Preliminary photochemical studies of fluorene in various aqueous media

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ABSTRACT

The current study investigates the direct photochemical degradation of aqueous fluorene with the aid of a 125W polychromatic medium, pressure Hg lamp. The purpose was to test the effectiveness of the lamp in irradiation using fluorene spiked solution as substrate. A 700 ml volume of fluorene solution of 0.002 mg/l was irradiated batch-wise at 1, 3, 6, 12, 18, 24 and 48 h. The amount of fluorene removal was studied for fluorene solutions prepared from , neutral (distilled water), acidic (by adjusting pH with hydrochloric acid, HCl), basic (by adjusting pH with sodium hydroxide, NaOH) and saline (addition of sodium chloride, NaCl) solutions and there was 95.95, 92.35, 96.65 and 97.15 % removal respectively after 48 h of irradiation. The major degradation product identified was fluorenone. The different media did not significantly affect the rate of fluorene degradation.

Keywords: Direct photolysis, aqueous fluorene, ultraviolet light, degradation, media

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have two or more fused aromatic rings in linear, angular, or cluster arrangements and are of either natural (biogenic and geochemical) or anthropogenic (oxygen deficient combustion of carbon based materials) origin (Bamforth & Singleton, 2005).

PAHs show relatively low water solubility (Abd-Elsalam et al., 2009) and concentrations in the range between 0.1-830 ng are normal in fresh water (Kabzinski et al., 2002), but they are both toxic and carcinogenic and their finding in industrial and municipal effluents (Shemer & Linden, 2007) together with a tendency to bioaccumulate in aquatic organisms (Sabate et al., 2001) makes them prime targets for remediation. A number of chemical and biological methods have been used for this (Srujana

& Khan, 2012; Gasron et al., 2004; Ferrarese et al., 2008; Hughes et al., 1999) with bioremediation being widely explored due to its low cost and technical advantages (Yuzeng et al., 2000). Advanced oxidation processes (AOPs) for water treatment which involve the use of O_3, H_2O_2, and/or UV light for removing organic contaminants are also widely used (Shemer and Linden 2007; Ledakowicz et al., 1999).

Hydroradicals which are generated in AOP's destroy organic contaminants in situ. The free radicals generated can react to mineralise the pollutants completely and may also lead to the formation of highly polar and soluble products including phenols, quinones and acids (Shemer & Linden, 2007).

A variety of UV sources have been used directly in photodegradation (Sanches et al., 2011). The efficiency of UV light for degradation depends on the

structure and properties of the target molecule(s) and low pressure UV sources have proved to be most effective for PAH degradation (Sanches *et al.*, 2011). UV degradation studies of PAHs have given positive results for anthracene, phenanthrene, fluoranthene, pyrene and their benzo-substituted homologues (Sanches *et al.*, 2011; Beltran *et al.*, 1995) with the higher molecular weight PAHs undergoing more rapid rates of degradation than the lower and less condensed ones (Dabrowska *et al.*, 2008). The present study extends this theme by exploring the use of a medium-pressure Hg lamp for the direct photo-degradation of fluorene, a relatively low molecular weight tricyclic PAH, in an aqueous environment and examines the effect of pH and the presence of NaCl on the observed rate of degradation.

MATERIALS & METHODS

Fluorene (98%) and analytical grade dichloromethane were obtained from Sigma Aldrich, St. Louis, MO 63103-USA. Concentrated hydrochloric acid (HCl) and sodium hydroxide (NaOH) were from Riedel-de Haen (Seelze-Germany) and sodium chloride (NaCl) from Merck (Darmstadt, Germany).

The lamp used in this study was an old version manufactured in the 1970s by Photochemical Reactors Limited, UK. It was calibrated with the aid of a Ramses-ACC-UV- Hyperspectral UVA/UVB Irradiance Sensor: 280 - 500 nm from Germany. The detector was placed ~ 5 cm away from the lamp (corresponding to the distance from the reactor wall to the lamp when immersed) during the irradiance measurements.

A standard solution of 20 mg/ml was prepared in dichloromethane (DCM). A 0.1 ml aliquot of the standard solution was used to spike 1000 ml of distilled water to make 0.002 mg/ml solution. The resultant solution was stirred continuously with a magnetic stirrer for 2 h to ensure homogeneity. The pH of the solution was ~7.0 (that of the distilled water used).

