

State: PR

Project Number: 2005PR21B

Title: Removal of Inorganic, Organic and Antimicrobials Contaminants from Aqueous Solutions by Waste Tire Crumb Rubber

Project Type: Research

Focus Category: Treatment, Water Quality, Toxic Substances

Keywords: water treatment, water quality, organic compounds, heavy metals

Start Date: 3/1/2005

End Date: 2/28/2006

Congressional District:

PI: Perales-Perez, Oscar J
email:oscar@ge.uprm.edu
phone:1-787-8324040 (x3087)

Co-PI(s): Arocha, Marco A.
email:marocha@ge.uprm.edu
Roman, Felix
email:froman@uprm.edu

Abstract

The present proposal is focused on the systematic evaluation of crumb rubber as a suitable material to remove inorganic, organic solvents and antimicrobials from aqueous effluents through a low-cost and easy-to-scale technology based on the sorption properties of this waste material. We propose to investigate not only the conditions leading to maximization of uptake capacity and sorption rate, (including chemical and physical activation of rubber particles as a pre-treatment to enhance its sorption capability) but also the conditions to re-extract the contaminants (desorption), a factor of critical importance to determine the potential use of the proposed sorbent on a large scale remediation application. The remediation option addressed by this proposal is based on the presence of carbon black, zinc oxide, and sulfur in crumb rubber, with potential capability to absorb/adsorb and precipitate hazardous species from aqueous solution. This fact has been verified by preliminary results obtained in the first part of our work with Cu(II), Cd(II) and Pb(II) species. The sorbent 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. The applicability of crumb rubber as a sorbent will expand the recycling options for this material towards the treatment of polluted effluents (surface and underground) and remediation of contaminated soils where eventual superficial or underground water streams could have mobilized the contaminants into the aqueous phase.

Project Number:

1. Title: 'Removal of Inorganic, Organic and Antimicrobials Contaminants from Aqueous Solutions by Waste Tire Crumb Rubber'

2. Focus Categories: TRT, TS, WQL

3. Keywords: water treatment, water quality, organic compounds, heavy metals

4. Duration: March 1, 2005 - February 28, 2006

5. Federal funds requested: \$20,000.00

6. Non-Federal (matching) funds pledged: \$40,000.00

7. Principal Investigators:

Oscar Perales-Perez ¹, Department of General Engineering, UPRM, Mayagüez

Felix Roman ², Chemistry Department, UPRM, Mayagüez

Marco A. Arocha ³, Department of General Engineering, UPRM, Mayagüez

8. Congressional District : N/A

9. Statement of the Critical Problem

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 (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 through a single-step operation. In Puerto Rico, main problems of heavy metal pollution (mainly Pb and Cd) have been reported in effluents from municipal wastewater, electroplating, metal finishing and printed circuit board manufacturing plants. The mercury pollution problem in Juncos and the presence of lead in some wells in Gurabo are also examples of the aquifers contamination issue. The described situation is even more dramatic when the decontamination process deals with organic contaminants, as those detected in some laundries and gas stations in Puerto Rico, where traditional precipitation and ionic exchange processes are not applicable. Antimicrobials such as Sulfonamides (SAs) and Tetracycline (TCs), are of common veterinarian use to prevent epidemics and increase the weight gain in the animals. Very recently, the presence of these antimicrobials in water streams has been verified in Europe and the United States. This type of water pollution has raised environmental concerns based on the fact that up to 90% of the antibiotics fed to animals can be excreted in their active form. Therefore, the use of manure from antibiotic-treated animals as fertilizer and their wash-off by irrigation of rain precipitation should alter the microbial composition and ecology in the receptor soil as well as the quality of receptor water bodies. Diluted concentrations of antimicrobials can also selectively kill susceptible bacteria and favor the growth of resistant microorganisms, which in turn can become a pool of resistant genes. On a local basis, it has been detected that Puerto Rican tissues

samples of cattle, calf and swine tissue samples contained excessive levels of agricultural residues. The violations were due to the presence of excessive antimicrobials in the animal tissue.

Accordingly, the development of a low-cost, environmental friendly and efficient cleaning process for effluents bearing inorganic and organic contaminants becomes indispensable.

On the other hand, about 4-million tires are discarded annually in Puerto Rico, of them approximately 800,000 tires are reused each year, and the remainder is land filled, stockpiled or illegally dumped. Land filling is a poor management option for scrap tires. Whole tires take up large amounts of valuable space in a landfill, coming up to surface shortly. New environmental regulations eliminate land filling as a disposal method, greatly increasing the environmental treat of scrap tires. Accordingly, the search of different alternatives to expand the re-use possibilities for scrap tires sounds justified. The present proposal is focused on the systematic evaluation of crumb rubber as a suitable material to remove inorganic, organic solvents and antimicrobials from aqueous effluents through a low-cost and easy-to-scale technology based on the sorption properties of this waste material. The remediation option addressed by this proposal is based on the presence of carbon black, zinc oxide, and sulfur in crumb rubber, with potential capability to absorb/adsorb and precipitate hazardous species from aqueous solution. This fact has been verified by preliminary results obtained in the first part of our work with Cu(II), Cd(II) and Pb(II) species. The sorbent 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.

10. Statement of Results or Benefits

The present proposal deals with the detailed study of the sorption capability of waste tire crumb rubber for inorganic, such as Cu, Cd, Hg, Cr and As, organic (hexane, toluene and trichloroethylene) and SAs and TCs species of environmental concern. We propose to investigate not only the conditions leading to maximization of uptake capacity and sorption rate, (including chemical and physical activation of rubber particles as a pre-treatment to enhance its sorption capability) but also the conditions to re-extract the contaminants (desorption), a factor of critical importance to determine the potential use of the proposed sorbent on a large scale remediation application.

The applicability of crumb rubber as a sorbent will expand the recycling options for this material towards the treatment of polluted effluents (surface and underground) and remediation of contaminated soils where eventual superficial or underground water streams could have mobilized the contaminants into the aqueous phase. Based on the results from the batch and columnar tests, process development options including filter beds or cleaning columns containing packed granular crumb rubber, will be proposed. The results of this investigation would benefit directly the crumb-rubber recycling industry on the Island (e.g., REMA, Inc) and represent a new option for the local and federal government agencies dealing with the solid waste management, and the treatment of waste water and contaminated soils (e.g., the Autoridad de Desperdicios Sólidos, ADS, and the Junta de Calidad Ambiental). Furthermore, the students working for this project will get well-trained to improve their opportunities in the job market in the area of recycling and environmental remediation, and will in turn contribute to the consolidation of a 'green-culture' and related educational efforts in Puerto Rico. Based on the technical and social importance of the two involved fields (cleaning of polluted water streams and recycling of waste tires crumb rubber), the national impact of the present work becomes evident.

11. Scope and Objectives of the Research.

11.1 General scope

11.1.1 Effluent pollution by inorganic and organic species in aqueous phase.

Heavy metal contamination is a major source of environmental concern, and existing technologies are not always adequate for meeting regulatory limits. The toxic metals like Cd, Pb, Hg and As are biologically non-degradable and tend to accumulate in various vital animal organs and plant tissues; therefore, even exposure to trace concentrations of various of these toxic metal ions can lead to long term toxic effects. In the particular case of arsenic, most current environment concerns about this element are related to its presence in drinking water and to the clean up of severely contaminated but localized sites of soil pollution. As of late 2000, the maximum contaminant level (MCL) for As in the US was 50 µg/l, but EPA has proposed reducing the MCL by an order of magnitude. Major sources of aqueous effluents polluted with heavy metal ions in Puerto Rico are municipal wastewaters treatment plants and the electroplating, metal finishing and printed circuit board manufacturing industries. Typical concentrations of toxic inorganic species in those aqueous effluents range from 0.1-100 ppm. Aquifers can also be polluted with heavy metal ions when pristine underground water or percolating rain water pass through soils contaminated with toxic chemicals, causing their leaching and mobilization into the water bodies. The mercury pollution problem in Juncos and the presence of lead in some wells in Gurabo (Revista Domingo, El Nuevo Dia, Junio 15, 2003), can be considered local case-studies. More recently, a local newspaper Vocero (August 25, 2004) has raised concerns on the mercury pollution problem related to its presence in coastal waters in the Vieques area and the consequent bioaccumulation by local fish consumed by the population. This problem was conducive to the recommendation to limit the consumption of local sea food, especially by pregnant women. On the other hand, the demonstrated presence of organic hazardous compounds like trichloroethylene (TCE) contained in the wastes from laundries facilities and the contents of hexane, toluene that could be released from gas tanks into underground water, also justify any effort on the evaluation of options to remove those organic compounds from water bodies and/or contaminated soils.

