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ScienceDirect
Journal of Hazardous Materials 153 (2008) 792–798
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Promoted wet air oxidation of polynuclear aromatic hydrocarbons

F. Javier Rivas*, Ruth García, Juan F. García-Araya, Olga Gimeno

Departamento de Ingeniería Química y Química Física, Edificio José Luis Sotelo, Facultad de Ciencias,
Universidad de Extremadura, Av. Elvas S/N, 06071 Badajoz, Spain

Received 25 June 2007; received in revised form 5 September 2007; accepted 5 September 2007
Available online 8 September 2007

Abstract

The treatment of an aqueous solution of four polycyclic aromatic hydrocarbons, namely acenaphthene, phenanthrene, anthracene and fluoranthene, under moderate conditions of temperature and pressure has been conducted in the presence and absence of free radical promoters (hydrogen peroxide or potassium monopersulfate). With no addition of promoters, the process achieves PAH conversion values in the range 80–100% at 190 °C and 50 bars of air pressure (80 min of reaction). Similar results are obtained in the presence of hydrogen peroxide, however, in this case, the time required is just 60 min with a sharp decrease in PAH concentration in the first 10–20 min. Additionally, temperature can be lowered to values in the range 100–150 °C. If potassium monopersulfate is used instead of hydrogen peroxide, an analogous behaviour is experienced, in the latter case, temperatures above 120 °C lead to an inhibition of anthracene oxidation, likely due to ineffective decomposition of the monopersulfate molecule.

Keywords: WAO; OXONE®; Hydrogen peroxide; PAH

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals naturally occurring in coal, crude oil and gasoline. Additionally, PAHs can appear in products derived from fossil fuels, such as coal-tar pitch, creosote and asphalt, and can also be released into the environment during the incomplete burning of fossil fuels and garbage [1]. Given the hydrophobic nature of PAHs (especially high molecular weight PAHs), these compounds tend to be adsorbed onto suspended solid particulates and sediments. PAH contaminated soil remediation technologies include two different processes: direct PAHs removal with no extraction or, alternatively, PAHs can be first extracted from soils and further treated in a fluid phase. Thus, for instance, gaseous ozone can be injected into contaminated soils with no need of extraction [2] or, contrarily, an organic or inorganic extracting agent can be used previously to remove PAHs from soils and thereafter the solvent is regenerated by oxidation of organics or adsorption onto a suitable adsorbent [3].

One of the technologies that can be used to simultaneously extract and oxidise organics from soils is the subcritical wet air oxidation (WAO) under moderately elevated temperatures (150–300 °C) and pressures (30–200 bars). The process is normally performed in the presence of water and an oxygen containing gas as the oxidising agent, although other possibilities include the use of inorganic peroxides (promoted wet air oxidation). Several works have detailed the results of applying the WAO technology to polluted soils [4–8], however, the efficiency of WAO in the remediation of contaminated soils depends not only on the extraction capability but also on its potential to oxidise the target contaminants. In this sense, most of the literature has reported the PAHs removal level attained in the specific soils treated with none or little attention paid to the oxidation degree and kinetics occurring in the water phase. The present study is focused on the fate of four selected PAHs under WAO conditions in the presence and absence of oxygen and with the addition of free radical promoters, for instance a hydroxyl radical promoter (hydrogen peroxide) and a sulfate radical promoter (peroxymonosulfate).

2. Experimental

Wet air and promoted (either H_2O_2 or OXONE®) oxidation experiments were carried out in a PARR stainless steel autoclave of 600 mL of capacity. A titanium vessel was placed inside the reactor to avoid corrosion of the reactor walls. The rest of

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* Corresponding author. Tel.: +34 924 289300x6951; fax: +34 924 289385.
E-mail address: fjrivas@unex.es (F.J. Rivas).

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doi:10.1016/j.jhazmat.2007.09.025

components inside the reactor were kept in 316 SS. The experimental set-up consisted basically of the following components: sampling port equipped with a heat exchanger to cool down samples, injection port, meant to inject the promoter after reaching the working operating conditions, a magnetic system to agitate the reaction mixture and finally the corresponding pressure and temperature sensors. Reaction temperature was kept constant by a digital PI controller. The operating procedure was as follows: 325 or 350 mL of PAH saturated water were placed inside the reactor and pressurized to 5 bars with air (or nitrogen). Thereafter, the heating system was switched on to reach the desired operating temperature. Once the temperature achieved the set point, the reactor was finally air (or nitrogen)-pressurized to the working pressure and this was taken as time zero. When a promoter was added, a 25 mL solution of a predetermined concentration was injected immediately after reaching the operating temperature. Steadily and after flushing of the injection port, 2 mL of sample were withdrawn from the reactor to analyse the remaining PAH concentration. Further details of the experimental setup can be found elsewhere [9].

