

**EVALUATION OF WASTE TIRE CRUMB RUBBER AND
DEWATERED SLUDGES AS ADSORBENTS OF HEAVY
METALS IONS IN THE MIRADERO WATER TREATMENT
PLANT AT MAYAGUEZ, PUERTO RICO**

by

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ABSTRACT

Water pollution by heavy metal species is a major environmental concern, and existing technologies are not always adequate for meeting regulatory limits. Major sources of pollution of aqueous effluents with heavy metal ions (mainly Pb, Cu, and Zn) in Puerto Rico are municipal wastewater treatment plants and the discharges from electroplating, metal finishing, and printed circuit board manufacturing industries. Typical concentrations of toxic inorganic species in those aqueous effluents range from 0.1 to 100 ppm. The mercury pollution in Juncos and the presence of lead in some wells in Gurabo (newspaper, *El Nuevo Dia*, June 15, 2003), can be considered local case-studies. In this regard, the presence of Cu, Pb and Zn species in the final discharge generated at the water filtration facility in Mayaguez (as stated by the Puerto Rico Aqueduct and Sewer Authority, PRASA, the Puerto Rican Agency in charge of the potable water facilities) represents an incomparable opportunity to test the capability of waste tire crumb rubber (WTCR) and dewatered sludge to solve an actual environmental problem. The main difference between both is in the sorption rate: the sorption rate of Cu and Pb was faster when WTCR was used than the sludge. The sludge was capable of removing Zn ions whereas the WTCR was not. A combination of these methods and chemical precipitation resulted in the removal of the heavy metals to achieve compliance with the NPDES permit. The engineering recommendation involves the installation of a helicon tank where the settled sludge will contribute to the adsorption of the aqueous metal species. This infrastructure is similar to others installed at Añasco filtration plant and other facilities of potable water treatment in Puerto Rico. As shown in the laboratory, using coagulant incites colloidal particles precipitate and remove in the last Thickener.

RESUMEN

La contaminación del agua por metales pesados es una fuente importante de preocupación ambiental. Las tecnologías existentes no siempre son adecuadas para cumplir con los límites reglamentarios. Las principales fuentes de contaminación de los efluentes acuáticos con iones de metales pesados (principalmente Pb, Cu y Zn) en Puerto Rico son las plantas municipales de tratamiento de aguas residuales y las descargas de las industrias de galvanoplastia y de circuitos de computadoras. Las concentraciones típicas de especies inorgánicas tóxicas en los efluentes acuáticos están entre 0.1 a 100 ppm. La contaminación por mercurio en Juncos y la presencia de plomo en algunos pozos en Gurabo (periódico El Nuevo Día, 15 de junio de 2003), son casos locales. En este sentido, la presencia de Cu, Pb y Zn especialmente en las descargas generadas por la planta de filtración de aguas en Mayagüez (según lo declarado por la AAA, la Agencia de Puerto Rico a cargo de las instalaciones de agua potable) representa una oportunidad inigualable para poner a prueba la capacidad del polvo de neumático (WTCR, por sus siglas en inglés) y lodos deshidratados para resolver un problema ambiental real. La principal diferencia entre ambos está en la tasa de absorción: la tasa de absorción de Cu y Pb fue más rápida cuando se utilizó WTCR en comparación con los lodos. El lodo fue capaz de eliminar los iones de zinc, mientras que el WTCR no resultó serlo. La combinación de estos métodos y la precipitación química permitió obtener la eliminación de metales pesados y así lograr el cumplimiento de las regulaciones en los permisos NPDES, por sus siglas en inglés. La recomendación ingenieril es la instalación de un tanque cónico para formar una capa de lodo que absorba los metales pesados. Esta infraestructura es similar a otras instaladas en la planta de filtración de Añasco y otras instalaciones de tratamiento de agua potable en Puerto Rico. Como se demostró en las pruebas de

laboratorio, la aplicación de un coagulante precipita las partículas coloidales presentes y pueden ser eliminadas en el último tanque clarificador.

