# Report as of FY2006 for 2006PR28B: "Use of Waste Tire Crumb Rubber to Remove Inorganic (Arsenic, Mercury) and Polycyclic Aromatic Hydrocarbons (PAHs) Species from Aqueous Solutions"

## Publications

- Conference Proceedings:
  - Alamo Luis; Perales, Oscar; Roman, Felix, 2007, Sorption of ethylbenzene, toluene and xylene onto crumb rubber from aqueous solutios Sorption of ethylbenzene and xylene in CLEANTECH, NSTI, Santa Clara, CA, p. 22-36.
- Other Publications:
  - Perales, Oscar; Roman, Felix; Alamo, Luis; Sanchez, Diana; Cruz, Jose, 2007,Evaluan nuevas opciones para reciclaje de goma, GACETA OF THE U OF PUERTO RICO AT MAYAGUEZ (V9, Y1,January07) (in Spanish)
  - Perales, Oscar; Roman, Felix; Alamo, Luis; Sanchez, Diana; Cruz, Jose; 2007, Evaluan nuevas opciones para reciclaje de goma, DIALOGO (MAGAZINE OF THE UNIVERSITY OF PUERTO RICO). February07.
  - Sanchez, Diana; Roman, Felix; Perales, Oscar 2007, Removal of Copper Ions from Aqueous solutions using waste tire crumb rubber as sorbent PRISM 2007, Cayey, PR (poster presentation)
  - Alamo, Luis; Roman, Felix; Sanchez, Diana; Perales, Oscar, Jose, 2007, Use of recyled crumb rubber to remove organic pollutants from aqueous solutions, PRISM 2007, Cayey, PR (poster presentation)
  - Torres, Heidy; Roman, Felix; Alamo, Luis; Perales, Oscar, 2007 Comparison between GC-MS Ion Trap, GC-MS Quadrupole and GC-FID techniques used in sorption studies of xylene onto crumb rubber, PRISM 2007, Cayey, PR (oral presentation)
  - Lopez, Jose; Nieto, Sorelis; Perales, Oscar; Roman, Felix; 2007, Sorption of Tetracycline onto waste tire crumb rubber, PRISM 2007, Cayey, PR (poster presentation)
  - Alamo, Luis; Sanchez Diana; Perales, Oscar; Roman, Felix, 2007, Use of recycled crumb rubber to remove inorganic and organic contaminants from aqueous solutions, EXPOCHEM 2007, Mayaguez,, PR (poster presentation)
  - Lopez, Jose; Nieto, Sorelis; Perales, Oscar; Roman, Felix, 2007, Sorption of Tetracycline onto waste tire crumb rubber, EXPOCHEM 2007, Mayaguez, PR (poster presentation)
  - Alamo, Luis; Sanchez, Diana; Roman, Felix; Perales, Oscar, 2007, Sorption of ethylbenzene, toluene and xylene onto crumb rubber from aqueous solutios, ACS 233rd National Meeting & Exposition, Chicago, March 25-29, 2007
  - Lopez, Jose; Sanchez, Diana; Alamao, Luis; Perales, Oscar; Roman, Felix, 2007, Renoval of tetracycline, organic solvents and metal ions from from Aqueous solutions using waste tire crumb rubber as sorbent, USDA, Mayo 2007, Washington DC, (poster presentation)
  - Alamo, Luis; Perales, Oscar; Roman, Felix 2007, Sorption of ethylbenzene, toluene and xylene onto crumb rubber from aqueous solutions, CLEANTECH, Santa Clara, CA, May 24-25, 2007 (poster presentation)

- Dissertations:
  - Alamo, Luis, 2006, Sorption of ETX from aqueous solutions, MS Thesis, Dept. of Chemistry, UPR-Mayaguez, Mayaguez, Puerto Rico, 100 pages Nieto, Sorelis, 2006, Removal of antimicrobials from aqueous solutions, MS Thesis, Dept. of Chemistry, UPR-Mayaguez, Mayaguez, Puerto Rico, 140 pages

## Report Follows

## Problem and Research Objectives:

Protecting water bodies from contamination is essential for health and safety. Typical inorganic pollutants are heavy metals that form highly soluble solid products (e.g., Hg), or no solid at all (As-oxyanions like arsenite and arsenate), after conventional alkaline precipitation. The limitations of conventional approaches become more evident at very dilute concentrations of contaminants as those observed in effluents from water treatment plants using conventional alkaline treatment, or ground waters polluted by hazardous species mobilized by leaching and/or percolation throughout soil substrates. Optional solvent extraction and ionic exchange systems are very expensive and they are tailored for high ion selectivity, which limits the removal of all contaminants in a single-step operation. In Puerto Rico, main problems of heavy metal pollution (e. g., Pb and Cd) have been reported in different types of effluents. The mercury pollution problem in Juncos and the presence of lead in some wells in Gurabo are also examples of the aquifers contamination issue.

