Report for 2004PR18B: Sorption Behavior of Crumb Rubber to Remove Inorganic and Organic Contaminants from Aqueous Solutions.

- Other Publications:
  - The Puerto Rican main newspaper EL NUEVO DIA (June 20th, 2005) published an interview to the research group.
  - Perales, O; Roman, F, and Alamo,'Use of Recycled Crumb Rubber to Remove Heavy Metal Ions and Solvents from Aqueous Solutions', Poster presented at the 229th National Meeting of the ACS in San Diego, March 12-17, 2005

Report Follows

REPORT YEAR 1

Sorption Behavior of Crumb Rubber to Remove Inorganic and Organic Contaminants from Aqueous Solutions

Oscar Perales-Perez, Felix Roman, Marco Arocha

1. Project Summary

The present work was focused on the systematic evaluation of crumb rubber as a suitable material to remove inorganic and organic species from aqueous effluents through a low-cost and easy-to-scale technology based on the sorption properties of this waste material.

The capability of waste tires crumb rubber to remove metal ions of environmental concern in aqueous solutions was verified by adsorption studies at room temperature and quantified by ICP-OES. The chemical stability of mesh 14-20-crumb rubber was investigated for pH 1.5, 3, 6 and 9, before adsorption experiments. Final solutions were analyzed for Cd, Pb, Cr, Zn, As, Cu. In all cases, analyzed solutions reported concentration of those metals far below EPA regulations for drinking water. Sorption experiments verified that rubber particles (mesh 14-20 and mesh 30) were capable to adsorb Cu, Cd and Pb ions at different concentrations. The removal efficiency and metal-uptake levels were dependent on solution pH and metal concentrations. For instance, up to 98% of Cu(II) and Pb(II), and 37% of Cd(II) were removed from 1 ppm solutions of those ions and pH 6. It was also observed the continuous release of Zinc ions (from ZnO constituent in tires) during sorption tests. The adsorption capacity of crumb rubber was Pb > Cu > Cd, whereas higher metal concentration enhanced the metal uptake. Maximum uptake capacity for Cu and Pb ions at pH 6.0, were close to 0.6 mg/g rubber when the concentration of starting solutions varied from 1-20ppm. The adsorption efficiencies and metal up-takes were negligible at pH 1.5. Besides, crumb rubber was also used to remove xylene and toluene from aqueous solutions. The concentration of xylene dropped from 30 ppm down to 7 ppm in the first 30 minutes of contact. The terminal final concentration of xylene was as low as 2 ppm in a two-step operation. Preliminary results also suggested that sorbed metal ions can be desorbed by contacting 'pregnant' rubber particles with acidic solutions (pH 1-1.5) at room temperature.

2. Statement of the Critical Problem

Protecting water bodies (surface, aquifers and coastal) from contamination is essential for health and safety. Typical inorganic pollutants are heavy metals which form highly soluble solid products (e.g., Hg), or no solid at all (oxyanions like arsenite and arsenate, among others), after treatment of effluents by conventional alkaline precipitation. The limitations of conventional cleaning approaches become more evident when the contaminants are at very dilute concentrations as observed in effluents coming out from water treatment plants using conventional alkaline precipitation, or in 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 by Pb, Cu, Zn and Cd) have been reported in effluents from municipal wastewater, electroplating, metal finishing and printed circuit board manufacturing plants. In turn, the mercury pollution problem in Juncos and the presence of lead in some wells in Gurabo are examples of the aquifers contamination problem issue. The described situation is even more dramatic when the decontamination process deals with hazardous organic compounds, as those reported in some laundries and gas stations in Puerto Rico, where traditional precipitation and ionic exchange processes are not applicable at all. Accordingly, the development of a low-cost, environmental friendly and efficient cleaning process for effluents bearing inorganic and organic contaminants becomes indispensable.

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. Under this premises, the search of different alternatives to expand the re-use possibilities for scrap tires sounds justified.

The remediation option detailed in this proposal is based on the presence of components in crumb rubber, such as carbon black, zinc oxide, and sulfur, embedded in an elastomeric matrix, with potential capability to absorb/adsorb and precipitate hazardous species from aqueous solution. This fact has been verified by several investigations such as the research undertaken by Dr. James Donovan, a collaborator in this proposal. 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. On this basis, the Phase-I of the present project dealt with the systematic investigation of the practical applicability for this 'waste material' to remove different inorganic, such as Cu(II), Cd(II), and Pb(II), as well as organic species of environmental concern. 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.