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1 INTRODUCTION

1.1 Motivation

This project addressed the evaluation of two recycled materials: waste tire crumb rubber (WTCR), and dewatered sludge as potential sorbent for heavy metal ions in the clarified water of the Gravity Thickener Tanks in Miradero Water Treatment Plant in Mayagüez, Puerto Rico.

Currently, Miradero Water Treatment Plant in Mayagüez, Puerto Rico has reported high heavy metals concentration incidents in the clarified waters of the Gravity Thickener Tanks. The clarified waters are discharged to Pitillos Creek, which works under NPDES Permit 32835001 granted by the Environmental Protection Agency (EPA). Because of the mentioned reports, the plant is frequently in compliance violation of the National Pollutant Discharge Elimination System (NPDES) on lead (Pb), zinc (Zn), and copper (Cu). It is a well-known fact that heavy metals could be hazardous to the aquatic systems and consequently affect human's life.

The problem from the effluent supernatant waters is that they exceed the heavy metal concentration limits from Pitillos Creek. The following table summarizes the averaged heavy metals concentrations and the corresponding regulation levels.

Table 1. Existing average concentrations since January 1998 to June 2008 and regulated concentrations since December 1994 to present

Heavy Metals	Existing Average Concentrations (µg/L)	Regulated Concentrations (µg/L)
Copper (Cu)	114	8
Lead (Pb)	14.6	1.6
Zinc (Zn)	74.5	50

Environmental contamination by heavy metal species in Puerto Rico's waters is not common except for extraordinary cases. An example of heavy metals contamination is the case of Frontier in Quebrada Humacao where industrial wastes were discharged from 1971 to 1981. It was not

until 1977 that investigation of this incident began after 30 cows were found dead on land adjacent to the creek. Mercury was among the contaminants identified. To make it worse, the adjacent Ciudad Cristiana housing development, with about 500 residents, was there by 1979. These residents exhibited health problems associated to exposure to high levels of mercury. Evidently, the need to identify simple and cost-effective options to prevent pollution of water and soil by dissolved species becomes indispensable.

On the other hand, the process of setting fines and penalties depends on the action plan that is referred to the regulatory agency, in this case EPA. The action plan encompasses the strategies to be implemented in order to comply with regulatory requirements. If the tasks and milestones described in the action plan are not achieved, important penalties are established; for instance, if the concentration of Cu exceeds the regulated concentration, the corresponding fine could be between \$ 500 and \$ 1000 per month of violation.

As mentioned above, the three heavy metals that are to be addressed by this project are:

- Lead (Pb).- It is a neurotoxin that bioaccumulates in the food chain (fish) that deleteriously affects the aquatic ecosystem. In human beings, the ingestion or accumulation of lead affects the brain and the liver and destroys the blood building tissue in the bone marrow. (Fundación Eroski, 2008)
- Copper (Cu).- It is very toxic in aquatic system at large concentrations. In human being, it could damage the liver, kidneys and can provoke anemia. (Fundación Eroski, 2008)
- Zinc (Zn).- This species can produce muscular weakness and pain in excess quantities. Loss of taste, growth failure, and hypogonadism are also among its main effects on human health. (Fundación Eroski, 2008)

Under the above considerations, it becomes clear the need to identify a simple and cost-effective alternative to clean up water polluted with heavy metal species. In this regard, the use of waste tire crumb rubber and dewatered sludge also offer a new opportunity to reuse those, otherwise waste, materials instead of their final disposal in a landfill. The economic impact of the recycling industry is noted in the prices of materials that are recovered, because they are always lower than those made using virgin materials. The successful re-use of these materials will, therefore, have a

strong impact on two areas: first, finding new recycling options for waste tire crumb rubber and dewatered sludge, and next, to develop a novel alternative to clean up polluted waters.

