse and toxic gases, and it allows immediate transmission electricity as well as storage.

Under this scenario, this work is focused on performing the feasibility of the photo-Fenton process treating a natural water containing a mixture of two representative PAHs, consisting of 12 µg/L of AN and 3 µg/L of BaP, using the electric energy provided by a photovoltaic (PV) array.

2. EXPERIMENTAL

2.1. Chemicals

H_2O_2 (30%, w/w) was supplied by J.T. Baker (ECATEPEC, Estado de Mexico, Mexico), Fe_2SO_4 $7H_2O$ was purchased from Sigma-Aldrich (St. Louis, MO, USA) and AN (99%) and BaP (96%) from Alfa Aesar (Ward Hill, MA, USA). In addition, sulfuric acid (95-97%) was used for pH adjusting purposes and was provided by Merck (Darmstadt, Germany). HPLC-grade acetonitrile was also supplied by Merck and AN (99%) and BaP (98%) certified analytical standards from Dr. Ehrenstorfer (Augsburg, Germany) were used during HPLC analyses; being the latter ones as controls of the performance of the chromatographic system.

All chemicals were used as received and all solutions were prepared with deionized water obtained from a Millipore system (Bedford, MA, USA).

2.2. Working solution

The water utilized was taken from “El Peñol” dam, located in Guatapè (Antioquia, Colombia). The water was a relatively clean natural matrix with a low organic matter load, circumneutral pH and highly transparent, due to it low turbidity.

Water samples were always kept in dark conditions and refrigerated at 4 ºC. None previous treatments were applied

2.3. Photolytic reactor

An annular multi-lamp photoreactor was used for the photo-Fenton experiments. The reactor has an effective storage tank of 2 L and is equipped with an external jacket to maintain constant the temperature within the reaction solution. In Rubio-Clemente et al (2017b), a further description of the photoreactor used is reported. The radiation intensity values from 0.33 to 0.82 mW/cm^2, corresponding to the use of UV-A black-light lamps (Philips, Amsterdam, The Netherlands), emitting primarily at 365 nm and ranging from 1 to 4, was used. These radiation values were measured using a UVX radiometer with a UVX-25 sensor (UVP Inc., Upland, CA, USA).

In order to take profit to the efficiency of the photo-Fenton system, pH solution was adjusted at 2.8 (Pignatello et al. 2006; Rubio-Clemente et al. 2015). After that, Fenton’s reagents were added (first, iron salt was added followed by H_2O_2 addition) and lamps were turned on. They were warmed previously.

The electrical needs of the photoreactor were provided by a PV array without batteries composed of 9 modules.

A CM 6B solar radiation meter supplied by Kipp & Zonen B. V. (Delft, The Netherlands) was used to measure solar radiation reaching the PV array located at 6º15’39.7’’N 75º34’03.5’’W.

2.4. Analytical procedures

High performance liquid chromatography with fluoresce detection was used to identify and quantify AN and BaP concentration in water samples. For this purpose, a HPLC-FLD system series 1100/1200 (Agilent Technologies Inc., Palo Alto, CA, USA) was employed. Further details of the system, equipment and analytical procedure carried out are reported in Rubio-Clemente et al (2017a). On the other hand, total organic carbon (TOC) determination was performed in a TOC–Apollo 9000 analyzer purchased from Teledyne Tekmar Instruments (Mason, OH, USA).

3. RESULTS AND DISCUSSION

There are different factors affecting photo-Fenton system. In this work, the effect of UV-A radiation acting alone on AN and BaP removal was initially studied to select the best radiation arrangement obtaining the highest PAH conversion. Once the radiation conditions were fixed, 0.21 mg/L ferrous ions (Fe^{2+}), obtained by the addition of Fe_2SO_4 $7H_2O$ salt in the working solution were used and combined with different doses of the oxidizing agent (H_2O_2) for the Fenton's reaction to take place. The feasibility of the photo-Fenton process in removing AN and BaP, along with organic matter, by monitoring TOC evolution, was investigated.

3.1. Effect of UV-A radiation

One of the most important parameters for a photo-Fenton system to efficiently perform is the type of light and the intensity of radiation reaching the reaction solution. Considering the type of radiation, a great number of studies have been reported. As a matter of fact, Molkenthin et al (2013) investigated the organic matter mineralization of 50 mg/L bisphenol A using artificial UV-A and found about 100% of reduction compared to the conversion extent achieved by irradiation the experimental system with visible light. In turn, Kavitha and Palanivelu (2004) studied the percentage of 2.12 mM phenol degradation under natural and artificial light. Similarly to Molkenthin et al (2013), Kavitha and Palanivelu (2004) achieved higher removal extents of phenol under artificial radiation conditions compared to those obtained when exposed to sun light.

On the other hand, intensity radiation has also a significant role in the photo-Fenton process, as demonstrated Krutzler and Bauer (1999).

It should be highlighted that compounds undergoing photolysis, as it is the case of PAHs, the effect of this factor without the presence of neither the oxidizing nor the catalyzing agent must be previously studied. Consequently, in this work, the effect of UV-A radiation on AN and BaP transformation was examined by using 1, 2, 3 and 4 black-light lamps under the experimental conditions described above.

It was found that both of the target compounds underwent photolysis when irradiated with artificial UV-A light, being BaP the most affected compound. This could be thought to be ascribed to the different concentration of the target compounds tested, since as the compound is found in higher initial concentration, degradation extent is usually more reduced and removal rate is slower. However, in our research group, working with a solution spiked with a similar molar mixture of AN and BaP (3 µg/L), higher photolysis extents of BaP were observed in comparison with AN under the same operating conditions. This is likely due to the higher photolytical capacity of BaP when irradiated with 365 nm light in contrast to AN. Nonetheless, within the intensity radiation tested range, 0.82 mW/cm^2 was the radiation intensity allowing obtaining the highest AN and BaP removals, resulting in elimination extent values beyond 75 and 95%, respectively, as observed in Table 1.

