



## Novel photochemical advanced oxidation process for the removal of polycyclic aromatic hydrocarbons from polluted concrete



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### HIGHLIGHTS

- Concrete pollution with PAHs determined.
- Analytical method of PAH determination developed.
- FHO3AOP method of PAH removal.
- Substantial and uniform oxidation of PAH in concrete achieved.
- The FHO3AOP method is feasible, economically viable and environmentally acceptable.

### ARTICLE INFO

#### Article history:

Received 30 July 2016

Received in revised form 16 November 2016

Accepted 18 November 2016

Available online 24 November 2016

#### Keywords:

PAH

Advanced oxidation process

PAH remediation

Polluted concrete

### ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are denoted by International Agency for Research on Cancer as mutagens, teratogens and carcinogenic to humans. In 2013, Vinča Institute of Nuclear Sciences was hired to determine whether PAHs are present in significant quantities in the concrete walls of newly built residential buildings (about 15,000 m<sup>2</sup> of apartments), and to propose appropriate technical solution for PAH removal in this case. As PAH occurrence, determination and remediation in concrete is, to our knowledge, a completely new field, it was necessary to face a number of challenges, including lack of regulations considering contents of PAHs in concrete, investigation of the origin of PAH contamination in concrete (if established), as well as finding feasible and non-expensive remediation method, which would be appropriate for residential space. In first part of this study, a markedly high concentrations of 5 PAHs were detected by UPLC/PDA analysis in samples of both concrete walls and mineral oil used for coating of planks during formwork, while control concrete and mineral oil, taken from independent construction site, were taken as a reference. Such coincidence, as well as the fact that mineral oil has penetrated into the concrete which is proven by ASAP/MS analysis, pointed to the mineral oil as the most probable source of PAH contamination of the concrete. In the second part, an efficient and easy-applicable method for PAH oxidation in concrete (called FHO3AOP), using UV light, H<sub>2</sub>O<sub>2</sub> and ozone, was presented and discussed in terms of previous literature data.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. By definition, the PAH compounds contain only carbon and hydrogen atoms, however, the atoms of nitrogen, sulfur and oxygen can be easily substitute the benzene ring and form a heterocyclic aromatic compounds, which are grouped under the name of common polycyclic aromatic hydrocarbons [1]. Agency for Environmental Pro-

tection (EPA) has defined 16 priority PAH compounds from the group that is most often detected in samples of soil, air and water, basic environmental media [2]. These are: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (Ant) fluoranthene (Flu), pyrene (Pyr), benzo (a) anthracene (BAA), chrysene (Chr) benzo (b) fluoranthene (BBF), benzo (k) fluoranthene (BKF), benzo (a) pyrene (BaP), indeno (1,2,3-cd) pyrene (IP), dibenz (a,h) anthracene, and benzo (g, h, i) perylene (BghiP). Some PAHs are denoted by International Agency for Research on Cancer as mutagens, teratogens and carcinogenic to humans. The most significant health effect is an excess risk of lung cancer upon inhalation of PAHs [3,4].

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Sources of PAHs can be natural (volcanic eruptions, forest burning) or anthropogenic (use of fossil fuels, petrochemical industries, exhaust fumes of cars) [5]. A significant source of PAH emissions are plants for treatment of municipal and industrial waste. Generally, PAHs are the main byproducts of incomplete combustion of organic matter, and thus can be found, among other, in processed waste oils [6–8].

In 2013, Vinča Institute of Nuclear Sciences, University of Belgrade was hired to determine if PAHs are present in significant quantities in concrete walls of the newly constructed buildings in settlement “Dr. Ivan Ribar” in Belgrade, Serbia, (15,000 m<sup>2</sup> of residential space), and to propose a technical solution/remediation in this case. The examination of the concentration of PAHs in building materials such as concrete, as well as PAH remediation of residential buildings, has not been performed earlier to our knowledge. As a result, following challenges were imposed in this problem: 1) it was necessary to apply the appropriate method for PAH detection and determination in concrete as a rather complex solid medium 2) there is the lack of appropriate regulations and reference values considering concentrations of PAHs in concrete, 3) it was of interest to determine the origin/source of PAH contamination in the buildings, 4) finally, it was necessary to find adequate remediation method in order to eliminate PAHs from residential space. Until now, considering available literature, there were no attempts to remove PAHs from concrete walls by neither biological [9–11] nor chemical methods. Hence we will limit here to UV light, hydrogen peroxide and ozone, as efficient and relatively low-cost chemical agents that can be generally used for PAH degradation. Many studies dedicated to photolysis of individual PAHs, have shown that aromatic structures of these compounds strongly absorb UV radiation in the areas of  $\lambda$  240–400 nm, and thus PAHs can be decomposed under the influence of UV light [12–14]. Generally lighter PAHs are more rapidly decomposed by UV light than heavier ones [15]. Hydrogen peroxide under the influence of UV light deliberates highly reactive hydroxyl radical, that further interacts with PAHs (modified Fenton reaction) [16–23]. Fenton reaction used for remediation of polluted soils is carried out by a solution of H<sub>2</sub>O<sub>2</sub>, in controlled acidic pH and in presence of stabilizers, that allow controlled rate of peroxide depletion and better wetting of contaminated material [24–27]. Moreover, as H<sub>2</sub>O<sub>2</sub> decomposition is exothermic, volatility of polluting compounds is helped by deliberated heat.