A 700 ml volume of the fluorene spiked water was transferred into a 1 liter immersion well reactor furnished with a 125 W medium polychromatic Hg lamp (wrapped in a protective quartz jacket) and equipped with a water cooling system. The lamp was 240 mm long and 125 mm wide. Around 95 % of the lamp length was immersed in solution for every batch experiment. When the lamp was immersed in the reactor round bottom flask, the distance from the quartz jacket to the walls of the reactor was

approximately 5 cm. Batch irradiation was carried out for 1, 3, 6, 12, 18, 24 and 48 h. Irradiation was performed under static conditions at room temperature (25 ^{o}C ± 2) in a closed system.

The rate of photodegradation was monitored by determining the concentration of fluorene before and after each batch irradiation experiment. Three aliquots, 100 ml each, of spiked water solution were extracted with dichloromethane (3, 3, 4 ml, DCM) before and after each irradiation time by shaking in a separating funnel (Zeledon Toruno *et al.*, 2007).

The organic extracts were combined and analysed by GC-MS for peak identification. Sample concentration was achieved under nitrogen and fluorene concentration was determined by peak comparison with a calibration curve.

In order to test the effect of pH on the rate of degradation of aqueous fluorene, adjustments were carried out with concentrated hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions to pH values of ~ 2.0 (acidic) and ~ 14 (basic) respectively. The solutions were treated and irradiated according to the procedures described for the neutral spiked solution.

Saline solution was prepared by weighing 30 g of NaCl which was then dissolved in distilled water and made up to the mark of a 1000 ml volumetric flask. The resultant solution was spiked with 0.1 ml of 20 mg/ml solution of fluorene. The solution was treated and irradiated according to the procedures described for the neutral spiked solution.

GC-MS analysis was performed by means of a Thermo Scientific Trace GC Ultra equipped with an Ultra - 2 HP WCOT fused silica column (25 m x 0.2 mm, 0.33μm) by Agilent Technologies from J&W Scientific, USA. The GC was coupled to a Thermo Scientific DSQ II quadrupole mass spectrometer. Samples were injected at a rate of 1 μl min^{-1} by splitless injection mode and helium was used as the carrier gas at a constant flow rate of 1 ml min^{-1}. The oven program was started at 50 ^{o}C and held for 1 min, increased at a rate of 8 ^{o}C min^{-1} up to 220 ^{o}C and held for 1 min, and then increased at a rate of 10 ^{o}C min^{-1} up to 300 ^{o}C and held for 1 min. Mass detection was operated in a full scan mode (m/z ratio of range 50 - 400) at 3.86 scans s^{-1} for product identification. Ionisation was by electron impact at 70 eV. Ion source temperature was 250 ^{o}C.

The mass spectrometer operated in the positive mode at a constant resolving power of approximately 6000 FWHM (full width at half maximum). The

atmospheric pressure interface conditions were: orifice 1 = 18 V and both orifice 2 and ring lens = 7 V. The DART source was operated at 220 °C with a gas flow of 2.0 mL/min and a distance between the DART source exit and the cone inlet of 12 mm. The DART discharge needle voltage was set to +3000 V and a perforated electrode voltage of +150 V was applied. The grid voltage was set to 250 V. The total ion chromatogram (TIC) was acquired for 0.5 min and the data were processed by first creating extracted ion chromatograms with an m/z interval of ±0.1 which were then centroided and calibrated using a PEG 600 mass spectrum acquired during the same set of experiments.

The results presented are mean replicate values and quantification was done with a calibration curve with $R^2 > 0.9$. Blank experiments were performed for each batch and the extraction procedure recovers > 85 % fluorene in all the aqueous solutions. A control dark experiment which was performed for the near neutral

solution (pH~7) by leaving aqueous fluorene solution in an aluminum foil protected borosilicate bottle for 48 h yielded ~6% loss in initial concentration.

RESULTS AND DISCUSSION

The outcome of the degradation of aqueous fluorene is presented in this section.

The pH of the solution formed by spiking distilled water with fluorene was ~7.0. The rate of reduction of the amount of fluorene present in solution increased with time from the first hour through to 48 h (Figure 1). The amount of fluorene remaining in solution after 48 h was 4.05 % of the initial amount. The insufficient supply of oxygen to the reaction vessel due to the closed nature of the system could not have contributed to the low degradation rate since oxygen content has been proven to have only minor effects on the degradation rates of PAHs (Miller *et al.*, 2001; Lehto *et al.*, 2000).

Fig. 1: Percent fluorene degraded with time

The wave length at which PAHs usually absorb is around 253.7 nm (Figure 2) (Sabate *et al.*, 2001). Since the UV source used in the current study has only a small percentage of emitted radiation occurring

below 300 nm (Figure 3), this is likely responsible for the low rate of photodegradation of fluorene considering the long irradiation time. 9H-Fluoren-9-

one was identified as one of the products and the concentration seemed to diminish with duration.