2 OBJECTIVES

2.1 Main

Assess the use of two recyclable materials: waste tire crumb rubber and dewatered sludge as potential sorbents for heavy metal ions contained in aqueous samples.

2.2 Specifics

The specific objectives of this project are the following:

- Assess the chemical stability of waste tire crumb rubber and dewatered sludge for their potential use as adsorbents in water cleaning operations.
- Determine the optimum conditions to remove heavy metal ions (Cu, Pb, and Zn) from synthetic and actual water samples by using waste tires crumb rubber.
- Determine the optimum conditions to remove heavy metal ions (Cu, Pb, and Zn) from synthetic and actual water samples by using dewatered sludge generated in Miradero Water Treatment Facility in Mayaguez, PR.
- Evaluate the combined use of crumb rubber and dewatered sludges as sorbents for Cu, Pb, and Zn species.
- Propose a tentative flow-sheet considering the use of the evaluated adsorbents to remove dissolved metal species from water samples at Miradero Facility.

3 LITERATURE REVIEW

The features of each removal process, their applicability and limitations as discussed in available literature, is summarized as follows.

3.1 Chemical Precipitation

Thickening and dewatering operations are directed at removing suspended solids contained in sludge and backwash wastewaters. If the liquid effluents generated in these operations contain dissolved components, either organic or inorganic, which must be removed to comply with discharge or recycling requirements, additional processing of these liquids may be required.

Chemical precipitation is a powerful tool for removing dissolved components from water, accomplished by the formation of salts containing the target species to be removed, which have limited solubility in water. The precipitated salts may be separated by gravitational settling and removed as sludge.

Chemical precipitation is based on the solubility limits of the salts formed between the target component and its associated ion, and is a function of water temperature. Solubility in water is a chemical property which is specific for each species, and is indicated by the solubility product constant K_{sp} , calculated by multiplying the molar concentrations of each ion in solution.

$$K_{sp} = [\text{Cation}] \cdot [\text{Anion}] \quad (3.1-1)$$

From the above expression, it may be concluded that the lower the solubility product constant, the better removal that may be obtained by chemical precipitation.

For example, Zinc, Lead, and Copper may form distinct salts, some of which are presented in Table 2 below, with the corresponding solubility product constants (K_{sp}). Coincidentally, for all three metals, Zinc, Lead, and Copper, the salts with the lowest solubility products are the sulfides. Since all three salts contain one mole of the sulfide ion for each mole of metal, the residual concentration of metal is given by the square root of the solubility product constant, or 7.7×10^{-12} , 2.4×10^{-14} , and 7.7×10^{-19} moles/L, for Zinc Sulfide, Lead Sulfide, and Copper Sulfide, respectively, which would correspond to mass concentrations well below the NPDES

requirements for the Miradero WTP, as presented in Table 1. Note that although these metals would precipitate also as carbonate and hydroxides, the residuals left in solution would not be low enough to comply with permit requirements, and would in addition require operation pH values above 10. Also note that water pH values below 7 will affect precipitation, lowering removal efficiencies. Sulfide ions may be better to water in the form of Sodium sulfide (Na_2S) or Sodium Hydrosulfide (NaHS). Using chemical precipitation the solubility product of one of the metal compounds is exceeded so the metal may be removed separately or co-precipitated with phosphorus.

Common precipitants are hydroxide (OH^-), sulfide (S^{2-}) and carbonate (CO_3^{2-}). The metals are precipitated through the addition of lime or caustic to a pH of minimum solubility. The pH value at minimum solubility varies with the metal. For example, the optimum pH value for Copper, Zinc, and Lead removal are 8.8, 9.2 and 9.4, respectively (Environmental Protection Agency, EPA, 2007). Sometimes it is necessary to adjust the pH in order to achieve a desired result for metals precipitation.

