

## Removal of polyaromatic hydrocarbons from scrap tires by solvent extraction

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**Abstract**—This study analyzes polycyclic aromatic hydrocarbon (PAH) compounds released from scrap tires by GC/MS and introduces a simple extraction process at ambient conditions to remove PAHs from scrap tires. The PAH species released from scrap tires included seven PAH compounds with high molecular weight and 4- and 5-aromatic rings and total-PAH content of 159 mg/L. When scrap tires were extracted using hot water (180 °C) for 3 h, the overall removal efficiency was 53%, indicating that PAHs were not adequately removed by this method. However, using organic solvents, the overall PAH removal efficiency improved to 82% for propionic acid and 70% for acetic acid, because the mass transfer of PAHs within scrap tires increases with decreasing dielectric constant. The PAH removal efficiency was dependent on solvent type and temperature.

Key words: Scrap Tires, PAHs, Solvent Extraction, Removal

### INTRODUCTION

Scrap tire management is a global environmental issue. Europe, the USA and Japan generate more than  $5 \times 10^6$  ton of scrap tires per year [1,2]. Due to the growth of production and consumption of automotive tires that pollute the environment during storage and subsequent incineration for disposal, worldwide intensive studies are being constructed and installed according to their effective use. But most of these tires are simply dumped in the open or in landfills, which is environmentally not acceptable [3]. Therefore, recycling of organic matter of rubber-containing waste by using new technologies is of considerable practical importance, both in terms of minimization of environmentally harmful impact on the environment and because of continued growth in energy prices. However, scrap tires release organic substances, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and airborne particulates, all of which are potentially harmful. Specifically, PAHs released by scrap tires containing petroleum oil are major contaminants due to their high carcinogenic and mutagenic properties, and therefore, practical recycling solutions are limited [4-7].

Polycyclic aromatic hydrocarbons (PAHs), so named because they are composed of two or more fused aromatic rings, are the main toxic components of crude oil and petroleum compounds. Due to their highly hydrophobic and lipophilic natures, PAHs tend to strongly associate with soil and rubber. Some techniques that have successfully been used to remove PAHs in contexts ranging from in-lab to full-scale operations include thermal treatment, microbiological slurry processes, flotation, wet oxidation, and solvent extraction [4-6]. However, the degradation of PAHs achieved via these methods is only partial, and compounds even more toxic than their parent com-

pounds may be formed in the process [8]. As a consequence of improvements in quantitation methods, deeper attention is being focused on extraction methods [9]. The literature contains examples of extraction techniques for removing PAHs from environmental solids such as supercritical fluid extraction (SFE), soxhlet extraction, and microwave-assisted extraction (MAE) [7-10]. A relatively new technique is pressurized fluid extraction (PFE; 2000 psi, >100 °C and pressurized hot water extraction (PHWE; >250 °C) using conventional solvents at high pressure and temperature [9,11]. Comparison of the recovery efficiencies achieved by PFE, SFE, and MAE showed similar results, but PFE requires significantly less organic solvent than the other techniques [9]. However, these extraction techniques using water and conventional solvents require high pressures and temperatures, which may decompose rubber or polymer substances.

The solvents used in extraction techniques and the major compositions of the contaminated soils all affect extraction yield, although the selection of a suitable extraction solvent is probably the most important variable. The effectiveness of a solvent is mainly dictated by its polarity and solubility parameters [10]. The current trend is to replace toxic organic solvents with benign solvents in processes ranging from analytical extractions to chemical synthesis and environmental remediation at ambient conditions. Obviously, water is the first alternative choice if compatibility problems are solved. Water is an environmentally friendly solvent that has the additional advantages of being readily available, non-toxic, and low cost, but in its natural state it is not a good solvent for most PAH compounds.