Therefore, from these findings, 4 lamp arrangement was used in subsequent experiments to analyze the combined action of Fenton's reagents with UV radiation.

Compound	UV-A (4 lamps) Time= 90 min	UV-A/H_2O_2/Fe^{2+}(0.21 mg/L) Time= 240 min		
		5 mg/L H_2O_2	10 mg/L H_2O_2	15 mg/L H_2O_2
AN	> 75%	> 99%	> 99%	> 99%
BaP	> 95%	> 99%	> 99%	> 99%

Table 1. Removal percentages of AN and BaP through the photo-Fenton process.

3.2. Effect of Fenton's reagents

In addition to radiation, the amount of catalyst and oxidizing agent highly influences the oxidation system.

Taking into account the health risks associated with the presence of high levels of iron in aqueous environments (Papanikolaou & Pantopoulos 2005) and the restrictions concerning the residual amount of iron in drinking water and water to be released to the environment, an initial low dose of Fe_2SO_4 $7H_2O$ salt was used in order to have 0.21 mg/L of Fe^{2+} in the reaction solution. This amount of iron was combined with 5, 10 and 15 mg/L of H_2O_2 for Fenton's reaction to take place and the production of HO^o, which will interact with the pollutants of interest for their degradation.

As described previously, radiation will intervene in iron regeneration and acceleration with the subsequent increase in HO^o number within the bulk. Moreover, as observed in the previous section, AN and BaP can undergo photolysis. These two main transformation pathways are depicted in Figure 1. On the other hand, HO^o can also be produced from H_2O_2 photolysis. However, this mechanism of HO^o production is not expected to have a significant contribution in AN and BaP transformation because of the low absorbance capacity of H_2O_2 when irradiated with wavelengths under 300 nm.

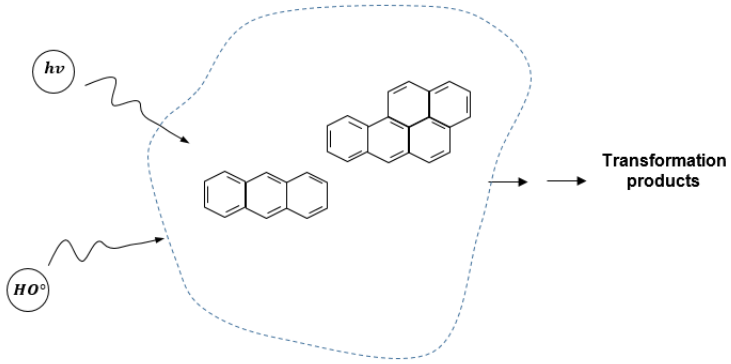

Figure 1. Main pathways for anthracene and benzo[a]pyrene to be converted to transformation products through the photo-Fenton process.

In Table 1, the results obtained after 240 min of treatment are also presented. Surprisingly, as evidenced irrespective of the H_2O_2/Fe^{2+} rata, a removal extent of AN and BaP higher than 99% is achieved. Nevertheless, a great difference in terms of time reaching this level was observed. When 0.21 mg/L Fe^{2+} were combined with 5 mg/L H_2O_2, this removal percentage value was achieved before 90 min of irradiation, while higher irradiation time was needed for the other catalytic and oxidizing agent concentration rata to obtain the same results. This can be explained from the side-reactions occurring within the bulk when the Fenton's reagents are present in excessive concentrations (Rubio-Clemente et al. 2014b).

Consequently, in this study, the action of 0.21 mg/L Fe^{2+} along with 5 mg/L H_2O_2 under UV-A radiation intensity of 0.82 mW/cm^2 provided by the use of 4 black-light lamps was used for analyzing the TOC mineralization extent. It was found that under the mentioned operating conditions, TOC elimination higher than 30% was obtained. Promising findings by applying photo-Fenton process also has already been reported (Kavitha & Palanivelu 2004; Molthenkin et al. 2013; Rubio-Clemente et al. 2014b, 2015).

However, since the removal of AN and BaP is not synonym of AN and BaP degradation, even if TOC in the samples is reduced by means of photo-Fenton application with 5 mg/L H_2O_2 and 0.21 mg/L Fe^{2+}, further analyses are required in subsequent studies to guarantee the feasibility of the PV system to obtain water of quality without the presence of harmful substances.

On the other hand, it is important to note that it could be interesting to test the photo-Fenton process under the direct action of solar light in the absence of the PV array, as the efficiency of this system for organic pollutant degradation has been successfully informed (Moncayo-Lasso et al. 2009; Duran et al. 2015).

4. CONCLUSION

Photo-Fenton process coupled with a photovoltaic array has been tested in the treatment of natural water from a Colombian reservoir containing AN and BaP at 12 and 3 µg/L, respectively. This study shows the potential of the coupled system that combines 0.21 mg/L of Fe^{2+} and 5 mg/L H_2O_2 irradiated with 0.82 mW/cm^2 UV-A light provided by 4 black-light lamps.

The PV-photo-Fenton system allows for a reduction of AN and BaP higher than 99% and a mineralization of the organic matter naturally contained in the water of study higher than 30% after 90 min of treatment. Nevertheless, further studies are needed for assuring the non-production of transformation compounds that could be more toxic than the parent compounds.

Additionally, the system would be tested directly driven by solar light in order to avoid the potential costs and pollution problems ascribed to the use of PV modules.

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