3. Objectives of the Research (Phase-I):

This proposal explored the following main objectives:

i. To determine the chemical stability of crumb rubber in aqueous solutions at different pH values and room temperature.
ii. To asses the sorption capability of crumb rubber for inorganic and organic species from aqueous solutions. Targeted species were selected based on their chemical speciation behavior. Then, the sorption capability of granular crumb rubber for Cu (II), Cd (II), Pb(II), toluene and xylene, was investigated.
iii. To asses the sorption rates and loading-capacity as a function of crumb rubber particles concentration, particle size, ions speciation and concentration, solution pH in single-species systems at room temperature.

Timeline of activities

Year 1: Systematic evaluation of sorption properties of granular crumb rubber
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 (M. A. Arocha, O. Perales-Perez, F. Roman).

3. Methods, Procedures and Facilities

Methods and Procedures

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

i. Chemical stability of granular crumb rubber

One 1 gram of screened crumb rubber (14-20 mesh) was contacted with 100 ml of distilled water under acid, neutral and alkaline solutions for 24 hours at room temperature. After contact, aliquots were withdrawn, passed trough a membrane filter and analyzed to determine the release of any inorganic species out from the sorbent.

ii. Experimental Procedures

The basic set-up for the sorption/desorption tests included temperature-controlled water shaker baths, stirrers, pH-meters and filtration and drying units. All quantitative analyses were carried out in Dr. Felix Roman's laboratory.

iii. Sorption experiments

The following parameters were evaluated in batch equilibrium sorption experiments: average size of rubber particles (mesh 14-20 and mesh 30), concentration of hazardous species (typically from 1 ppm to 30 ppm), pH (1.5 and 6.0, in inorganic sorption tests only). The typical crumb rubber concentration was 10g/l.

Synthetic solutions bearing targeted metal species were prepared in distilled/dionized water. Solution pH was adjusted by suitable amounts of NaOH or HNO_3 for the experiments with inorganic species. Synthetic metal ion solutions were prepared by dissolving suitable weights of $CuSO_4.5H_2O$, $CdCl_2$ and $Pb(NO_3)_2$ in de-ionized water. One-hundred ml of prepared solutions was contacted with 1 gram of crumb rubber in a temperature-controlled water bath shaker. Aliquots of 2.5 ml were withdrawn for different contact times to monitor the progress of the sorption process. All tests were run at room temperature conditions. Samples and blanks were run in triplicate. Depending on pH conditions, the solutions were acidified in order to retard hydrolysis reactions. The results of the sorption tests were used to determine the equilibrium uptake, sorption rates, and removal efficiency of target species.

The batch sorption tests for the organic compounds followed a procedure similar to that for inorganic species. However, screw cap vials with Teflon-lined septa were 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, was kept at approximately 1 ml. After contact period, samples were withdrawn, centrifuged in close vessels and submitted for quantitative analyses. Samples and blanks were run in duplicate.

iv. Quantitative analyses

Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was used in this project for the quantitative evaluation of the sorption experiments. ICP-OES has multi-elemental capabilities, good sensitivity, high precision, accuracy, wide dynamic range and cost effectiveness. US EPA method 200.7 is an ICP-OES method used for the determination of heavy metals including Cu, Cd, Pb, in aqueous solutions. Individual standards and Standard Reference Materials were purchased from NIST or any other company that sales certified standards. The concentration of targeted elements was measured before and after contacting the contaminants-bearing solutions with the crumb rubber to determine the sorption efficiencies and uptake capacities. The concentration of the organic compounds in the aqueous, gas and solid phases was determined by solid phase micro extraction (SPME) and gas chromatography mass spectrometry.

5. Principal findings and significance.

5.1 <u>Chemical stability o crumb rubber.</u>

Table 1 summarizes the obtained results. As seen, negligible release of toxic metals, such as lead or cadmium, was observed at pH 6.0 (typical pH value in surface and ground waters). In all cases, the concentrations are below EPA regulations for **<u>drinking water</u>**. Although Zn ions were released from the ZnO contents in crumb rubber, the concentrations were not above the accepted levels.

	Solution pH				
	1.5	**3**	**6**	**9**	**EPA regulation (mg/L)**
Cu	0.0828	0.0434	ND	0.0001	1.3
Cd	0.0023	ND	0.0010	ND	0.005
As	0.0372	ND	ND	ND	0.050
Zn	2.3842	1.1116	0.4080	0.2924	5
Pb	ND	ND	ND	ND	0
Cr	0.0518	0.0915	ND	ND	0.1

ND Not detected

Table 1. Concentration of metals released (mg/L) at different pH values. EPA regulations are for drinking water.