11.1.2 Effluent contamination by antimicrobials

Estimates of antibacterial use in US aquaculture alone vary from 92,500 to 196,400 kg/year [1-3]. Nawaz et al reported that 8.5 million kg of antimicrobials are used annually in the US for agricultural purposes. Mellon and Benbrook (2001) estimated that no therapeutic uses of antibacterial for livestock production alone account for 11.2 million kg/year. Some veterinarian medicines, including antimicrobials, are considered feed additives that allow animals to be brought to market faster and at a lower cost. Livestock farmers supplement their animal feed with several types of therapeutic drugs including antimicrobials, antiprotozoals, ecto- and endo-parasiticides, and hormones [4, 5]. Two commonly types of antimicrobials are sulfonamides (SAa) and tetracyclines (TCs). SAs compete with p-aminobenzoic acid to prevent the synthesis of folic acid in bacteria whereas TCs bind to bacterial ribosomes to prevent tRNA access to the receptor sites. These antimicrobials are applied by various forms such as injections, additives in animal feed and as water bathing agents for fish. For example, about 0.1 g of sulfamethazine is added per 1 kg of animal feed [6]. Very recently, the presence of these types of antimicrobials in water bodies and streams has been verified in Europe and the United States, which has raised new environmental concerns. Although antimicrobials degradation may help to minimize the presence of the parent compound, the degradation products can also be considered as harmful substances. The degree of metabolism of antimicrobials compounds will depend on the type of substance, the species treated and the age of the animal. The worst case scenario is represented by the non-metabolized medicament that will be excreted unchanged. In a more general case, urine and

feces from a treated animal would contain a mixture of the parent compound and the transformation products.

The operation of livestock farms bearing many animals produces large amounts of manure and slurry on a periodical basis. In a typical operation, manure is stored in pounds for certain lengths of time before its application to land as fertilizer [4]. If the storage pound floor has not been built properly, and depending on the partition to soil and sediment of the medicine, antimicrobials contained in the solid and liquid manure can get mobilized and pollute surface and groundwater bodies and streams. Moreover, the input of antimicrobials into natural waters will be promoted during rain events. Based on the fact that up to 90% of the antibiotics fed to animals can be excreted in their active form, the use of manure from antibiotic-treated animals as fertilizer should obviously alter the microbial composition and ecology in the receptor soil. In addition, diluted concentrations of antibiotics can selectively kill susceptible bacteria and favor the growth of resistant microorganisms, which in turn can become a pool of resistant genes. Therefore, antibiotic resistant pathogens will not respond well to therapy by ordinary antibiotics, and then new antibiotics must be developed which also represents an additional cost. Smith, K. E. [8] has demonstrated a link between antibacterial use in agriculture and antibacterial-resistance infections. As established by Lindsey et al [9], concern is growing about water pollution by antimicrobials, because they can accelerate the evolution of antimicrobial-resistant bacteria as well as to transfer this resistance to other bacteria. Although the antimicrobials used in humans often are not the same as those given to animals, their structures can be similar enough to promote the bacterial resistance in human applications. For example, when streptococci and staphylococci bacteria developed resistance to Tylosin, a common animal food additive, they also developed resistance to erythromycin used by the human caretakers.

Antibiotics and antimicrobials in water

SAs are negatively charged at neutral pH, have pK_2 values ranging from 5.4 to 7.5 and pK_1 of around 2.5, and therefore, they are highly soluble in water [9]. SAs also exhibit poor chelating ability and have a low binding constant for soil [3, 4, 9-11], and hence they have a high potential to get mobilized to surface and groundwater. On the contrary TCs, because of its chelating character, can be sorbed onto soil strongly, limiting –but not avoiding– its entering into water bodies. Steuer-Laudisen et al. [7], have demonstrated that the soil distribution coefficient in sludge was 1990. Therefore, it can be suggested that although TCs may be detected in surface water, they may not be contained in ground water. Other studies have demonstrated that non-sorptive medicines, such as SAs, appear to be quickly transported to surface waters, whereas the transport of highly sorptive compounds, like TCs, appears to be much slower, with concentrations measured in drainage outfalls many months after application [4]. Mechanisms other than hydrophobic partitioning, such as cation exchange, cation bridging at clay surfaces, surface complexation and hydrogen bonding may play a role in the sorption of veterinarian medicines to soils and sediments [11]. Recently, [4, 12], Kolpin and Giger have confirmed the occurrence of 95 organic wastewater contaminants, including pharmaceutical, in 139 streams across the USA. Among 31 antibiotics from the groups of TCs, macrolides, SAs and fluoroquinolones, erythromycin- H_2O and sulfamethoxazole at concentrations up to 1.7 and 1.9 $\mu\text{g/l}$, respectively, were detected in water samples. In another report, Lindsey et al [9] reported the analyses of 144 water samples. Their results showed that TCs and SAs were contained in samples from nine sites in concentrations from 0.07 to above 15 $\mu\text{g/l}$. Chlortetracycline was detected at 0.15 $\mu\text{g/l}$ in one water surface sample, and the most detected TC was oxytetracycline. The report also evidenced that several collection sites contained both SAs and TCs. Currently, USGS is leading the efforts to determine baseline information regarding these types of organic contaminants in water bodies inside US. Karthikeyan [12] have analyzed samples from wastewater treatment facilities, adjacent

groundwater monitoring wells, on-site wastewater treatment systems and water supply wells under the influence of surface water in Wisconsin area. He reported the detection of SAs (sulfamethazine, sulfamethoxazole, and sulfadimethosine), TCs (tetracycline, chlortetracycline), one fluoroquinolone (ciprofloxacin), one macrolide (erythromycin) and trimethoprim, all considered as organic contaminants by the USGS.

The Puerto Rican Scenario

Numbers of cattle, calf and swine tissue samples have been found in Puerto Rico containing prohibitive levels of agricultural residues out of the total number of tissues collected in 1999, 2000 and 2001. The rate of violations was mostly confined to cattle with 70 violations (Antibiotics - 68; Sulfonamide - 1) and was due to the presence of excessive antibiotics in the animal tissue, as stated in Food Safety and Antimicrobial Residues in Food Animals report (available at <http://www.fsis.usda.gov/OPPDE/animalprod/Presentations/Residue>). Evidently, the presence of antimicrobials in Puerto Rican agricultural soils and water bodies can not be ruled out.

11.1.3 Recycling of tire rubber.

In order to prevent waste rubber and in particular discarded automobile tires from damaging the environment, it is highly desirable to recycle this material. Recycling of waste materials is a most important goal for all industries and, specifically for the rubber industry. Large stockpiles of waste rubber (tires, scrap and by-products of rubber factories) are increasing as is their disposal charge. In the United States, approximately 240,000,000 tires were discarded in 1990 on the basis of the tire industry's estimation (U.S. EPA, 1991) and it has been estimated that the amount of discarded tires reaches 10 billion every year worldwide. In 2001, the United States generated approximately 273-million scrap tires [13-16]. Although, markets now exist for 76% of these scrap tires –up from 17% in 1990- the remaining scrap tires are still stockpiled, or land filled, however. Moreover, the total mass quantity of tires currently recycled in a given year (not including reuse, retreading, or combustion) is less than 7% of the annual tire generation rate [13-14]. Only a small portion of the waste tires are retreated, and a very small portion is devulcanized by tedious processes. The asphalt highway construction business holds the greatest potential for the demand of scrap and used tires in the form of ground rubber.

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, stockpiled or illegally dumped [17]. In turn, stockpiled scrap tires, pose potentially serious health and safety problems. Whole tires served as breeding grounds for diseases carrying mosquitoes and rodents. Uncontrolled tire piles are fire hazards and, once ignited, tire piles 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 mentioned facts, the still growing generation rate of new tires and the stricter controls onto used-tires disposal, the search of new options to re-use this waste material becomes indispensable, not only for Puerto Rico but also for continental US.

11.1.4 Crumb rubber composition and sorption properties

Crumb rubber is the result after shredding tires, separation of metals and fibers, and pulverizing of the clean rubber into different sizes. It can be reutilized to manufacture new products or used as aggregate on other products. Today's technology allows scrap tires be reduced to various sizes and consistencies depending upon the targeted end use market. Crump rubber is composed of a complex mixture of elastomers (natural and synthetic rubber), curatives (sulfur and peroxides), cure system-activators (stearic acid), fillers and reinforcing agents (carbon black, fibers, etc), process oils, plasticizers and additives (antioxidants, antiozonents). On a rubber-composition point of view, the major components of tires are rubber vulcanized with sulfur (0.07-2.22%), steel, ZnO (0.55% - 2.79%) and carbon black (10.97%-45.6%) [16]. Carbon black is used to strengthen the rubber and improve its abrasion resistance. This component should exhibit similar adsorbing characteristics as activated charcoal, a well known agent used to remove organics and inorganic compounds from aqueous and gaseous effluents, a fact that makes viable the removal of target species through sorption/adsorption mechanisms. Furthermore, the presence of acid functional groups, such as stearic acid, provides ion exchange sites for metal ions.

Non-polar organic compounds are expected to interact with the non-polar matrix of the rubber and other non-polar constituents such as carbon black and oils, mostly by van der Waals interactions. In turn, polar compounds are expected to interact through dipole-dipole interactions and hydrogen bonding. The kinetics of the sorption process will depend on the access of sorbate species to the sorption sites, the number of sorption sites and the nature of the sorption interactions. An important factor related to the sorption process is the fact that crump rubber is vulcanized and therefore its molecular structure contains a large number of cross-links. The amount of solvent that will diffuse into the rubber depends on the number of cross-links and the compatibility of the solvent and rubber at a molecular level. Moreover, the lower the molecular weight of the compound the faster it will diffuse into the rubber. A possible mechanism for the sorption of the TCs in the crumb rubber matrix is formation of chelates with metals presents within these particles such as zinc in ZnO. Water soluble antimicrobials of the type SAs, which are negatively charged at neutral pH, are expected to interact by a pH-dependent ion exchange mechanism. Furthermore, Van der Waals interactions with the carbon black contained in the crumb rubber are expected for TCs and SAs antimicrobials.