Finally, oxidation of polluting compounds by ozonation can be performed through either a direct route (reaction between ozone and compounds), or indirectly (via free radicals formed by decomposition of ozone) [16,28–31]. Most of the advanced oxidation processes use a combination of strong oxidants such as O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and a suitable catalyst [32–35].

The aim of this paper was to establish if PAHs are present in significant quantities in examined buildings, as well as to propose and discuss the origin of PAH contamination in this case, in order to avoid similar problems in future. In addition, a new method for PAH removal (called FHO3AOP) based on oxidation of PAH by combination of UV radiation and application of ozone and H<sub>2</sub>O<sub>2</sub> as oxidation agents, is presented. The efficacy of presented methods is discussed in light of previous literature data considering PAH degradation in aqueous solution and solid media.

## 2. Experimental

### 2.1. Reagents and material

The following chemicals were used: stock standard PAH-Mix 14 (1-methylnaphthalene (1-Mnapt), 2-methylnaphthalene, naphthalene, acenaphthene, acenaphthylene, fluorene (Fluo), phenan-

threne, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene) in solvent mixture acetone/benzene, concentration 2000 ng/ml (Dr. EHRENSTORFER GmbH), sodium dodecylbenzenesulfonate (Sigma Aldrich), trimethylhexadecyl ammonium chloride (Sigma Aldrich), UPLC grade ACN (J.T. Baker, UPLC Gradient Grade), *n*-hexane (Carlo Erba p.a.), hydrogen peroxide (Zorka Pharma p.a.), dimethyl-formamide (Merck), acetone (Zorka Pharma p.a.), sodium sulphate anhydrous (Merck) and deionized water.

### 2.2. Instruments and methods

Tests by liquid chromatography were performed on a Waters Acquity UPLC System, with PDA (Photodiode Array) detector, using the chromatography column suitable for testing PAHs manufacturer Restek, Pinnacale DB PAH 1.9 mm, 100 × 1.2 mm. Column was heated at 35 °C, with gradient elution combining two phases, 10% aqueous solution of acetonitrile (A) and pure acetonitrile (B). Flow rate was 0.25 ml/min with the following elution conditions: from 0 to 0.5 min, 45% of solution A and 55% solution B; from 0.5 to 3.5 min, 35% of solution A and 65% solution B; from 3.5 to 11 min, 2% of solution A and 98% solution B and from 11.0 to 12.0 min, 45% of solution A and 55% solution B. The samples and standard (10  $\mu$ L, prepared as described) were injected via sample manager.

In addition, the samples of oil and concrete were evaluated with Waters ASAP (Atmospheric Solids Analysis Probe) in conjunction with a tandem quadrupole mass spectrometer (ACQUITY TQ Detector). The samples (extracts of oil and concrete in acetonitrile) are directly loaded onto ASAP and MS results are obtain within the minute. MS full scan data from 0 to 1000 amu were acquired with the following MS tune page parameters: ionization mode: ESCi positive; corona current (APCI): 4.2  $\mu$ A; source temp.: 150 °C; desolvation temp.: 350 °C; desolvation gas: 694 L/h.

### 2.3. Sampling and extraction of PAHs from concrete and oil

Every analyzed sample is obtained by averaging of individual samples taken from randomly chosen sites on each wall in the room. Samples were taken by cutting piece of the wall of dimensions 10 × 10 cm, with a drill with diamond plate, to the depth of 2 cm.

Samples for UPLC/PDA analysis were prepared using modification of standard methods for the preparation of samples and extraction of organic pollutants (ISO 11709 and ISO 18287) in order to insure the efficient extraction of the PAHs from the concrete.

The concrete samples were pulverized in a stainless steel mold on the hydraulic press, and the obtained powder was sieved until homogeneous sample with particles <100  $\mu$ m was obtained. 20 g of the prepared powder was put in erlenmeyer with 100 ml of acetone on the magnetic stirrer for 1 h. Afterwards, 100 ml of hexane was added and was left under vigorous stirring for 18 h, thus providing a complete conversion of non-polar PAHs from the solid phase to the liquid phase. After the extraction process, the polar and non-polar phases were separated using 400 ml of deionized water. In order to remove traces of water from non-polar phase, the anhydrous Na<sub>2</sub>SO<sub>4</sub> was added. The separated liquid phase is concentrated on a rotary evaporator (Buchi, Flawil, Switzerland) to a volume of 2 ml. The sample was transferred to a vial suitable for evaporation in a stream of nitrogen gas, and then acetonitrile was added and evaporated under a stream of nitrogen gas to a volume of 1 ml.

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