5.2 <u>Sorption of inorganic species.</u>

The purpose of these 'screening-tests' was 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 ongoing Phase-II. 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. Following figures show the variation of metal ions concentration with contact time for two different levels of initial concentrations of metal ions (1 and 5ppm).

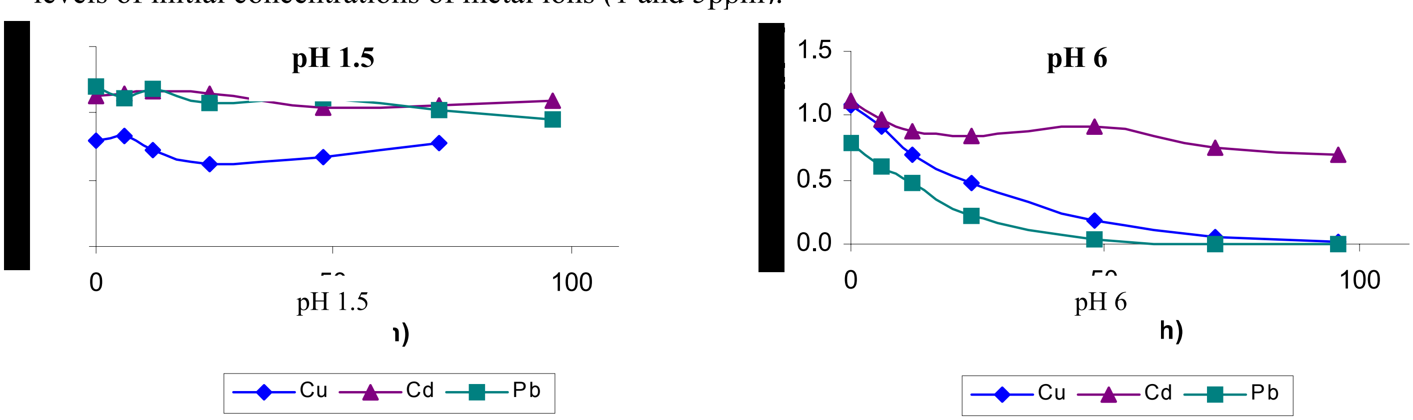

Figure 1. Sorption of Cu, Cd and Pb ions by 14-20 mesh crumb rubber (10 g/l). Initial concentration of metals ~ 1ppm.

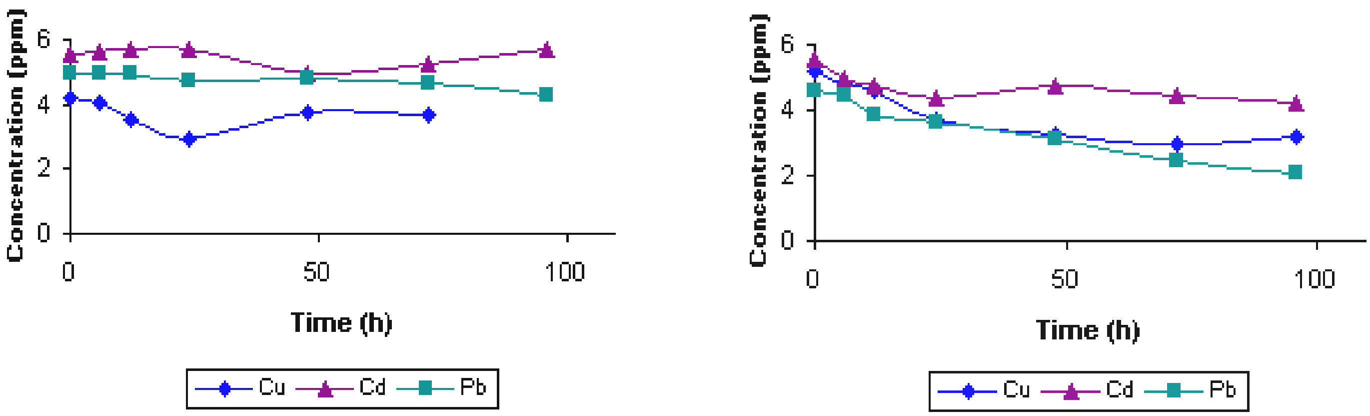

Figure 2. Sorption of Cu, Cd and Pb ions by 14-20 mesh crumb rubber (10 g/l). Initial concentration of metals ~ 5ppm.