Activation pre-treatment of crumb rubber

In order to enhance the sorption capability of crumb rubber, two schemes of activation will be attempted. In the chemical activation route, crumb rubber will be contacted with a concentrated zinc solution, dried and contacted with solutions bearing target species. It is expected that the increase of Zn contents in rubber particles would benefit the ionic exchange reactions between Zn ions and heavy metal ions as suggested by Rowley et al. The thermal activation route will promote the availability of pores. This activation pre-treatment is based on a carbonization and volatile removal process under inert atmosphere at 500-900°C followed by a mild oxidation of the substance with steam, CO₂ or air at 800-1000°C. This latter option is based on well-know thermal activation of commercial charcoal.

11.2 Objectives

The proposed research focuses on the systematic evaluation of granular waste rubber tires as sorbent material for inorganic, organic and antimicrobials species of environmental concern in aqueous solutions. Fundamental concepts related to equilibrium and kinetics during the sorption and desorption stages will be addressed. The stability of crumb rubber particles under acid neutral and alkaline conditions in aqueous phase will be evaluated. Next, the maximum uptakes and sorption

rates of granular crumb rubber in single and multi-components systems will be investigated. Options for sorbent activation by chemical and thermal means will also be attempted. The detailed investigation of the reversibility of the sorption process, will also be an essential step in the research plan since: a) a highly reversible desorption of sorbed species would allow the re-use of the sorbent and the appropriate handling of recovered contaminants, or b) if reversibility is poor to null, make the final disposal of the crumb rubber a safe option, discarding any possibility to release the sorbed species back into water bodies.

Therefore, this proposal will explore the following main objectives:

- i. To optimize the sorption capability of crumb rubber for inorganic and organic species from aqueous solutions. In order to maximize the up-takes and sorption rates of crumb rubber, alternatives for its activation (chemical or thermal) will be studied. Then, the sorption capability of granular crumb rubber for Cu (II), Hg (II), Cd (II), Cr(III), oxyanions of As (III, V) and Cr (VI), hexane, toluene and trichloroethylene, will be systematically investigated.
- ii. To assess the sorption capability of crumb rubber for antimicrobials from aqueous solutions. Targeted species were selected based on their common veterinarian use; then, the sorption capability of granular crumb rubber, with and without activation, for different types of SAs and TCs will be evaluated.
- iii. To assess the sorption rates and loading-capacity as a function of crumb rubber particles concentration, particle size, ions speciation, concentration, solution pH (for inorganics and antimicrobials) and temperature.
- iv. To determine the desorption behavior of crumb rubber.
- v. To develop of explanatory models for the sorption-desorption stages and selectivity of hazardous species (inorganic, organic and antimicrobials).

11.3 Timeline of activities

Although funds are requested for one-year, the general plan is summarized as follows:

Year 1: Preliminary evaluation of sorption properties of granular crumb rubber (Ongoing)

- 1) Physical and chemical stability of granular crumb rubber in aqueous media (O. Perales-Perez, F. Roman).
- 2) Batch equilibrium and kinetic tests for sorption of inorganic species in single-species system (O. Perales-Perez, F. Roman)
- 3) Batch equilibrium and kinetic tests for sorption of organic species in single-species system (F. Roman, M. A. Arocha, O. Perales-Perez,).

Year 2: Optimization of the sorption process and sorption of antimicrobials species from aqueous solutions. (This proposal)

- 1) Physical and chemical stability of granular crumb rubber in aqueous media. (O. Perales)
- 2) Activation of crumb rubber (F. Roman, O. Perales)
- 2) Optimization for sorption of heavy metal ions: Cu, Cd, Pb, Cr, As. (O.Perales, F. Roman)
- 3) Optimization for sorption of organic compounds: hexane, toluene and trichloroethylene. (F. Roman, M. Arocha, O. Perales)
- 4) Batch equilibrium and kinetic tests for sorption of SAs and TCs (antimicrobials) compounds. (F. Roman, O. Perales, M. Arocha)
- 5) Desorption behavior of up-taken species (F. Roman, O. Perales)

Year 3: Desorption, Modeling and Scaling-up

- 1) Sorption of inorganic and organic species in multi-species systems and columnar tests (Competitive sorption tests)
- 2) Desorption behavior of crumb rubber for inorganic, organics and antimicrobials compounds.
- 3) Sorption/desorption modeling of single-species systems.
- 4) Scaling-up of sorption and desorption results. Application to real effluents.

The scheduled activities for one year are presented as follows:

PLANNED ACTIVITIES	MONTHS												
	1	2	3	4	5	6	7	8	9	10	11	12	
Crumb rubber chemical stability tests													
Activation of crumb rubber													
Sorption Inorganics													
Sorption organics													
Sorption antimicrobials													
Desorption tests (preliminary)													
Preparation of final report													

12. Methods, Procedures and Facilities

12.1 Methods and Procedures

Granular crumb rubber, screened at different mesh sizes, will be kindly provided by REMA Corp. a tire rubber recycling company located in Caguas, Puerto Rico. It is estimated that a maximum of 4-kilograms of dry crumb rubber will be used for the sorption tests. This crumb rubber will be stored in appropriate containers.

12.1.1 *Chemical stability of granular crumb rubber*

The screened crumb rubber will be contacted with aqueous solutions under acid, neutral and alkaline solutions at fixed pH values for a suitable time at different temperatures. After contact, aliquots will be withdrawn, passed through a membrane filter and analyzed by ICP to determine the release of any inorganic species out from the sorbent. These simple experiments will provide important information regarding the chemical stability of the sorbent material, as a function of its particle size, before contacting it with test solutions.

12.1.2 *Experimental Procedures*

The basic set-up for the sorption/desorption tests includes temperature-controlled water shaker baths, stirrers, pH-meters and filtration and drying units. All quantitative analyses will be carried out in Dr. Felix 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.

i. Sorption experiments

The following parameters will be evaluated in batch equilibrium sorption experiments: average size of rubber particles, concentration of hazardous species, pH, crumb rubber/solution w/w ratio, ionic

strength and temperature. To evaluate the role of carbon black on the different compounds sorption, a reference carbon black used by the rubber industry will be tested as sorbent to estimate its sorption capacity. Synthetic solutions bearing the targeted species will be prepared in distilled/dionized water, which will also bear a background electrolyte. Solution pH will be adjusted by suitable amounts of NaOH or HNO₃ for the experiments with inorganic species. At the end of the equilibrium period, the pH of each suspension will be determined. Prepared solutions will be then contacted with granular crumb rubber in Erlenmeyer flasks (inorganic species) immersed in a temperature-controlled water bath shaker. Samples and blanks will be run in duplicate. After determining the pH of the solutions after the contact period, they will be filtered through membrane filters and submitted for quantitative analyses by atomic absorption and/or ICP-OES techniques. In the sorption kinetic experiments, aliquots will be obtained at different time intervals and submitted for quantitative analyses of the residual species contents right after filtration. Depending on the pH conditions, the solutions could be acidified in order to retard hydrolysis reactions. During the first step of the experimental work, the sorbent will be contacted with solutions containing a single species. Based on information provided by these experiments further experimentation will investigate the sorption behavior of granular crumb rubber in contact with solutions containing more than one target species to evaluate their competitive sorption behavior. The results of the experimental work will permit to determine the equilibrium uptake, sorption rates, and removal efficiency. Obtained data will be used to investigate the sorption behavior in columnar (bed) experiments and evaluate the number of stages needed for sorption.

The batch sorption tests for the organic compounds and antimicrobials will follow a procedure similar to that for inorganic species. However, screw cap vials with Teflon-lined septa will be used instead of common glass beakers and agitated on a hematological mixer. In order to minimize vapor loss and allow a suitable mixing, the head space in the vial after addition of the sorbent and sorbate, will be kept at approximately 1 ml. A background solution will also be used (CaCl₂ or NaNO₃) and HgCl₂ will be used as a biocide to avoid degradation of the organic compounds by bacteria or fungi. After contact period, samples will be withdrawn, centrifuged in close vessels and submitted for quantitative analyses. Samples and blanks will be run in duplicate.

ii. Activation experiments

In the chemical activation option, rubber particles will be contacted with a concentrated Zn solution at room temperature and at 85°C for 24 hours. Dried particles will then be contacted with solutions bearing inorganic contaminants. In turn, crumb rubber will be directly carbonized in N₂-CO₂ atmosphere at 850°C for 15-30min, in the physical activation option. Treated crumb rubber will be maintained in an oven at 110-120°C to dryness.

iii. Desorption experiments

In the case of inorganic species, the reversibility of the sorption reaction as a function of pH at 25°C will be evaluated. Granular crumb rubber containing sorbed species will be contacted with distilled water at different pH values and/or ionic strengths. Samples will be withdrawn at different contact times, filtered and submitted for analyses by the above mentioned techniques. The desorption capacity will be quantified based on the mass balance between the contents of target species in the solid and liquid phases. Depending on their sorption behavior, granular crumb rubber bearing organic species could be contacted with aqueous solutions at different values of pH, ionic strength as well as temperature. In this latter case, a suitable condensation unit will be implemented.