In this paper, we analyze PAH compounds released from scrap tires and introduce two simple treatments to remove PAHs from scrap tires using a solvent extraction process, both of which are environmentally friendly and cost-effective extraction methods. Two treatment types to remove PAHs were used: hot water, as raising the temperature decreases the dielectric constant of water, and organic

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solvent, which increases the affinity and mass transfer of PAHs.

## EXPERIMENTAL

Scrap tires were supplied as powdered material with a grain size of approximately 1 mm produced by crumbling waste tire treads. HPLC grade dichloromethane suitable for GC/MS analysis was obtained from J.T. Baker (USA). Certified A.C.S. grade acetic acid and isopropyl alcohol were purchased from Sigma Aldrich Chemical (USA).

The hot-water and solvent extraction was carried out in a 200 ml sealed vessel. For hot-water extraction, 20 g of scrap tire (20 wt%) was loaded in 100 ml of water and then heated at various temperatures from 25 °C to 180 °C for 3 h. For solvent extraction, 20 g of scrap tire was loaded in 100 ml of each solvent such as water, isopropyl alcohol, acetic acid, and propionic acid and then stirred at room temperature for 8 h. After hot-water and solvent extraction, the scrap tire materials were filtered and dried in an oven at 50 °C for 24 h.

The US-EPA 8100 method was used to determine the concentration of PAHs through gas chromatography/mass spectrometry (GC/MS) using a Fisons Instrument MD-800 equipped with a fused-silica capillary column, DB-5MS J&W Scientific (30 m×0.25 mm×0.25 μm), with helium as a carrier gas and a flow rate of 30 cm/s. The oven temperature program started at 40 °C (held for 4 min) and was increased to 300 °C at 10 °C/min (final holding time for 15 min). Thermogravimetric analysis (TGA) was performed using TA Instruments TGA-2950, which was run in a flowing nitrogen atmosphere.

## RESULTS AND DISCUSSION

### 1. Analysis of PAHs in Scrap Tires

The identification and quantification of PAHs released from scrap tires was performed via gas chromatograph/mass spectrometer (GC/MS). The seven PAH species observed included benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbFA), benzo(j)fluoranthene (BjFA), benzo(k)fluoranthene (BkFA), and dibenzo(a,h)anthracene (DBaA) (Table 1). The mean content of total-PAH in the scrap tire materials was 159 mg/L.

Fig. 1 shows the structures of the seven PAH compounds released from scrap tires. As shown, we found that PAH species in scrap tires are characterized by high molecular weight with 4- and 5-aromatic rings. Usually, lower molecular weight PAHs (light PAHs)

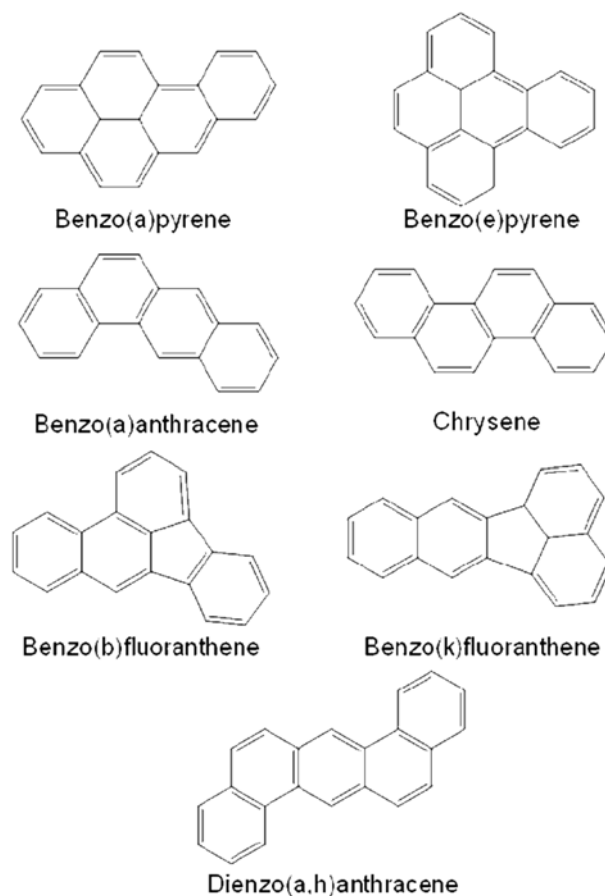


Fig. 1. The structure of the 7 PAHs released from scrap tires.