Other products detected include phenols and carboxylic acids. The pH of the solution after every irradiation was in the acid range of ~ 3.0. This could be attributed to the presence of dissolved phenols (Encyclopaedia Britannica, 2012) and acids. DART analysis confirmed the presence of fluorene and 9H-fluoren-9-one in the products of irradiation.

Fig. 2: Absorption spectrum of fluorene

Fig. 3: Emission spectrum of the Hg lamp used in the study

The destruction by photo-irradiation of aqueous fluorene solution with or without any additive increased with time in all cases. In the case of fluorene solution which had been adjusted with HCl

to a pH of ~2.0, the rate of fluorene removal increased from 82.39 - 92.35 % from 1 - 48 h respectively. In the case of fluorene solution with pH of 14 (from adjustment with NaOH), the rate of removal was from 73.32 - 96.65% from 1- 48 h respectively. The saline solution (which had near neutral pH) proceeded steadily with 59.19 % removal of fluorene at 1 h duration and ended with 97.15 % at 48 h. Overall, the amount of fluorene degradation in 48 h was fastest for the solution containing 3 % NaCl followed by that containing NaOH, and the solution with no additive. The slowest rate was observed with the solution containing HCl (Figure 1). However, when Figure 1 is examined carefully, it is clear that all the curves of the four irradiation media lie in close proximity although that with NaCl lies above the others. It is quite clear that the adjustment of the composition of the aqueous solution does not significantly affect the extent of fluorene degradation. GC-MS analysis of the extracts from all the other irradiated samples showed 9H-Fluoren-9-one as well as other products which could not be identified by their mass spectra but had indications of seemingly phenolic structures. The final pHs of the irradiated solutions were all ~3.0, with the exception of the NaOH solution which remained basic with a pH of 13.0 after irradiation. Results reported on the photo-degradation of fluorene, chrysene and benzo[a]pyrene indicated that pH did not affect the degradation of fluorene, although that of the two other PAHs was influenced by pH (Miller & Olejnik, 2001).

The way in which ultraviolet light induces the chemical oxidation of organic compounds is not well understood. However, it is generally agreed that UV radiation produces sensitizers in the solution and that these sensitizers induce the formation of among others OH radicals (Shemer & Linden, 2007). Hydroxyl radicals are believed to be the main species involved in the oxidation of fluorene (Beltran *et al.*, 1995).

The initial reaction of fluorene with hydroxyl radicals is expected to give rise to 9H-fluoren-9-one by a reaction like that previously described as occurring on silica gel (Barbas *et al.*, 1997). 9H-Fluoren-9-one can then undergo a Baeyer-Villiger type oxidation to provide the corresponding ring expanded lactone which would suffer a rapid oxidative scission to provide 2'- hydroxybiphenyl-2-carboxylic acid (Cavani *et al.*, 2010). The substituted biphenyl is expected to be cleaved through photooxidation to yield 2-hydroxybenzoic acid and pyrocatechol (El Anba-Lurot

et al., 1995). Further oxidation would result ultimately in the formation of oxalic and formic acids (Naffrechoux *et al.*, 2000). The entire reaction pathway is presented in Figure 4.

The slow rate in the degradation of fluorene in the photooxidation experiments can be attributed to the nature of solutions used in this work. The solutions used in the present work provided environments which are relatively unsuitable for the generation of the photosensitizers that are needed for the production of a vigorous supply of hydroxyl radicals.

Fig. 4: Suggested pathway for fluorene photolysis

CONCLUSION

The study explores the potential of an old fashioned medium pressure polychromatic Hg lamp (an artificial source of light) for the removal of aqueous fluorene by direct photolysis in a closed system under static conditions. The removal efficiencies for neutral, acidic, basic and saline media were 95.95, 92.35, 96.65 and 97.15 % respectively after 48 h, thus the nature of the aqueous media does not have a significant effect on the rate of degradation of fluorene. The degradation of aqueous fluorene might be more effective under indirect photolysis conditions in the presence of a photo-sensitizer or catalyst and or with a low pressure lamp which emits radiation of ~ 254 nm suitable for the reactivity of PAHs. Further work will be carried with other extraction solvents to check for possible products retained in the aqueous phase as well as the use of other instrumental methods for the explicit identification of further products. This will help to obtain a definite

mechanism for the reactions processes involved. Though the results of this study are preliminary and might not mimic exactly what happens in the environment, they still give an insight into the possible establishment of methods for UV-treatment of waste water.

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