12.1.3 Quantitative analyses

Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption Spectroscopy (AAS) are widely used in the determination of toxic metals in environmental matrices and will be used in this project for the quantitative evaluation of the sorption and desorption experiments. ICP-OES has multi-elemental capabilities, good sensitivity, high precision, accuracy, wide dynamic range and cost effectiveness. US EPA method 200.7 is based on the ICP-OES technique and used for the determination of heavy metals including Cu, Cd, Pb, Cr, Hg and As in aqueous solutions. AAS is a selective and very sensitive technique for the determination of trace amounts of metals in the environment. It is superior in sensitivity to ICP-OES and will be used for traces determination. US EPA has published methods (SW 846) for the determination of toxic elements in environmental matrices. Some of these methods are EPA method 7000 (general information), 7060 (arsenic), 7130 (cadmium), 7190 (chromium) and (7470) lead. The concentration of the organic compounds in the aqueous, gas and solid phases will be determined by solid phase microextraction (SPME) and gas chromatography mass spectrometry. A Finnigan Gas Chromatography-Mass/Spectrometry/Mass Spectrometry system will be used for quantitative analyses of organic solvents in aqueous solutions. In turn, EDTA has been used to increase extraction of higher concentrations of TCs in order to improve recovery by chelating metal ions in solution. The methods developed by Lindsey et al. at 2001 and Moats 2000 using HPLC [18-19] will be adapted and used to quantify the levels of TCs and SAs in aqueous solutions.

12.1.4 Modeling the sorption behavior (year 3)

Sorption isotherms will be obtained and fitted to different sorption models, such as, linear, Langmuir, Freundlich, and BET. We are also interested in modeling the toxic uptake as a function of radial position r , and time, t , for spherical (or assumed spherical) particles. Absorption into the polymeric phase might be occurring simultaneously as adsorption into carbon black, likely at two different rates. The different rates of sorption could be modeled using a two-compartment model (Arocha et al., 1997). As an initial approximation, the two-compartment model will use a linear or nonlinear Freundlich isotherm as a constitutive equation to describe the sorption behavior. The main mass transfer effects for a two-compartment crumb rubber particle are the diffusional resistance of the polymeric matrix, the transport of contaminant through the polymeric matrix and adsorbent carbon black, and the external surface mass transfer resistance. The 'porous macrosphere with embedded microsphere-model', is an adaptation of a model developed by Arocha et al. [20] to describe nonlinear sorption for soil-VOCs systems. Arocha's model in turn is an adaptation of the Ruckenstein et al, [21] linear sorption-diffusion model for ion exchange resins. A tire-rubber particle is pictured as a large spherical aggregate of a tire-rubber matrix in which small microspheres of uniform size of carbon black are embedded. The embedded adsorbents (i.e., carbon black) which contain small pores are exclusively contained in the small spheres, while the macropore spaces facilitate the contaminants to travel across the polymeric matrix for reaching the surface of the adsorbents. The adsorbent fraction, made up of particles of carbon black, with estimated diameter of less than 100 nm, would contain most of the active pores for adsorption in the tire-rubber matrix and adsorbs organic and inorganic contaminants strongly. Adsorption, absorption and diffusion in a two-compartment sorbent can be described by one compartment dealing with the transport processes occurring within the rubber matrix and another with that occurring within the embedded porous carbon black. Implementing the Ruckenstein et al. and Arocha et al. extended nonlinear model, the macropore aqueous-phase rubber-matrix concentration field is governed by the mass balance equation:

$$\varepsilon_a \frac{\partial C_a}{\partial t} + S_a \frac{\partial \tilde{C}_{S_a}}{\partial t} = D_{a,eff} \frac{1}{r_a^2} \frac{\partial}{\partial r_a} \left(r_a^2 \frac{\partial C_a}{\partial r_a} \right) - \eta 4\pi R_i^2 D_{i,eff} \left(\frac{\partial C_i}{\partial r_i} \right)_{r_i=R_i} \quad (1)$$

It includes terms for accumulation in the aqueous-phase macropore structure and at the macrosphere surface, diffusion into the macrosphere volume, and diffusional flux from the macropore aqueous phase to the microspheres surfaces (carbon black). Subscripts a and i stand for transport through macrospheres and microspheres, respectively. For a unit microsphere, the mass balance for the micropore aqueous-phase concentration is,

$$\varepsilon_{i,p} \frac{\partial C_i}{\partial t} + S_{i,p} \frac{\partial \tilde{C}_{S_i}}{\partial t} = D_{i,eff} \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial C_i}{\partial r_i} \right) \quad (2)$$

This equation includes terms for accumulation in the aqueous phase and at the surface, and diffusion into the micropore volume. In equations (1) and (2), $D_{i,eff} = \varepsilon_{i,p} D_i / \tau_i$ and $D_{a,eff} = \varepsilon_a D_a / \tau_a$ are the effective diffusivities, and τ_a and τ_i are the tortuosity factors for macropores in the rubber matrix and micropores in the carbon black adsorbents, respectively. The pore diffusivities, D_a and D_i , account for the contributions of Knudsen, molecular, and surface diffusion.

12.2 Facilities

Major equipment and instrumentation are already available in Dr. Felix Roman's (Co-PI) Laboratory, Chemistry Department. The set-up for sorption tests includes a shaker water bath, pH-meters, filtration units and drying ovens. These minor pieces of equipment were purchased thanks to a seed-money grant assigned to Dr Oscar Perales by PRWRERI for the first year of this project. A brief description of available instruments and their capabilities is presented as follows:

- 1) Finnigan Polaris GC/MS/MS system equipped with direct insertion probe and electron impact and chemical ionization modes. This system will be used to measure the levels of volatile organics in the proposed project.
- 2) Leeman Labs Inductive Coupled plasma-Optical Emission Spectroscopy system equipped with a high resolution Echelle Monochromator and auto sampler. It will be used to measure the levels of the toxic metals involved in the project.
- 3) Two Varian Spectra 400 Atomic Absorption units. They are excellent for elemental analysis at trace levels (low ppb levels).
- 4) A CEM microwave digestion system will be used for fast acid digestions of solid samples such as rubber particles.

13. Related Research.

Publications related to the specific use of granular crumb rubber to remove inorganic ions and organic species from aqueous solutions are scarce. Available literature are mostly focused on batch experiments involving Cd(II), Pb(II), Hg(II), without considering the influence of the speciation and oxidation state of the targeted inorganic species or organic structure, factors that are strongly related to sorption behavior in most of existent sorption/adsorption systems. To our knowledge, there is no reported attempt to use crumb rubber to remove antimicrobials compounds from aqueous solutions.

Although the potential use of rubber particles to remove organic compounds and aqueous Cd, Pb and Hg ions has been preliminary evaluated [22-26], available literature lacks of a more comprehensive discussion of involved mechanisms and explanations to observed results. Knocke et al., [22] conducted studies to evaluate the sorption behavior of waste tire rubber for inorganic Hg from aqueous solution. In these experiments ground samples of vulcanized tire rubber was used in batch sorption studies. The results showed that, pH was the most important factor, with an optimum range of 5.5-6.0. It was suggested that the diffusion of Hg through pores in the rubber sorbent was the rate-limiting step regarding final uptake. We suggest that using higher porosity crumb rubber will increase inorganics sorption. Rowley, Husband and Cunningham [23] proposed tentative mechanisms of adsorption of Cd(II), Hg(II) and Pb(II) onto shredded rubber. The suggested mechanisms were dependent on the type of metal ion; Hg and Cd uptake took place with a simultaneous release of native embedded Zn suggesting an ion exchange mechanism. On the other hand, Pb adsorption did not involve any Zn displacement. Gunasekara, Donovan and Xing [24], have shown that ground discarded tires can remove inorganic mercury ions from aqueous solutions. Two types of ground tire rubber, a mixture of natural and synthetic rubbers and a completely natural rubber were used in the form of black powder. The sorption of mercury was slower in comparison to organic compounds and its sorption affinity was found to be concentration dependent. Preliminary results showed that for 1 g of rubber powder in 100 ml of Hg (II) solution, complete sorption occurred for all Hg concentrations below 4 µg/ml. Although the effect of solution chemistry on the ‘binding’ of Hg to rubber powder was studied, the authors stated the need for a more detailed evaluation of the process rate and a better explanation of the involved sorption mechanisms in this system.