As evident, the sorption behavior was dependent on the type of ion and pH of the starting solutions. The general trend showed 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 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: Pb, Cu>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 A) 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 (1.32A), expected to be strongly complexes 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.

Other results for different initial concentrations of Cu(II) and Pb(II) species at pH 6.0 and mesh 14-20 crumb rubber are summarized in Figure 3. As seen, the lower the initial concentration, the higher the removal efficiency. These results evidence the capability of crumb rubber to adsorb/absorb heavy metal ions from aqueous solutions. The sorption kinetics and uptake capacities were enhanced even further when smaller particles size of crumb rubber (mesh 30) were used.

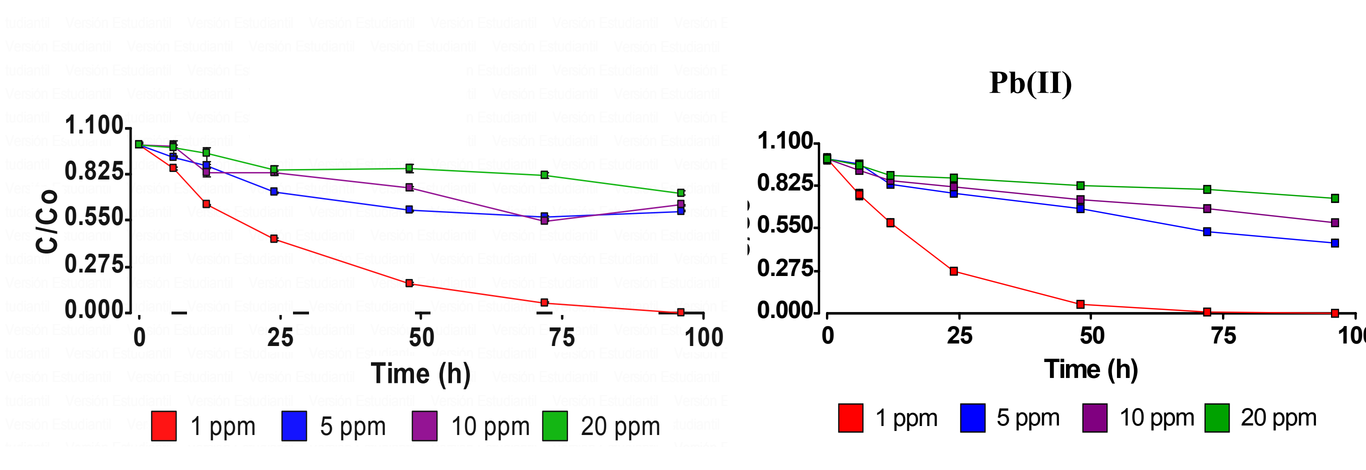

Figure 3. Sorption tests for Cu, Cd and Pb at pH 6.0 as a function of contact time at 25°C. The crumb rubber concentration was 10g/l for all tests.

On the other hand, the negligible sorption of Cu (II) and Pb (II) at pH 1.5 evidences the strong dependence of sorption capability with pH. The competition between H^+ and metal ions for available sorption sites could explain this behavior.

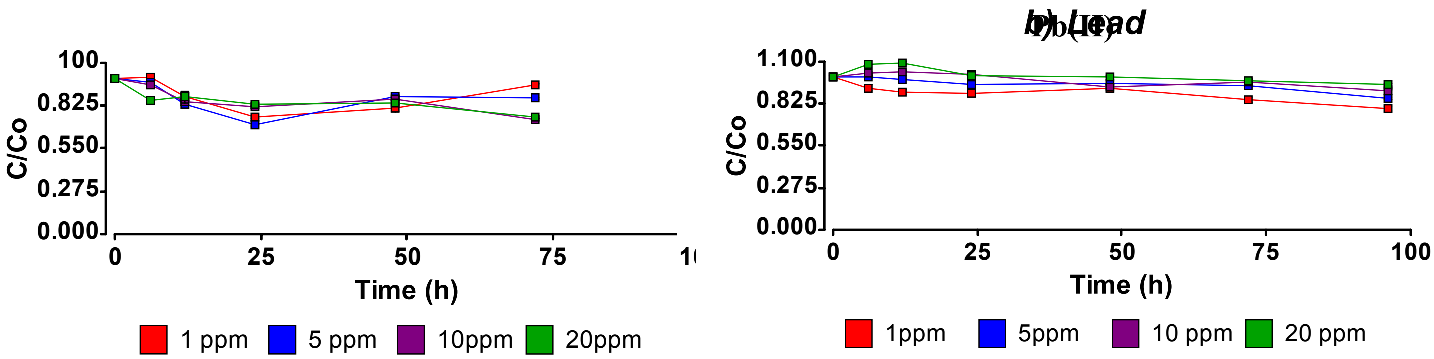

Figure 4. Sorption tests for Cu, Cd and Pb at pH 1.5 as a function of contact time at 25°C. The crumb rubber concentration was 10g/l for all tests.