are more volatile, water soluble, and less lipophilic than high molecular weight PAHs (heavy PAHs) [12]. These physico-chemical properties also determine the environmental behavior of different PAH species, as the transfer and turnover of low molecular weight PAHs will be more rapid than those of heavy PAHs [13]. Higher numbers of aromatic rings in the PAH molecule increase resistance to removal.

### 2. Effect of Hot Water Extraction

The key observation explaining the effectiveness of hot water extraction is the change of dielectric constant indicating that the affinity of PAHs and water increases with increasing temperature. At ambient conditions, the dielectric constant of water is about 78, which is much too polar to dissolve most organic pollutants of interest, such as PAHs. PAH solubility in water at ambient conditions is low and decreases rapidly with molecular weight [14,15]. On the other hand, hot water above 250 °C has a low dielectric constant and is therefore an extremely effective solvent for most organic contaminants. Scrap tires formed with rubber, however, began to decompose below 250 °C in hot water (Fig. 2). As seen in Fig. 2, the weight loss below 250 °C gradually decreased compared to the initial sample weight, which was attributed to the decomposition of rubber.

The extraction efficiencies for PAHs of scrap tires according to different treatment temperatures at 80 °C, 130 °C, and 180 °C are shown in Fig. 3. The PAHs were inefficiently extracted at ambient temperature in water compared to that of untreated scrap tires. The remaining total PAHs at 80 °C, 130 °C, and 180 °C are 117 mg/L,

Table 1. Contents of individual PAHs in the scrap tires

Compounds	Mean concentration (mg/L)	Solubility in water (25 °C) (μmol/L)
Benzo(a)pyrene	21	0.0063
Benzo(e)pyrene	20	0.0072
Benzo(a)anthracene	30	0.041
Chrysene	43	0.0079
Benzo(b)fluoranthene	26	0.0059
Benzo(k)fluoranthene	16	0.032
Dibenzo(a,h)anthracene	3	0.018

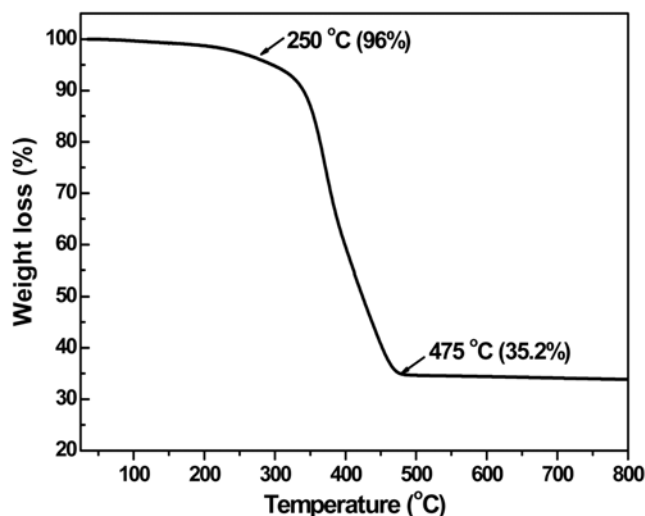


Fig. 2. Thermodynamic analysis (TGA) for the scrap tires.