Concerning the sorption capability of rubber for organic compounds, J. Y Kim et al. [25] conducted batch sorption tests for m-Xylene, ethylbenzene, toluene, trichloroethylene, 1, 1, 1-trichloroethane, chloroform and methylene chloride. The corresponding partition coefficients decreased from 977 L/kg for m-Xylene down to 13 L/kg for the methylene chloride. Although different experimental conditions were tested, e.g. ionic strength, pH, ground tire particle size and temperature, no significant effect on the sorption behavior was observed. It was suggested that the organic compounds sorbed primarily onto tire rubber polymeric materials and partially carbon black. Gunasekara *et al* [24] also investigated the sorption of naphthalene and toluene by granular crumb rubber. The sorption of organic compounds was relatively fast and thirty minutes of contact time was enough to achieve an 80% of naphthalene removal from an initial concentration of 15 µg/l. Results suggested that rubber particles had a greater affinity for naphthalene than toluene. Even though the sorption of inorganic and organic compounds onto granular crumb rubber has been observed, still there is a lack of quantitative information concerning the real equilibrium uptakes and sorption kinetics for the design of practical systems involving the use of crumb rubber as a sorbent material for environmental remediation.

13.1 Preliminary Results Phase-I (Sorption of inorganic species)

Phase-I of our ongoing work is focused on the determination of sorbing behavior of crumb rubber in presence of different types of heavy metal ions. The purpose of these ‘screening-tests’ is to determine the sorption capability of crumb rubber in presence of select contaminant species in aqueous phase. Based on the obtained results, the contaminants up-take and sorption rate will be optimized during Phase-II (this proposal).

As suggested by the data showed in figures 1 and 2, our preliminary results confirmed the capability of waste tire crumb rubber to up-take Cu(II), Cd(II) and Pb(II) ions from aqueous

solutions at room-temperature. Synthetic metal ion solutions were prepared by dissolving suitable weights of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, CdCl_2 and $\text{Pb}(\text{NO}_3)_2$ in de-ionized water. The pH of the metal solutions were then adjusted at 1.5 and 6.0. 100-ml of prepared solutions was contacted with 1 gram of 14-20 mesh crumb rubber in a temperature-controlled water bath shaker room-temperature. Aliquots of 2.5 ml were withdrawn for different contact times to monitor the progress of the sorption process. Samples were acidified and analyzed for Cu, Cd or Pb by using an inductively coupled plasma optical emission spectroscopy unit (ICP-OES Leeman Labs, Inc.). Samples and blanks were run in duplicate. Quality controls were carried out as it indicates the method 200.7. U.S. EPA. Following figures show the variation of metal ions concentration with contact time for two different levels of initial concentrations of metal ions (1-5ppm). Due to space restrictions, other results including the data from sorption of organic compounds will be presented in the final Phase-I full report to PRWRERI.

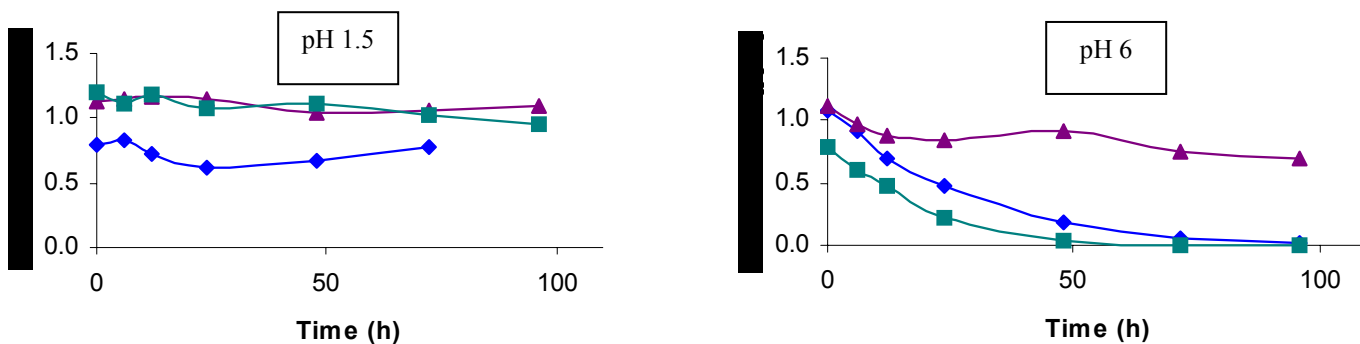


Figure 1. Sorption of Cu, Cd and Pb ions by 14-20 mesh crumb rubber (10 g/l). Initial concentration of metals ~ 1ppm.

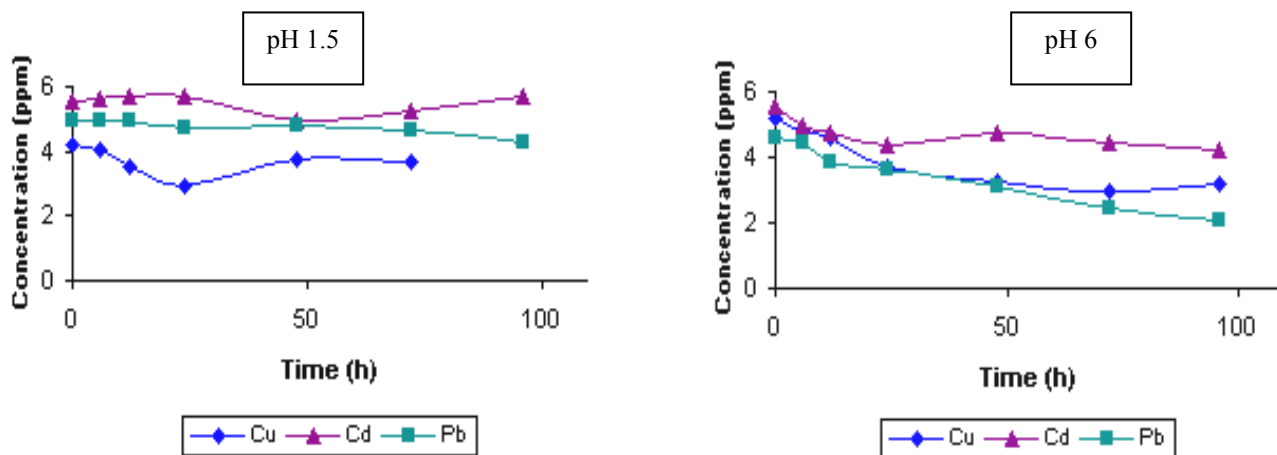


Figure 2. Sorption of Cu, Cd and Pb ions by 14-20 mesh crumb rubber (10 g/l). Initial concentration of metals ~ 5ppm.

As evident, the sorption behavior was dependent on the type of ion and pH of the starting solutions. The general trend was to achieve a significant removal of metal ions at pH close to 6.0, which is in good agreement with the behavior observed in different adsorption systems where the a more neutral pH favors the metals up-take and sorption rates. The sorption behavior was also dependent on the type of ions and an order of preference of crumb rubber for investigated metals was observed: $\text{Pb}, \text{Cu} > \text{Cd}$. The sorption trend becomes more evident for the most diluted initial metal ions concentration (~ 1 ppm), where hazardous Pb species was removed completely. The less mobility and large ionic size (0.97\AA) of Cd species at pH 6 can explain the observed faster saturation of crumb rubber when Cd ions were adsorbed. In turn, the fast and continuous sorption of large-sized Pb ions (1.32\AA), expected to be strongly complexed by OH^- ions in neutral solutions, could be related to a different

mechanism, that may involve ionic exchange with Zn sites available from ZnO in crumb rubber, as suggested by Rowley et al. [23].

13.2 Sorption of antimicrobials from aqueous solutions

Current studies aim at understanding better the elimination of antibiotics during municipal wastewater treatment facilities including sorption onto sewage sludge and bio-transformation. Giger [27] studied the behavior of antibiotics in a waste water treatment plant, in which conventional activated sludge treatment followed by a sand filter was operated in parallel with a pilot-scale membrane bioreactor. However, recent results and the type of evaluated antimicrobials have not been published yet. Pedersen [28] have investigated the sorption of sulfamethazine (SMZ) and sulfamethoxazole (SMX) to smectitic clays and natural organic matter (NOM) in batch sorption tests. SAs sorption was strongly pH dependent with neutral species exhibiting maximal association with both smectitic clays and NOM. SMZ adsorption to smectitic depended on the type of exchangeable cations whereas the type of exchangeable cation did not affect the extent of SMX adsorption. D. Aga et al. [29] have developed quantitative techniques to determine TCs and SAs in aqueous phase, as well as the sorption behavior of TCs on activated clay in an effort to understand the interaction of this type of compound with soil particles. Their research interests deal with the degradation of TCs in soil fertilized with manure, microbiodegradation of tetracycline antibiotics, fate of sulfonamides in the aquatic environment and factors that affect the mobility of tetracycline in soil. Analysis of the soil extracts showed the presence of non-degraded chlortetracycline and transformation products that include isochlortetracycline and anhydrochlortetracycline. They have also investigated the interactions of oxytetracycline, a popular TCs antibiotic, with model clay adsorbents as a function of suspension pH. The adsorption of oxytetracycline in the natural and sodium forms of montmorillonite clay decreases with increasing pH in the order $\text{pH } 1.5 > \text{pH } 5.0 > \text{pH } 8.7 > \text{pH } 11.0$, suggesting that cationic exchange interactions are dominant at lower pH values, when oxytetracycline has a net positive charge. Karthikeyan [30] have investigated the sorption of tetracycline and fluoroquinolone (ciprofloxacin) to Fe and Al hydroxides, well-known soils components, and by humic substances. The sorption behavior of ciprofloxacin took place with strong pH dependence, with a maximum sorption of 72% unaffected by reaction time around neutral pH. In turn, tetracycline sorption exhibited mild-pH dependence and a significant difference between LSC and HPLC-determined removal levels.