Acenaphthene (Ac), phenanthrene (Ph), anthracene (An) and fluoranthene (Fl) (Sigma–Aldrich) were used as received. Saturated solutions were obtained by vigorous stirring of an excess of PAHs in MilliQ ultrapure water in the dark. After 3 days the non-dissolved fraction of PAHs was removed from solution by consecutive filtrations on Schleicher & Schuell 589^3, 2° filtration paper and 0.47 mm diameter Millipore membranes (MF Millipore 0.45 μm). Hydrogen peroxide and OXONE® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) were purchased from Aldrich and used as received. OXONE® is a double potassium salt being the active ingredient the peroxymonosulfate, commonly known as monopersulfate. It derives from the peroxymonosulfuric acid H_2SO_5 (also known as Caro's acid, $pK_1 = \infty$, $pK_2 = 9.4$) whose structure is a tetrahedron with a S atom in the centre surrounded by a perhydroxyl group and two oxygen atoms.

Aqueous PAHs were analysed by injecting 25 μL of a sample into a HPLC system (Rheodyne injector, 1050 Hewlett Packard pump, 1046A, Alltech Prevail C18 column (4.6 mm × 150 mm), Hewlett Packard fluorescence detector, Chromjet Spectra Physics integrator) in isocratic mode using an acetonitrile–water mixture 70:30 (v/v) as mobile phase.

3. Results and discussion

3.1. Wet air oxidation experiments

3.1.1. Inert atmosphere

Although in most of cases the absence of oxygen in WAO processes avoids the elimination of organic contaminants, the literature reports several examples in which the hydrolysis or other non-oxidising processes (i.e. isomer transformation) might take place to a significant extent [10,11]. Consequently, due to the aforementioned non-oxidising reactions, in this work it was decided to check for the possibility of PAH removal under typical WAO conditions in the absence of oxygen. For this purpose, once the reactor was filled with the PAH solution, it was thereafter purged with nitrogen for 60 min, previous to the heating and pressurising stages. Fig. 1 shows the results obtained for a run conducted at 180 °C and 16 bars of total pressure. As observed, the different PAHs tested partially disappear after 70 min of reaction. Thus an average removal of approximately 30, 35, 25 and 50% for acenaphthene, phenanthrene, anthracene and fluoranthene was experienced, respectively. Since adsorption of PAHs to the reactor walls is unlikely at this temperature, it seems that the hydrocarbons have suffered some type of hydrolysis reaction. In this sense, hydrolysis of pyrene at 300 °C has been reported by detecting the presence of 2-methyl-pyrene, 1,3-dimethylpyrene, 1-pyrene-carboxaldehyde and some phenol derivatives [12].

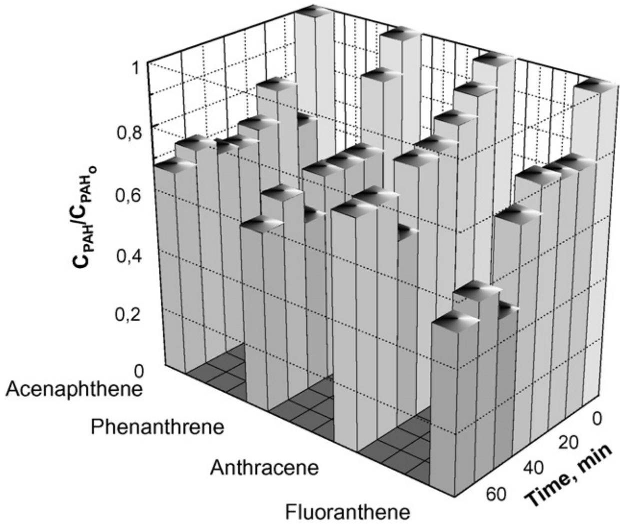

Fig. 1. Wet nitrogen treatment of PAHs. *Experimental conditions*: $V = 0.350$ L, $T = 180\,^{\circ}C$; $P_T = 16$ bars, pH 6.0, $C_{Ac_o} = 1.20$ ppm, $C_{Ph_o} = 0.26$ ppm, $C_{An_o} = 5.77 \times 10^{-3}$ ppm, $C_{Fl_o} = 1.86 \times 10^{-2}$ ppm.

3.1.2. Oxygen containing atmosphere

The next step in this study was to assess the effect of oxygen presence at high temperature and pressures. The most important parameter in WAO processes is temperature; accordingly, the influence of this parameter was checked in the interval 170–200 °C. Fig. 2 illustrates the results obtained. The presence of oxygen significantly enhances the conversion of PAHs. PAH removal even starts in the heating period, which takes approximately 40–50 min (see embedded figure for the 170 °C run). Broadly speaking, it can be inferred a positive effect of temperature. After 70 min of treatment, PAH conversion values are located in the interval 45–60% at 170 °C, while if temperature is raised to 180 or 190 °C, the conversion range increases to values in the interval 80–100%. In terms of mol of PAH reacted per unit of time, acenaphthene seems to be the most reactive hydrocarbon. It is noticeable the considerable elimination of this PAH in the heating period when the starting temperature is 190 °C. In any case, at the latter temperature the rest of PAHs also suffer a significant 40% depletion in the aforementioned heating period if compared to the 10% observed at 170 °C. Reactivity order, under the operating conditions investigated, follows the order: Ac > Ph > Fl > An. This order coincides with the solubility sequence. Likely, a more accurate analysis