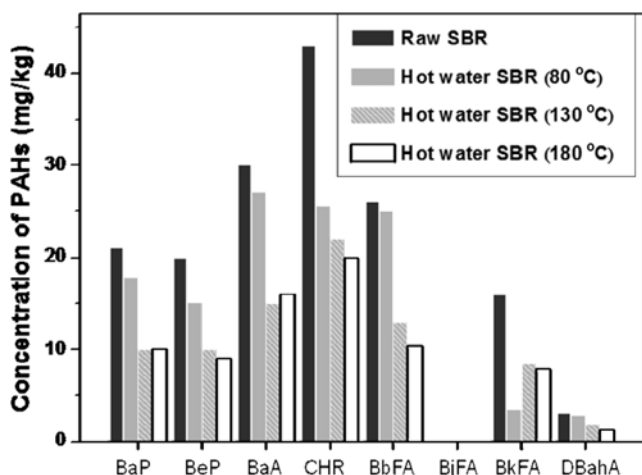


Fig. 3. Individual PAHs contents extracted from scrap tires in hot water at 80 °C, 130 °C and 180 °C for 3 h, respectively. PAHs: Benzo(a)pyrene (BaP), Benzo(e)pyrene (BeP), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b) fluoranthene (BbFA), Benzo(j)fluoranthene (BjFA), Benzo(k)fluoranthene (BkFA), Dibenzo(a,h) anthracene (DBAhA).

80 mg/L, and 74 mg/L, which represent 26%, 50%, and 53% removal efficiencies, respectively. From this result, it is observed that the extraction efficiencies increase at higher temperature due to the decreased dielectric constant of water. In this case, Bonten et al.

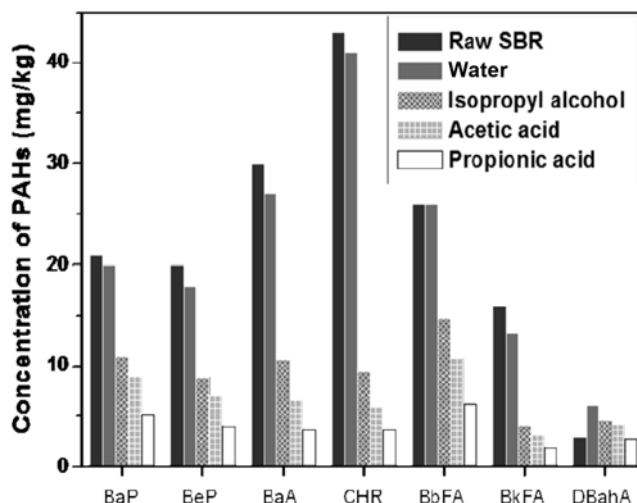


Fig. 4. Individual PAHs contents extracted from scrap tires in different organic solvents at room temperature for 8 h. PAHs: Benzo(a)pyrene (BaP), Benzo(e)pyrene (BeP), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b) fluoranthene (BbFA), Benzo(j)fluoranthene (BjFA), Benzo(k)fluoranthene (BkFA), Dibenzo(a,h) anthracene (DBAhA).

[14] investigated the possibilities for enhancing the bioavailability of hydrophobic organic contaminants in soil. They reported that temperatures above 95 °C led to significantly sharper decreases in residual concentrations, but that pretreatment at 70 °C showed no effect on residual PAH concentrations. Consequently, higher temperatures result in the dissolution of more contaminants, because the mass transfer of PAH within a soil particle increases with increasing temperature. Hartonen et al. [11] reported that PAHs and n-alkanes from sea sand were successfully extracted using liquid water or steam at different temperatures. The PAHs and n-alkanes are well extracted at higher temperature because the dielectric constant is the key factor in understanding solvent-solute interactions and can be related to polarity. A lower dielectric constant favors the solubility of low polarity compounds. From the above results, we confirm that when water temperatures were increased, the removal efficiency of PAH species from scrap tires was improved because of the decrease in dielectric constant. However, in our study, the removal efficiency for PAHs was 53% at 180 °C, suggesting that the use of water alone was not satisfactory for extraction of PAHs of scrap tires.