14. Training Potential

On a training basis, the successful execution of this project will strengthen the education in disciplines related to environmental chemistry, applied chemistry, materials, and remediation and therefore strengthening the new doctoral program in Applied Chemistry. The project will also strengthen the research base of the Ph.D. program in Environmental option administered by the Civil Engineering Department. Lately, an advanced undergraduate course in Materials Recycling has been approved. This course will also be a part of the MS Curriculum in Materials Science and Engineering (MSE) hosted by General Engineering Department. It is expected that at least two graduate student, paid with non-federal matching funds, will be involved in the proposed research. Two undergraduate students will be part of the research activities through their participation in the Undergraduate Research Course. Involved PI's will be in charge of training participant students whom will be exposed to a multidisciplinary research environment and get hands on experience by their deep involvement in training and research activities in experimental design, quantitative chemical analysis, mathematical modeling, on-field activities, and implementation of environmental protection

technologies. Also, students and faculty are welcomed to field-trip REMA facilities and get exposed to operational aspects of tire recycling. Consequently, the students working for this project and the ones affected by the educational modules will get well-trained to improve their opportunities in the job market in the area of recycling and remediation, and will in turn contribute to the consolidation of a 'green culture' in Puerto Rico.

Field of study	Undergraduate	Master's degree	PhD degree	Post PhD	TOTAL
Chemistry	01	01			02
Civil Engng.	01	01			02

General References

- [1] C. M. Benbrook. Antibiotic Drug Use in US Aquaculture. 2002. Information Available at: <http://www.iatp.org>
- [2] T. L. Jones-Lepp, D. A. Alvarez et al. Analytical Chemistry Research Needs for Mapping Trends of Pharmaceutical and Personal Care Product Pollution from Personal Use: Some Current Research and Future Needs, September 2001. Paper available in <http://www.epa.gov/nerlesd1/chemistry/ppcp/trends.htm>
- [3] D. Kolpin, E. Furlong, M. Meyer, E. M. Thurman, et al. Pharmaceutical, Hormones and Other Organic Wastewater Contaminants in US Streams, 1999-2000: A National Reconnaissance. *Environm. Sci. Technol.*, 36, 6, 1202, March 2002.
- [4] A. Boxall, D. Kolpin, et al. Are Veterinary Medicines Causing Environmental Risks? *Environm. Sci. Technol.* A287, August 1, 2003.
- [5] E. Golet, I. Xifra, H. Siegrist, et al. Environmental Exposure Assessment of Fluoroquinolone Antibacterial Agents from Sewage to Soil. *Environ. Sci. Technol.*, 37, 15, 3243, 2002.
- [6] D. Kim, J. Choi, J. S. Kim, and D. W. Lee. Determination of Sulfonamides in Meat y Liquid Chromatography Coupled with Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Bull. Korean Chem. Soc.*, 23, 11, 1590, 2002.
- [7] F. Stuer-Lauridsen, M. Birkved, L. P. Honsen, et al. *Chemosphere* 40, 783, 2000.
- [8] Smith, K. E., *N. Engl. J. Med.*, 340, 1525, 1999
- [9] M. E. Lindsey, M. Meyer, et al. Analysis of Trace Levels of Sulfonamide and Tetracycline Antimicrobials in Groundwater and Surface Water Using Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry. *Anal. Chem.* 73, 4640, 2001.
- [10] T. Christian, R. Schenider, H. Farber, D. Skutlarek and H. Goldbach. Determination of Antibiotics Residues in Manure, Sol and Surface Waters. 2003. Report available in: <http://www.fate.uni-bonn.de/netscape/download/Manuskript-Minneapolis.pdf>
- [11] J. Tolls. Sorption of Veterinary Pharmaceutical in Soils: A Review. *Environ. Sci. Technol.*, 35, 17, 3397, August 2001.
- [12] W. Giger, A. Alder, et al. Occurrence and Fate of Antibiotics as Trace Contaminants in Wastewaters, Sewage Sludges and Surface Waters. *Chimia* 57, 485, 2003.
- [13] US EPA: Municipal Solid Waste: Tires, EPA, 2003. <http://www.epa.gov/epaoswer/non-hw/muncpl/tires.htm>
- [14] Rubber Recycling Rolls Along, Institute of Scrap and Recycling Industries, Inc., <http://www.isri.org/industryinfo/rubber.htm>
- [15] V. L. Shulman, Tyre Recycling After 2000: Satis and Options, The European Tyre Recycling Association, France, 2000.
- [16] Waste Tires. *Report of California Integrated Waste Management Board and Department of Energy*. December 11, 2003.
- [17] E. Velasquez, Reciclaje de neumáticos: una gran industria, Dimensión, *Revista del Colegio de Ingenieros y Agrimensores de Puerto Rico*, Vol. 15, 4, 2001.
- [18] M. E. Lindsey, M. Meyer, et al.. Analysis of Trace Levels of SAs and TCs Antimicrobials in Ground and Surface Water Using Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry. *Anal. Chem.* 73, 4640, 2001, and T. Christian, R. Schenider, et al. Determination of Antibiotics Residues in Manure, *Sol and Surface Waters*. 2003.
- [19] W. A. Moats. Determination of Tetracycline Antibiotics in Beef and Pork Tissues Using Ion-Paired Liquid Chromatography *J. Agric. Food Chem.*, 48 (6), 2244 -2248, 2000.
- [20] Arocha MA, Jackman AP, and McCoy BJ. Adsorption Kinetics of Toluene on Soil Agglomerates: Soil as a Biporous Sorbent, *Environ. Sci. Technol.* , 30, 1500-1507, 1996.
- [21] Ruckenstein, E; Vaidyanathan, et al. Sorption by Solids with Bidisperse Pore Structure, *Chem. Eng. Sci.* 26, 1305-1318, 1971.
- [22] Knocke, W. R. and Hemphill L. M., Mercury (II) sorption by waste rubber, *Eater Res.*, 15(2), 275, 1981
- [23] Rowley A. G., Husband, et al., Mechanisms of metal adsorption by waste tire rubber, *Water Res.*, 18(8), 981, 1984
- [24] Gunasekara, A. Donovan J., et al., Ground tires remove naphthalene, toluene and Hg from water, *Chemosphere* 41, 1155, 2000
- [25] Kim, J. Y., Park J. K., et al., Sorption of organic compounds in the aqueous phase onto tire rubber, *J. Env. Engng.*, Sept. 1997, 827
- [26] Unnikrishnan G, Thomas S., et al., Sorption of aromatic hydrocarbons through filled natural rubber, *Polymer*, 37, 2687, 1996.
- [27] W. Giger, A. Alder, E. Golet et al. Occurrence and Fate of Antibiotics as Trace Contaminants in Wastewaters, Sewage Sludges and Surface Waters. *Chimia* 57, 485, 2003.
- [28] J. Pedersen, J. Gao, H. Bialk. Sorption of SA Antimicrobial Agents to Clays and Natural Organic Matter. *G. Soc. Am. Abs.*, Ann. Meeting, 35, 6, 370, September 2003.
- [29] D. Aga. Available at: <http://www.chem.buffalo.edu>
- [30] K. G. Karthikeyan, W. F. Bleam, et al. Occurrence of Antibiotics in Wastewater Effluents and Their Mobility in Soils: A Case Study for Wisconsin. DNR Research Abstract. Annual Summary, 2003. Available in http://bse.wisc.edu/Updates_121203_012104

15. Investigators' Qualifications

Oscar J. Perales-Perez (PI)

Department of General Engineering
University of Puerto Rico at Mayagüez

a. Education

University of Engineering, Lima, Peru Metallurgical Engineering B. Sc., (honors), 1986
University of Engineering, Lima, Peru Metallurgical Engineering P. E., 1992
Tohoku University, Sendai, Japan Materials Processing (Anticontamination Lab) Dr. Eng., 1998

b. Professional experience

Assistant Professor, (tenure-track) Dept. of General Engr., Univ. of Puerto Rico – Mayagüez [Aug. 2002 to date]

Professor, Environmental Assessment and Remediation Alternatives, Graduate School National Engineering University, Lima, Peru. [Dec. 2001-July 2002].

Visiting Assoc. Prof. in Materials Processing, Center for Interdisciplinary Research, Tohoku University, Japan [Dec. 1998- Nov. 2001].

Consulting Engineer, SGS-Peruvian branch, Division of Environmental Issues, [Sept. 1994-Sept. 1995].

Project Engineer, Newmont Gold Corporation, Metallurgical Operations, Peru, [Nov.1990-Aug.1991].

External consultant, Peruvian National Council on Science and Technology, Purification of Maras' brines by fractional crystallization, Peru, [Dec.1989-Dec. 1990].