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of more than a hundred organic compounds composed of two or more carbon rings derived from benzene. These compounds have received a significant attention due to their suspected mutagenic and carcinogenic nature. PAHs arise mostly form incomplete combustion processes and are ubiquitous in the environment. The main outdoor sources of PAHs include combustion from gasoline and diesel engines, combustion of coal and oil for power generation, wood burning and incineration, among others. In turn, major indoors sources of PAHs include cooking, smoking, and burning of natural gas and incense. Indoor PAH concentrations in air as high as 1000 ng/m3 and 110 ng/m3 for 2 member rings-PAH have been reported in Japan and USA. It has been confirmed that PAHs can enter water directly from the air with dust and precipitation, or on particles washed from the soil by runoff. PAHs dissolved in water can be "taken up" by plants, and are released into soil and water when the plants die, decompose or are burned. PAHs can also be mobilized into the aquatic environment through discharges from industrial and domestic sewage effluents, leaks of PAHs-containing materials (e.g. oils), runoff from paved roads, parking lots, and the grounds of wood preservation plants, among other sources. Accordingly, the development of a low-cost, environmental friendly and efficient removal process for PAHs compounds from effluents (gas and water) becomes indispensable.

In the United States, approximately 240 million tires were discarded in 1990 on the basis of the tire industry's estimation (U.S. EPA, 1991) and it has been suggested that discarded tires reaches 10 billion every year, worldwide. In 2001, the United States generated approximately 273-million scrap tires. Although, markets now exist for 76% of these scrap tires –up from 17% in 1990- the remaining are still stockpiled, or land filled. On a local basis, over 4-million tires are discarded annually in Puerto Rico. It represents near to 15,000 tires per day, which makes the problem of solid waste management even more difficult to handle. Approximately 800,000 tires are reused each year, the remainder is land filled or illegally dumped. Stockpiled scrap tires pose potentially serious health and safety problems. Whole tires served as breeding grounds for diseases carrying mosquitoes and rodents. Also, tire piles are fire hazards and, once ignited, they can burn out of control for months, producing acrid black smoke and a hazardous oily residue. Widespread illegal dumping poses the same problem associated with stockpiling. Thousands of abandoned scrap tires are found in streams, rivers and roadsides throughout the Island. The mismanagement of millions of scrap tires every year represents a significant waste of resources. A very recent example is the case of the 8,000 tons of chopped-up tires in the barge docked in Guayama since July 23rd, 2002, a problem without a definitive solution, at least in the short term.

Based on the above premises, the search of alternatives to expand the re-use possibilities for waste tires sounds justified. The present proposal addressed the systematic evaluation of crumb rubber as a suitable material to remove extremely toxic PAHs compounds from aqueous solutions through a low-cost and easy-to-scale technology based on the sorption properties of this waste

material. The present remediation option is based on the presence of carbon black, zinc oxide, and sulfur in crumb rubber, with potential capability to absorb/adsorb hazardous species from water or gaseous streams. This fact has been verified in preliminary results reported in our previous works where the very efficient removal of inorganic Cu(II), Cd(II) and Pb(II) as well as organic BTEX (ethylbenzene, xylene, toluene) species have been demonstrated. Sorbent waste tire crumb rubber will be kindly provided by Rubber Recycling and Manufacturing Corp., REMA, a Puerto Rican company that produces crumb rubber at different particle sizes from scrap tires.
Accordingly, the present proposal dealt with the detailed study of the sorption capability of waste tire crumb rubber for PAHs compounds, e. g. naphthalene, among others, of environmental concern. We proposed to investigate the conditions leading to maximization of uptake capacity and sorption rate, a factor of critical importance to determine the potential use of the proposed sorbent on a large scale remediation application.

## Methodology:

Methods and Procedures

Granular crumb rubber, screened at different mesh sizes, was provided by REMA Corp. a tire rubber recycling company located in Caguas, Puerto Rico.