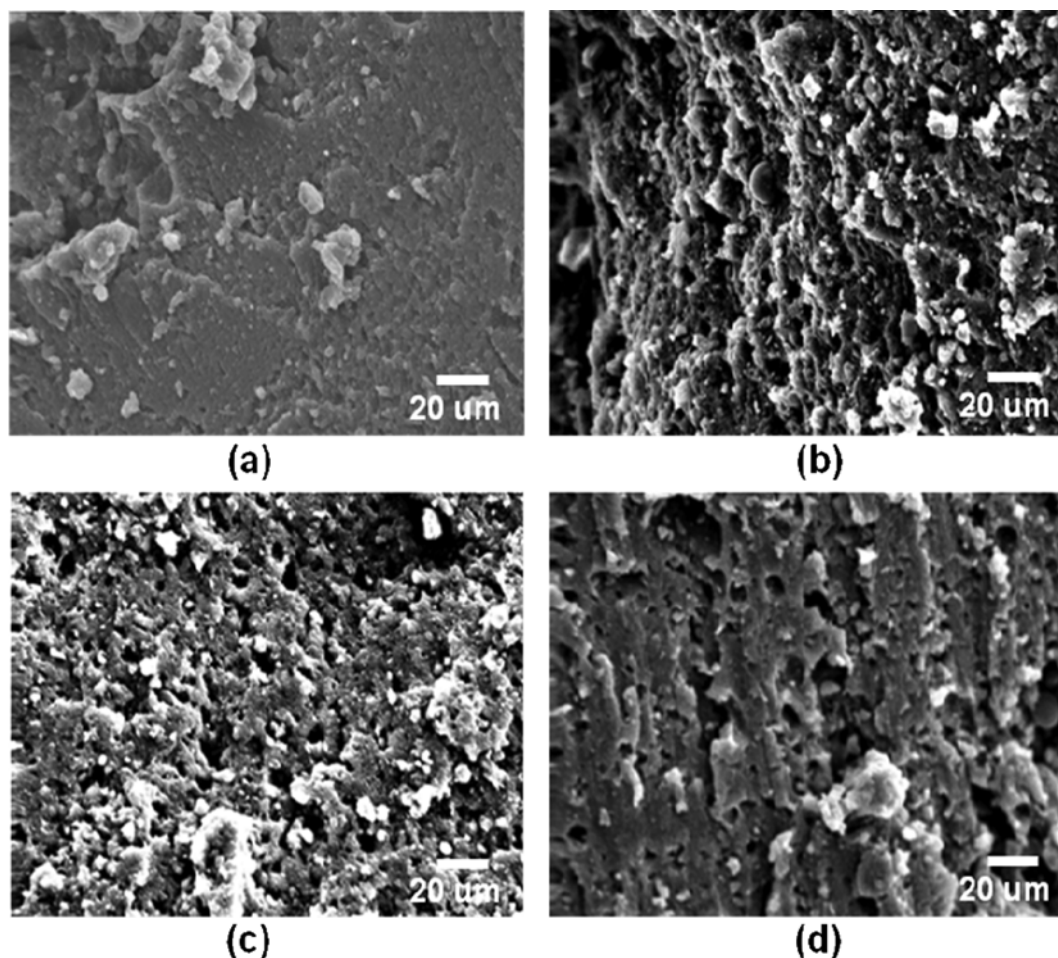
### 3. Effect of Organic Solvent Extraction

We investigated the PAH extraction efficiency of four extract-

Table 2. Individual and total PAHs contents extracted from scrap tires in different organic solvents at room temperature for 8 h

Extractant	Individual PAHs compounds (mg/L)							Total contents
	BaP	BeP	BaA	CHR	BbFA	BkFA	DBAhA	
Water	20	17.9	27.1	41	26	13.3	6.1	151 (5%)
Isopropyl alcohol	11	8.9	10.7	9.5	14.8	4.2	4.7	64 (60%)
Acetic acid	9	7.1	6.6	6	10.8	3.2	4.3	47 (70%)
Propionic acid	5.2	4.1	3.7	3.7	6.2	1.9	2.8	28 (82%)