Assistant Professor in Aqueous Processing and Environmental Protection Technologies, Department of Metallurgy, National Engineering University, Lima, Peru, [Oct. 1989-July 2002].

Lecturer, Metallurgy, Department of Metallurgy, National Engineering University, Lima, Peru [Oct. 1986-Sept. 1989].

Research Engineer, De-Re Metallica Laboratory: Hydrometallurgical processing and environmental protection technologies, Lima, Peru, [Dec. 1985-Oct. 1986].

c. Selected Publications (over 35 in referred Journals and conferences)

- 1) Perales, O., Sasaki, H. and Umetsu, Y. Precipitation and densification of magnetic iron compounds at room-temperature. *Hydrometallurgy* 50 (1998) 223-242
- 2) Perales O. and Umetsu, Y. ORP-monitored magnetite generation from aqueous solutions at low temperatures. *Hydrometallurgy* 55 (2000) 35-56.
- 3) Perales O., Tohji, K., and Umetsu, Y. Ambient-temperature synthesis of Metal-bearing ferrite: How and Why?. *J. Alloys and Compounds* 290(1999): 129-136.
- 4) Perales O. and Umetsu, Y. Ambient-temperature precipitation of Zn ions as ferrite-type compounds from aqueous solution. *Hydrometallurgy*. Vol. 63, Issue 3, March 2002, p. 235-248.
- 5) Perales O., Kasuya A., Umetsu Y. and Tohji K. The relationship between the reaction conditions and the characteristics of the metal-bearing ferrite produced at ambient temperature. *Ultrafine Grained Materials* (R. S. Mishra, S. L. Semiatin, C. Suryanarayana and T. C. Lowe Book Editors). TMS, USA, 2000. P. 41-49.
- 6) Perales O. and Umetsu, Y. Ambient-temperature precipitation of heavy-metal ions from aqueous solutions as ferrite-type compounds. *Proceedings of 2000 PMP II: Processing Materials for Properties*. TMS, 5-8 November 2000, San Francisco, USA.
- 7) Perales O., Tohji K., Umetsu Y. Room-temperature precipitation of metal-bearing ferrites from aqueous solutions. *Quarterly of the Mining and Materials Processing Institute of Japan*. Vol. 40, 2002
- 8) Perales O., Sasaki H., Jeyadevan B., Kasuya A and Tohji K. Production of Monodispersed Particles by Using Effective Size Selection Methods at the Nanosize Level. *Jap. J. Institute of Pure and Applied Physics, IPAP Series 3*, pp. 101-104, June 2001.

- 9) Kasuya, G. Milczrek, Perales O., et al., Size- and shape-controls and electronic functions of nanometer-scale semiconductors and oxides. *Colloids and Surfaces. A: Physic. and Engn. Aspects*, 202, 2-3, 2002, p. 291-296.
- 10) Perales O., Sasaki H., Jeyadevan B., Kasuya A and Tohji K. Production of Monodispersed Magnetic Particles by Using Effective Size Selection Methods at the Nanosize Level: Size-dependent Magnetic Properties. *J. Appl. Phys. Vol. 91, No. 10*, pp. 6958-6960, 2002.
- 11) Chinnasamy C.N., Jeyadevan, B., Perales-Perez O., Kasuya, A., and Tohji, K. Growth Dominant Co-Precipitation Process to Achieve High Coercivity at Room Temperature in CoFe_2O_4 Nanoparticles. *Trans. IEEE Magnetics*, 38, 5, 2640-2642 (2002).
- 12) C. N. Chinasammy, M. Senoue, B. Jeyadevan, O. Perales-Perez, K. Shinoda and K. Tohji. Synthesis of size-controlled CoFe_2O_4 particles with high coercivity and squareness ratio. In press.. *J. Colloids and Interface Sci.*
- 13) L. Alamo, O. Perales-Perez, F. Roman. Use of Crumb Rubber to Remove Heavy Metal Ions from Aqueous Solutions. To be presented at the ACS Conference, March 13-17, 2005, Washington DC.

d. Synergistic Activities (selected)

1. Member Materials Committee to create a interdisciplinary Materials Sci. & Engr. graduate program at the Univ. of Puerto Rico – Mayagüez [Aug. 2002 to date].
2. Member of UPRM Research Task Force to evaluate the environmental conditions in Vieques' agricultural areas [Sept. 2002 to date].
3. Principal Investigator, PRWRERI-USGS: Investigation of Sorbing Behavior of Crumb Rubber to Remove Inorganic and Organic Contaminants from Aqueous Solutions (PHASE-I) [March 2004-Feb 2005].
4. Invited Panelist for NSF-SBIR/STTR Program, March and September 2003, September 2004, Washington D.C.
5. Invited reviewer USGS-NIWR competitive grant program. USGS-NIWR. April 2004
6. Consultant for Environmental Impact Assessment. Ministry of Energy and Mines, Peru. Jan 2003-Dec 2003

C. Information Transfer Plan

The area of the proposed research addresses critical issues regarding the removal of hazardous compounds from water and the recycling of used rubber tires, solving two problems simultaneously and creating not only technological but also social expectations. There will be several strategies to foster education and the dissemination of results and activities related to this proposal:

- i) Presentation of results in local and international conferences hosted by professional organization such as The Minerals, Metals and Materials Society (TMS), The American Chemical Society, The American Institute of Chemical Engineers (AIChE) and The American Institute of Civil Engineers.
- ii) Inclusion of the subject: *Recycling waste tires to solve environmental problems* in a new course on Materials Recycling (to be hosted by General Engineering) and Environmental Chemistry (hosted by the department of chemistry).
- iii) Development of a teaching experimental module addressing the water pollution problem by inorganic, organic and antimicrobials species and the tire rubber recycling issue.
- iv) Presentation of the results to local and federal environmental protection agencies, the Puerto Rico Farm Bureau and other interested parties.
- v) Industry partnership with REMA Inc., fostering student field trips and Coop for training in real recycling and remediation problems.

An upper-level undergraduate course in Materials Recycling to be offered by the Department of General Engineering at UPRM has been approved. The pilot course will be offered affecting initially 30 students (one section class) but with the potential to reach about 300 students (ten class sections) when fully established.

In addition, the proponents will prepare a Class Module which will be made available to the Civil and Chemical engineering students going through the curriculum of the undergraduate Certificate in Environmental. The module, addressing the inorganic, organic and antimicrobial pollution in water bodies and streams and the proposed solutions, could be a topic or a discussion problem within such classes as, Water Resources Engineering (INCI 4138) a in Civil Engineering and Materials Recycling (INGE4XXX).

Our results will be presented not only to scientific community (TMS, ACS Conferences, among others) but also to local and federal environmental protection agencies, the Agriculture Extension Program of UPRM, and the Puerto Rico Farm Bureau and other interested parties. The idea is to disseminate the knowledge base available to agricultural and rural communities and to improve management practices. In the particular case of the antimicrobials problem, The Poultry Producers Chapter has expressed their support for this project. They are also willing to participate in workshops and seminars that will address poultry waste management and conservation practices to reduce soil erosion and potential contamination of soil and nearby water resources. It is also expected a tight interaction with the Waste Management Board of Puerto Rico, the Puerto Rican Chapter of EPA and the Junta de Calidad Ambiental (the local environmental regulation agency.)

Cooperation and institutional units involved

This proposal is the result of a multidisciplinary collaboration among the **Departments of General Engineering, and Chemistry**. A strong and very active interaction between these Departments, through the Graduate Program in Materials Science and Engineering (MSE) to be hosted by the later,

has also been established. Nowadays, the proposed Master program in MSE is at the UPRM Senate level. In particular, General Engineering faculties are collaborating actively with the Department of Chemistry in the area of Materials & Environmental Engineering in both, research and curriculum development. Furthermore, the **Departments of Food Science and Technology and Agronomy** and Soils are also actively collaborating with the Chemistry Department and have laboratory space within the new chemistry building. Several chemistry faculty members are research advisors to graduate and undergraduate students from these departments.

The sorbent material already cleaned and downsized to different particle sizes, 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. Furthermore, as stated in the letter received from REMA, Inc., participant personnel can field-trip REMA facilities, and get exposed to the operational aspects of tires recycling. Some experiments could also be run in REMA's laboratories.

The **Puerto Rican Poultry Producers** Chapter has also expressed their support for this project. The Chapter has also expressed availability of the poultry operation facilities for any study or evaluation of the antimicrobials problem that this project addresses. There will be also interaction with the **Waste Management Board** of Puerto Rico and the Puerto Rico Chapter of **EPA** and the **Junta de Calidad Ambiental** (the local environmental regulation agency.)

Felix R. Roman
Department of Chemistry
University of Puerto Rico at Mayaguez

a. Education

Post Doctoral, summer 1991 and 1995, Armed Forces Institute of Pathology in Washington, D.C.
Ph.D. in Chemistry, May 1989, University of Nebraska-Lincoln
M.S. in Chemistry, May 1986, University of Nebraska-Lincoln
B.S. in Chemistry, May 1981, Inter American University of Puerto Rico at San Germán

b. Professional experience

Professor-July 1996 to Present

Department of Chemistry, University of Puerto Rico at Mayagüez Campus.

