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Leaching of DOC, DN, and inorganic constituents from scrap tires

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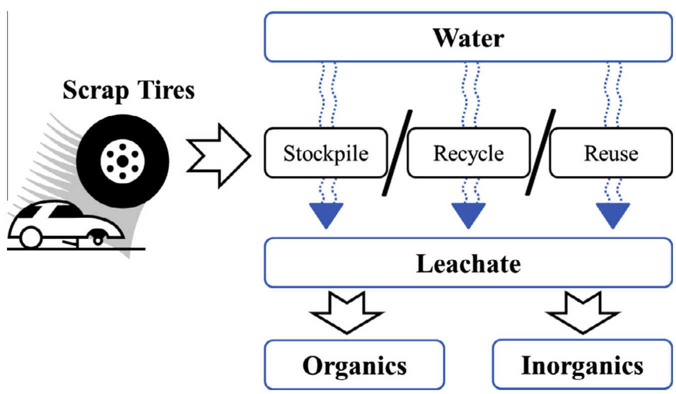
HIGHLIGHTS

- Leaching of organics increased with decreasing tire chip size.
- Minimum leaching of organics and inorganics were observed at neutral pH conditions.
- Iron and zinc were the highest inorganics in the leachates.
- Leaching rate of components associated with the rubbery portion decreased with time.
- Recommendations were developed for safer reuse of scrap tires.

GRAPHICAL ABSTRACT



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ABSTRACT

One concern for recycle and reuse of scrap tires is the leaching of tire constituents (organic and inorganic) with time, and their subsequent potential harmful impacts in environment. The main objective of this study was to examine the leaching of dissolved organic carbon (DOC), dissolved nitrogen (DN), and selected inorganic constituents from scrap tires. Different sizes of tire chips and crumb rubber were exposed to leaching solutions with pH's ranging from 3.0 to 10.0 for 28 days. The leaching of DOC and DN were found to be higher for smaller size tire chips; however, the leaching of inorganic constituents was independent of the size. In general, basic pH conditions increased the leaching of DOC and DN, whereas acidic pH conditions led to elevated concentrations of metals. Leaching was minimal around the neutral pH values for all the monitored parameters. Analysis of the leaching rates showed that components associated with the rubbery portion of the tires (DOC, DN, zinc, calcium, magnesium, etc.) exhibited an initial rapid followed by a slow release. On the other hand, a constant rate of leaching was observed for iron and manganese, which are attributed to the metal wires present inside the tires. Although the total amounts that leached varied, the observed leaching rates were similar for all tire chip sizes and leaching solutions. Operation under neutral pH conditions, use of larger size tire chips, prewashing of tires, and removal of metal wires prior to application will reduce the impact of tire recycle and reuse.

1. Introduction

During past two decades, the generation rate of scrap tires in the United States (US) was approximately one tire per person per year, which is equivalent to 290 million scrap tires annually (EPA, 2013). Disposal of these large numbers of scrap tires becomes problematic, as scrap tires are non-biodegradable, non-compactible, and they float to the surface in landfills. Due to these challenges, nearly two billion tires have already ended up in stockpiles in the US (Popovic, 2000). Unregulated stockpiling of tires can lead to (i) fire hazard and toxic emissions (poly-aromatic hydrocarbons

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(PAHs), metallic oxides etc.), (Downs et al., 1996; Liu et al., 1998) and (ii) health hazards by providing an ideal breeding habitat for mosquitos that transmit serious diseases (Manchon-Vizuete et al., 2004).

Within the last decade, many state programs were established in the US to promote good management practices, including cleanup and remediation of illegal tire stockpiles (Alabama-DEM, 2013) and requirements on shredding tires prior to landfilling (Arkansas-PCEC, 2012; Florida-DEP, 2012). Furthermore, following waste hierarchy principle, recovery and reuse alternatives are gaining popularity. It is reported that in 2013, markets existed for approximately 80% of scrap tires, a shift from 17% in 1990 (USEPA, 1991, 2013). According to recent reports, the State of California achieved a recovery rate of 80% in 2010 (California-Recycle, 2012), while the rate of recovery in Colorado was up to 111% in 2012 (Colorado-DPHE, 2013).

Scrap tires can be used in tire-derived fuels, civil/environmental engineering applications, electric arc furnaces, reclamation projects, devulcanisation, rubber reclamation, and pyrolysis (Tang et al., 2006; RMA, 2013). For some civil/environmental engineering applications, size reduction is required for the scrap tires to be used in highway construction, septic systems, ballast water filtration systems, and molded rubber products, as well as adsorbent media or daily cover in solid waste landfills (Amoozegar and Robarge, 1999; Tang et al., 2006, 2009, 2011; RMA 2013). One major concern, particularly with the direct use of crumb rubber and tire chips, is the leaching of tire constituents over time and subsequent potential harmful impacts in environment. The inorganic constituents in the leachate may include some heavy metals and sulfur, while the organics are expected to consist of PAHs used in the rubber (Wik and Dave, 2005). A comprehensive understanding of leaching from tires is critical for developing reuse alternatives for waste tires as fillings, sorbents, and construction materials.