\*PAHs: Benzo(a)pyrene (BaP), Benzo(e)pyrene (BeP), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbFA), Benzo(j)fluoranthene (BjFA), Benzo(k)fluoranthene (BkFA), Dibenzo (a,h) anthracene (DBAhA)



**Fig. 5. SEM micrographs on the surface of scrap tires untreated and treated in different organic solvents at room temperature for 8 h: untreated scrap tire (a), solvent-treated scrap tire with isopropyl alcohol (b), acetic acid (c) and propionic acid (d).**

ants--propionic acid, acetic acid, isopropyl alcohol, and water at room temperature--for 8 h. The dielectric constants of propionic acid, acetic acid, isopropyl alcohol, and water were about 3.1, 6.2, 18, and 78 at 25 °C, respectively. The content of total and individual PAHs is noted in Fig. 4 and Table 2. As shown in Fig. 4, the total PAH content in water, isopropyl alcohol, acetic acid, and propionic acid was 151 mg/L, 64 mg/L, 47 mg/L, and 28 mg/L, respectively. The PAHs removal efficiency was observed to be 82% in propionic acid, 70% in acetic acid, 60% in isopropyl alcohol, and 5.0% in water (Table 2). From this result, it can be observed that propionic acid and acetic acid were more effective solvents than isopropyl alcohol and water. Jeffrey et al. [6] reported the rates of degradation and formation of products using an advanced oxidation process (AOP) employing peroxy-acids as oxidizing agents to degrade toxic  $\alpha$ -methylnaphthalene in lake sediments. They found that within 24 h,  $\alpha$ -methylnaphthalene was reduced to 70% and 100% of its original concentration when propionic acid and acetic acid were used, respectively. Their results showed varied degradation rates depending on acid type. However, compared to our process, which does not include an oxidizing agent such as  $H_2O_2$ , propionic acid demonstrated higher removal efficiency than acetic acid, which strongly depends on the solvent dielectric constant. From this result, we conclude that the dielectric constant of solvents was a domi-

nant factor when removing PAHs in a single solvent system. This demonstrates a clear tendency of increased PAH removal efficiency when using an extractant with lower dielectric constant at ambient conditions.

Fig. 5 shows the SEM micrographs of particle surfaces between untreated and treated samples in isopropyl alcohol, acetic acid, and propionic acid at room temperature for 8 h. From the SEM images in Fig. 5(a)-(d), one can see the high surface porosity after solvent extraction in isopropyl alcohol, acetic acid, and propionic acid as compared with the particle surfaces of untreated scrap tires. As shown in Fig. 5, the pore sizes after solvent extraction in propionic acid, which demonstrated a high PAH removal efficiency, were larger than that in other solvents. In this result, we hypothesized that mass transfer of PAH species occurs via pores on the surface of scrap tires, and solvents with lower dielectric constant yielded larger pore volume. Therefore, we confirmed that removal efficiency increases by increasing the mass transfer kinetics of PAH species because of the formation of larger pores in solvents with lower dielectric constant.

## CONCLUSIONS

We analyzed the PAH compounds released from scrap tires and

introduced two simple extraction treatments to remove PAHs from scrap tires. The PAH species observed included seven compounds with total-PAH concentration (159 mg/L), with high molecular weight and 4- and 5-aromatic rings. When scrap tire material was extracted in hot water (180 °C) for 3 h, the overall removal efficiency was observed to be 53%, indicating that PAHs in scrap tires were not adequately removed. By using organic solvents, the overall removal efficiency of PAHs was improved to 82% in propionic acid and 70% in acetic acid at ambient conditions. This increase of removal efficiency was obtained by using an extractant with lower dielectric constant.

### ACKNOWLEDGEMENTS

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