Associate Professor June 1990 to July 1998

Department of Mathematics and Physical Sciences, Inter American University of Puerto Rico, San German Campus. Acting chairman of the Mathematics and Physical Sciences Department at the Inter-American University at San Germán during August 1995 to July 1996

Participated in the development of a curriculum for the establishment of a B.S. in Environmental Technology and a M.S Environmental Science at the Inter American University at San Germán. Also participated in the development of a Ph.D. program in Applied chemistry (includes environmental option) at the University of Puerto Rico at Mayagüez. This program is expected to begin next fall.

NASA consultant. Goddard Space Flight Center-Space Simulation Test Engineering Section. Assisted in the analysis of procedures for cleaning the Testing Vacuum Chambers at the Space Simulation Test Engineering Section resulting in a joint publication.

c. Selected publications

- 1) Juan A. Román, George Stitt and Félix R. Román. GSFC Space Simulation Laboratory Contamination Philosophy: Efficient Space Simulation Chamber Cleaning Techniques. 19th Space Simulation Conference; Cost Effective Testing for the 21st Century. NASA conference Publication 3341, Pages 23-40, 1996.
- 2) Richard J. Meyer, Félix R. Román, Ram B. Sharma Richard A. Ferrieri and Edward P. Rack. Stereochemical Consequences of Recoil Halogen Substitution. Radiochimica Acta 62, 181-187 (1993)
- 3) A.J. Blotcky, J.P. Claassen, E.P. Rack and F.R. Román. Determination of Aluminum by Chemical and Instrumental Neutron Activation Analyses in Biological Standard Reference Material and Human Brain Tissue. Analytical Chemistry Vol. 64, No. 23, 2910-2913 (1992)
- 4) Presentation: 9TH Ion mobility Spectroscopy Conference, Halifax, Canada, August 2000.
Evaluation of Filter Material as Sample Collectors for the Baringer 400 Ion Mobility Spectrometer.
- 5) Presentation: XXIII American Chemical Society Senior Technical Meeting, Palmas del Mar Humacao, PR, November 1999. Analytical Method Development for the Detection of Trace Amounts of Energetic Organic Peroxides by GC/MS and HPLC-PDA.

d. Research interests and synergistic activities

Present

Currently working in the following projects: 1) method development for the analysis of water, and soil pollutants such as polyaromatic hydrocarbons, pesticides and heavy metals using Gas Chromatography-Mass Spectrometry, High Performance Liquid Chromatography, ion chromatography, Atomic Absorption Spectrophotometry and Inductive Coupled Plasma-Optical Emission Spectrophotometry, 2) method development for the trace amount of explosives using chromatographic and spectroscopic techniques

Armed Forces Institute of Pathology; summers 1991, 1997.

Developed analytical methodology for the determination of trace amounts of aluminum, cadmium, iron and lead in human tissues using microwave dissolution and Zeeman furnace Atomic Absorption Spectrophotometry and Inductive Coupled Plasma-Optical emission Spectrophotometry.

Member of UPRM Research Task Force to evaluate the environmental conditions in Vieques' agricultural areas [Sept. 2002 to date].

Marco A. Arocha
Department of General Engineering
University of Puerto Rico at Mayagüez

a. Education

University of California-Davis	Ph.D.	Chemical Engineering	1995
University of Puerto Rico, Mayagüez	M.S.	Chemical Engineering	1989
National Polytechnic Institute	B.S.	Chemical Engineering	1978

b. Professional experience

2000-Present	Headperson, General Engineering Department
1999-Present	Associate Professor, General Engineering Department
1998-summer	Senior Fellow Researcher, Warner Lambert-Pfizer R&D
1999-summer, 2000	Headquarter, Morris Plains, NJ
1996-1999	Assistant Professor, General Engineering Department
1982-1985	Plant Manager, Intra Industrial Group
1977-1982	Process Engineering, Intra Industrial Group

c. Selected publications

- 1) Arocha, MA, "Vapor Phase Contaminant Transport in Soil with Micropores, Macropores, and Organic Matter: A Diffusion Model for Sorption and Desorption Experiments," Environmental Science and Technology, submitted.
- 2) Arocha MA, Vargas FF, Ramirez-Vick JE. "Albumin Effect on the Permeability of Cultured Endothelium". Submitted to Journal of American Physiology.
- 3) Arocha MA, McCoy B, Jackman A. "Numerical Analysis of Sorption and Diffusion in Soil with Micropores, Macropores, and Organic Matter." Computers in Chemical Engineering, **1997**, 21, 489-499
- 4) Arocha MA, McCoy B, Jackman A. "VOC Immobilization in Soil by Adsorption, Absorption, and Encapsulation." Journal of Hazardous Materials, **1996**, 51, 131-149
- 5) Arocha MA, McCoy B, Jackman A. "Adsorption Kinetics of Toluene on Soil Agglomerates: Soil as Biporous Sorbent." Environmental Science and Technology, **1996**, 30, 1500-1507

d. Synergistic Activities

- 1) Member of the Ad Hoc Committee to establish a Master Science program in Materials Science and Engineering
- 2) Member of the Ad Hoc Committee to establish a Ph.D. program in Bioengineering
- 3) Co-PI of the DoEd funded project: "Materials Science and Engineering Education Improvement for a Hispanic-Serving Institution," MSEIP-US DoEd to create laboratory infrastructure for teaching Materials Science and Engineering
- 4) PI of the NSF funded project: "Bioengineering Research and Education (BReEd) Experiences at UPRM"

Budget Breakdown

Project Number: 2005PR21B

Project Title: Removal of Inorganic, Organic and Antimicrobials Contaminants from Aqueous Solutions by Waste Tire Crumb Rubber

Cost Category	Federal	Non-Federal	Total
Salaries and Wages			
-Principal Investigator(s):	3000	0	3000
-Graduate Student(s):	0	0	0
-Undergraduate Student(s):	0	0	0
-Others:	0	0	0
-Total Salaries and Wages:	3000	0	3000
Fringe Benefits	276	0	276
Supplies	6324	0	6324
Equipment	8400	0	8400
Services or Consultants	0	0	0
Travel	2000	0	2000
Other Direct Costs	0	0	0
Total Direct Costs	20000	0	20000
Indirect costs on federal share	XXXXXXXXXX	0	0
Indirect costs on non-federal share	XXXXXXXXXX	0	0
Total Estimated Costs	20000	0	20000
Total Costs at campus of the University on which the Institute or Center is located.	20000	0	20000
Total Costs at other University Name of University:	0	0	0

Budget Justification

**Project
Number:** 2005PR21B

Project Title: Removal of Inorganic, Organic and Antimicrobials Contaminants from Aqueous
Solutions by Waste Tire Crumb Rubber

Salaries and Wages. *Provide estimated hours and the rate of compensation proposed for each individual. (Tuition remission and other forms of compensation paid as or in lieu of wages to students performing necessary work are allowable provided that the tuition or other payments are reasonable compensation for the work performed and are conditioned explicitly upon the performance of necessary work.)*

The PIs will receive a one-time \$1,000 summer salary of support at a rate of \$25/per hour during 40 hours of work in the project. The following table details this information: PI/Co-PI Year 1 Oscar Perales Base Salary \$ 50,760 Summer Salary \$ 1,000 Felix Roman Base Salary \$ 57,360 Summer Salary \$ 1,000 Marco Arocha Base Salary \$ 57,360 Summer Salary \$ 1,000 Total \$ 3,000 Table 1: PIs base and summer salaries

Fringe Benefits. *Provide the overall fringe benefit rate applicable to each category of employee proposed in the project.*

The fringe benefits are computed as 9.2% of the PIs summer salaries.

Supplies. *Indicate separately the amounts proposed for office, laboratory, computing, and field supplies.*

Laboratory supplies to be purchased are: amber glass vials (42-ml, Fisher Scientific), septum-featured Teflon valves (Mininert®, Fisher), Gastight® microsyringes, high-purity Argon cylinders for the routine operation of the ICP, lab grade reagents, standard reference reagents, graphite tube reagents, high purity helium for the GC-MS, glassware, electrodes, and general lab supplies for the Atomic Absorption System and GC-MS.

Equipment. *Identify non-expendable personal property having a useful life of more than one (1) year and an acquisition cost of more than \$5,000 per unit. If fabrication of equipment is proposed, list parts and materials required for each, and show costs separately from the other items.*

Minor laboratory equipment to be purchased with NIWR funds includes three mechanical stirrers, a pH-meter, filtration and drying units, distillation unit, one electronic balance and one tubular furnace for crumb rubber activation experiments.

Services or Consultants. *Identify the specific tasks for which these services would be used. Estimate amount of time required and the hourly or daily rate.*

Travel. *Provide purpose and estimate costs for all travel.*

Travel expenses include support for the PIs to attend conferences and other education and research meetings within the US that bear direct relationship with this project.

Other Direct Costs. *Itemize costs not included elsewhere.*

It is expected that the results of this project yield one or two publications in referred journals. The requested amount (\$824) has been separated to cover for publication fees.

Indirect Costs. *Provide indirect cost rate.*

Facilities and Administration costs related to this project will be covered by UPRM as in-kind money.