Most previous works have focused on the leaching of selected PAHs, heavy metals and their ecotoxicological effects. In general, zinc and some PAHs (benzothiazole, butylated hydroxianisole, 2-methylnapthalene, fluorine, phenanthrene, etc.) have been detected frequently in the leachates of tires (Wik and Dave, 2005; Li et al., 2010; Llompart et al., 2013). These studies also showed that with increasing pH, leaching of PAHs increased while some metals exhibited an opposite trend (Minnesota-PCA, 1990). Unfortunately, detection and quantification of each individual PAH is challenging, therefore there is a necessity for an aggregate parameter to monitor the leaching of organics. Furthermore, it is essential to monitor for an array of metals. Overview of past studies reveals the importance of considering different specimen sizes (e.g., crumbs vs. chips) and conditions must be evaluated to represent a wide range of reuse alternatives. To ensure representativeness, a side-by-side comparison of tire sizes is needed while analyzing for different constituents.

The main objective of this study was to perform a systematic investigation on the leaching of selected inorganic and organics constituents from crumb rubber and tire chips in the aquatic environments expected to be encountered during reuse applications. The ultimate aim was to support tire-recycling programs by developing recommendations for safe and environmental friendly recovery of scrap tires.

2. Materials and methods

2.1. Tires

A mixture of scrap car and truck tires (approximately 90% car and 10% truck tires), were supplied by the Asphalt Rubber Technology Center at Clemson University. The tires were collected from stockpiles and shredded prior to experiments. All the tire chips were uniformly cut, and the experiments were conducted for five different particle sizes (Table 1). The average thickness of the tire chips was about one centimeter (0.4 in) and the steel wires at the sides of the chips were cut before the experiments. Crumb rubbers were pulverized at ambient temperature after the removal of wires, and 14–8 mesh sieve sizes were used in the experiments.

2.2. Leaching solutions

Leaching from scrap tires was investigated under six different conditions: in solutions at pH 4.0, 7.0 and 10.0, in acidic rainwater, and in hard and soft groundwater. For the leaching solutions, the pH of distilled and deionized water (DDW) was adjusted using high purity NaOH or HCl without using any buffer. Synthetic rainwater and groundwater solutions were prepared in DDW based on the values established in literature (Drever, 1982; Hem, 1985; Kim and Aneja 1992), and concentrations of the constituents are given in the Supporting information Table S1.

2.3. Experimental procedure

Toxicity Characteristic Leaching Procedure (TCLP) has been widely used to generate leachate concentrations for all types of solids for a number of metals and organic chemicals. The results of the TCLP for the scrap tires and crumb rubbers are given in the Text S1. The batch experiments in this study were based off of the USEPA's TCLP test method. In this study, same solid to liquid ratio was used as in TCLP test with the difference of leaching solution and contact times to simulate the behavior of scrap tires under different applications.

The crumb tires or tire chips were soaked in each leaching solutions at a constant solid to solution ratio of 1:20 by mass at room temperature (22 ± 2 °C) and mixed steadily on a rotary tumbler. For each size, number of tire chips was adjusted to correspond to a 100 g. These chips were placed in 2.5 L wide mouth amber bottles with Teflon lined cap and filled with 2 L of leaching solution. During each soaking cycle of one week, pH of the leaching solution was recorded daily and adjusted to its initial value by using high purity NaOH or HCl. At the end of one week period, tires were separated by filtration, and the leaching solution was replaced with a fresh solution in order to maintain high concentration gradient for leaching. Soaking cycles were repeated for one month, by that time leaching has slowed down significantly.

Following periodic removal of 30 mL of samples, same volume of fresh leaching solution was added back to reactors. Sampling days were set to 1, 3, 5, 7, 8, 10, 12, 14, 15, 17, 19, 21, 22, 25, and 28. Using plastic syringes, each sample was filtered through a pre-washed 0.45-μm membrane filter into two separate vials. High-density polyethylene vials, which were acidified with high purity nitric acid, were utilized for inorganic analyses, whereas borosilicate amber glass vials were used for organic analyses (dissolved organic carbon (DOC), and dissolved nitrogen (DN)).

2.4. Analytical methods

Several tests were performed to characterize tires. Nitrogen adsorption at 77 K and water vapor adsorption at 273 K were performed with a physisorption analyzer (Micromeritics ASAP 2010) to determine the surface area and pore volume of crumb rubber samples using the Brunauer–Emmett–Teller (BET) equation. Elemental analyses of carbon, hydrogen, nitrogen, sulfur, and oxygen contents of crumb rubbers were determined using CHNS-O analyzer (Thermo EA 1112). Dry ashing was conducted for both crumb rubbers and tire chips at 550 °C for 24 h for complete combustion of the sample, and samples were digested using a high purity