*1 Chemical stability of granular crumb rubber*

The behavior of crumb rubber in aqueous solutions at different pH values and particle sizes has been evaluated already. It has been verified that crumb rubber do not release any toxic inorganic species into the aqueous phase.

*2 Sorption tests in aqueous phase*

The basic set-up for the sorption tests includes temperature-controlled water shaker baths, stirrers, pH-meters and filtration systems, drying ovens and GC/MS and LC/MS systems, currently available in Roman's laboratory. The term sorption here is used to include both adsorption, which refers to the retention of solutes by the surfaces of a solid material, and absorption, which refers to the retention of the solutes within the polymeric matrix. Sorption processes result from physical, chemical and electrostatic interactions between the solid surfaces and the sorbate.
**In PAHs sorption tests** screw cap vials with Teflon-lined septa were used instead of common glass beakers and agitated on a hematological mixer until equilibrium will be reached. In order to minimize vapor loss and allow a suitable mixing, the head space in the vial after addition of the sorbent and sorbate, was kept at approximately 1 ml. $HgCl_2$ was employed as a biocide to avoid degradation of the organic compounds by bacteria or fungi. Vials will be samples periodically and analyzed for PAHs. Solid Phase Microextraction (SPME), GC/MS and LC/MS were used to determine the concentration of the PAH in the initial solution and at the end of the sorption stage. During the first step of the experimental work, the sorbent was contacted with solutions containing single species. The results of the experimental work permitted to determine the equilibrium uptake, sorption rates, and removal efficiency.

## Principal Findings and Significance:

Once the optimum conditions for the quantitative determination of PAHs by the GC-MS techniques were determined, our experimental work was focused on the evaluation of the sorption behavior of the following PAHs: phenanthrene (PN), acenaphtylene (ACN) and acenaphthene(ACNP) from aqueous solutions under room-temperature conditions. In order to minimize any loose of the PAHs by volatilization, all experiments were carried out at a fixed concentration of PAHs (500 ppb for PN and 900 ppb for CAN and ACNP).

The solution pH was kept constant at 6.0. The concentration of crumb rubber (mesh 14-20) was varied between 0.03 g/L and 10 g/L in all tests. The terminal concentration values (i.e., the concentration at the equilibrium) were used to determine the removal efficiency of the crumb rubber. Experimental values were fitted to Langmuir and Freundlich isotherms. In general, the sorption behavior of all systems was well described by Freundlich's equation.

The higher concentrations of crumb rubber (10 g/L and 5 g/L) allowed both, the highest removal efficiencies and extremely short contact times. For instance, 99.2% and 98.8% of PN was removed at the end of 30 minutes of contact for 10 g/L and 5 g/L of crumb rubber, respectively. The corresponding terminal concentrations were 4.2 ppb and 5.8 ppb. The equilibrium conditions were achieved only after 28 hours when the concentration of crumb rubber was 0.01 g/L. The removal efficiency was 77% (114 ppb of PN in the final solution). The experimental data were well fitted by Freundlich equation (r=0.988).

In the case of CAN, two hours were required to achieve a 95% removal when the crumb rubber concentration was 10g/L. The removal dropped to 55% (20 hours of contact) when 0.03 g/L of crumb rubber was used instead. Again, the terminal concentration were well fitted by both Langmuir (r=0.9994) and Freundluch (r=0.9969) isotherms.

Crumb rubber was also an excellent sorbent to remove ACNP from aqueous solutions. The terminal concentration of ACNP was as low as 18 ppb (from starting 900 ppb ACNP solutions) after 2 hours of contact and 10g/L of crumb rubber. The corresponding removal efficiency was 98%. Only 76% of starting ACNP was removed after 20 hours when 0.03 g/L of crumb rubber was employed. Langmuir (r=0.9769) and Freundlich (r=0.9854) equations fitted experimental data very well.

Based on the above comments, the capability and efficiency of waste tire crumb rubber (mesh 14-20) to remove the selected PAHs compounds have been experimentally verified. Obtained results suggest that crumb rubber can be considered an excellent sorbent to clean-up aqueous effluents polluted by PAHs compounds. Ongoing work will address the evaluation of the sorption behavior under competitive conditions (co-existence of two and three PAHs compounds in the same solution) in batch and continuous (column) tests.