The linear isotherms indicate the rise in crumb rubber uptake capacity (in mg/g) with the increase in the initial concentration of metal ions.

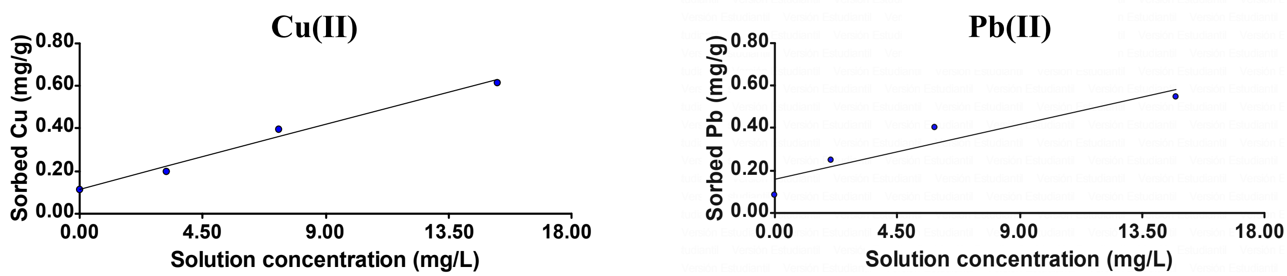

Figure 5. Sorption isotherms for Cu(II) and Pb(II) at pH 6.0.

5.3 <u>Desorption tests for Cu(II) ions</u>.

The presence of Cu in solutions after contacting 'pregnant' crumb rubber with distilled water at pH 1.5 suggested that desorption can be realized. An ionic-exchange mechanism should be involved with this process. Desorption option would enable crumb rubber to be regenerated and re-used in a subsequent sorption cycle. A more detailed evaluation of this option is included in ongoing Phase-II of the present project.

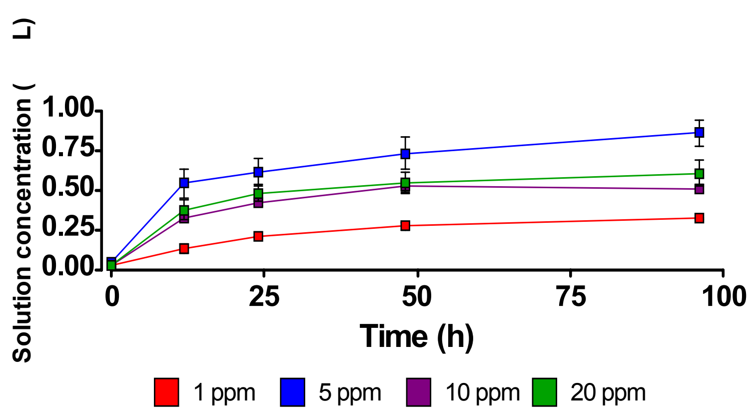

Figure 6. Cu(II) release after contacting crumb rubber, recovered from the sorption experiment at pH 6.0 and different initial concentrations, with an aqueous solution at pH 1.5.

5.4 Sorption of xylene and toluene

The sorption of organic species by crumb rubber was very fast. Most of the organics were sorbed within the first 30 minutes of contact. As evidenced by figure 7, the concentration of toluene can be decreased from 30 ppm down to 2 ppm in a two-step operation. Furthermore, the uptake capacity (in mg of xylene/g) of crumb rubber is high even at low concentrations of crumb rubber (Figure 8). Ongoing work addresses a more complete evaluation of the up taking capacity for toluene, xylene and benzene.

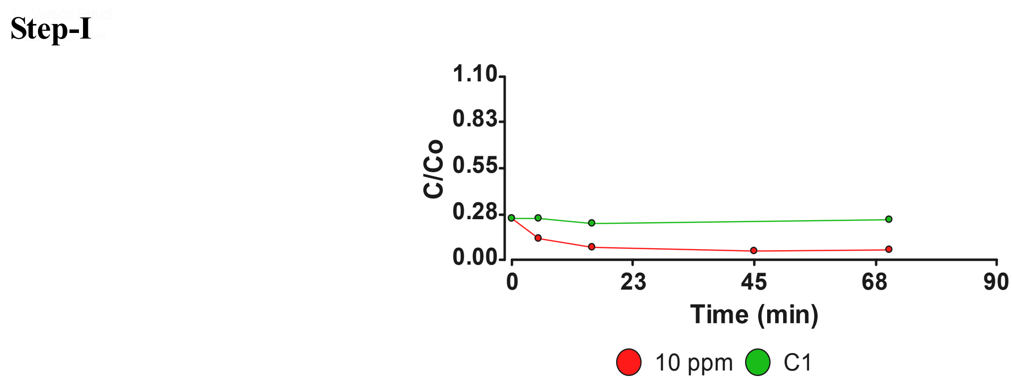

Figure 7. Sorption of Toluene by crumb rubber at pH 6.0. Initial toluene concentrations, 20 and 30 ppm (Step-I), and 10 ppm (Step-II). C1 and C2 correspond to control tests.

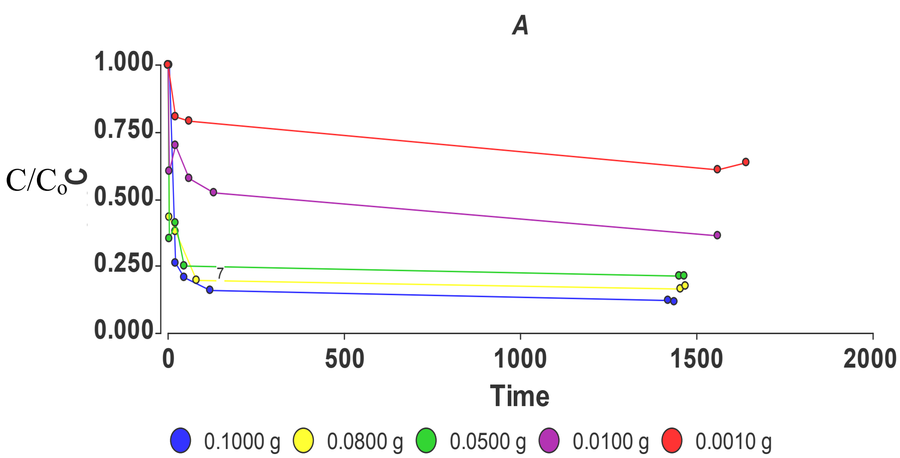

Figure 8. Sorption of Xylene with different amounts of crumb rubber in 10 ml of aqueous solutions at pH 6.0.

6. Publications:

6.1 A poster entitled: 'Use of Recycled Crumb Rubber to Remove Heavy Metal Ions and Solvents from Aqueous Solutions', was presented at the 229th National Meeting of the ACS (San Diego, March 12-17, 2005).

6.2 A poster entitled: 'Use of Recycled Crumb Rubber to Remove Heavy Metal Ions and Solvents from Aqueous Solutions' was submitted to PRWRERI. This poster included new data on sorption of organic species (xylene and toluene).

6.3 The Puerto Rican main newspaper EL NUEVO DIA (June 20th, 2005) published an interview to the research group.
6.4 A full paper with current findings is under preparation.

7. Other activities:

7.1 Toyota Foundation awarded to the research group the amount of $13,500 (01 year). The money is being used to cover stipends of graduate students participating in the project.
7.2 A full proposal was submitted to the Waste Solid Management Agency requesting funds for acquisition of state-of-the-art instrumentation. The proposal has been approved by the technical committee panel. Legal considerations to be included in the contract will hopefully be completed before July 2005.
7.3 A three-year proposal was submitted to USDA. Although the proposal got good reviews it was declined. The main observation was related to the lack of preliminary results at the time the proposal was submitted.
7.4 The PI plans to prepare a full proposal to be submitted to USGS and/or NWRI (November 2005).
7.5 Based on promising preliminary results, the research goals has been expanded to the evaluation of crumb rubber as potential sorbent for antimicrobials in aqueous solutions (Phase-II of the present Project).
7.6 The present research group involves: 03 faculties (02 from Materials Science and 01 from Environmental Chemistry) and 04 four graduate students from the UPRM-Chemistry Department. The PIs plan to include at least a couple of undergrad students from Chemistry and/or Civil Engineering Departments.