In the particular case of Zinc, Copper, and Lead, different types of chemical precipitants are available. For example, the Cu precipitation as CuS favor the drop in final Cu concentration down to the 0.01-0.02 mg/L whereas a terminal concentration in the 0.02-0.07 mg/L range is usually achievable when hydroxide precipitation on route is selected (Environmental Protection Agency, EPA, 2002). . The precipitation of Zn as its hydroxide at pH 11 favors terminal concentrations as low as 0.1 mg/L (Environmental Protection Agency, EPA, 2002). The achievable terminal concentration will be strongly dependent on the concentration of organic matter and temperature. Carbonates can also be used in chemical precipitation. Sodium carbonate (Na_2CO_3) is the most common chemical used. However, water softening is the main purpose to use carbonates.

Although the chemical precipitation route is a well-established-technology, main limitations are related to the need to achieve lower terminal concentration of the metal species. Also, the difficult handling of fine carbonates, hydroxides or sulfide powders will be a limiting factor. The chemical instability of metal hydroxides and carbonates are also of concern.

Table 2 summarizes the characteristics of each solid compounds produced after chemical precipitation of heavy metal ions. The table also indicates the solubility of the corresponding solid products.

Table 2. Solubility Product Constants for Selected Salts at 25°C

Species	Compound	Formula	K_{sp}	Residual Concentration		NPDES Limit ($\mu\text{g/L}$)
				moles/L	$\mu\text{g/L}$	
Copper (II)	Copper Hydroxide	$\text{Cu}(\text{OH})_2$	2.2×10^{-20}	2.8×10^{-7}	16.5	8.0
Copper (II)	Copper Sulfide	CuS	6.0×10^{-37}	7.7×10^{-19}	4.6×10^{-11}	8.0
Lead (II)	Lead Carbonate	PbCO_3	3.3×10^{-14}	1.8×10^{-7}	37.6	1.8
Lead (II)	Lead Sulfide	PbS	3.4×10^{-28}	2.4×10^{-14}	5.1×10^{-6}	1.8
Zinc	Zinc Hydroxide	$\text{Zn}(\text{OH})_2$	1.8×10^{-14}	2.6×10^{-5}	1546.2	50.0
Zinc	Zinc Sulfide	ZnS	3.0×10^{-23}	7.7×10^{-12}	5.1×10^{-4}	50.0

3.1.1 Chemical Precipitation using Sodium Trithiocarbonate

The use of Sodium Trithiocarbonate (Na_2CS_3) metals removal technology is designed to assist in removing heavy metals from wastewater to lower residual levels if compare with others traditional techniques.

The ammonium, alkali metal and alkaline earth metal trithiocarbonates are water soluble and provide the trithiocarbonate species CS_3 in solution capable of reacting with heavy metals to produce a metal sulfide precipitate. The most suitable trithiocarbonates are made with sodium (Na), calcium (Ca) or potassium (K) salts. The sodium salt was used in most of the initial testing of this project because it is the least expensive and most abundant.

Sodium trithiocarbonates are usually classified as:

1. Anhydrous salt, for example, Na_2CS_3 .
2. Acid salt, for example, $\text{CH}_2\text{S}_3\text{Na}$.
3. Hydrated salt, for example, $\text{Na}_2\text{CS}_3 \cdot x\text{H}_2\text{O}$

The sodium salt of the trithiocarbonates has several possible names such as: sodium thiocarbonate, sodium trithiocarbonate, sodium sulfocarbonate, or disodium carbonotrithioic. There are several methods for the synthesis of sodium and other trithiocarbonates. The most common method involves the reaction an aqueous solution of sodiumhydroxide (NaOH) with carbon disulfide (CS₂).

Any water soluble alkali metal or alkaline earth metal hydroxide may be substituted for the sodium hydroxide. A second method involves the reaction of sodium sulfide (Na₂S) with carbon disulfide (CS₂). Any alkali metal sulfide may be substituted for the sodium sulfide. A third method for obtaining sodium trithiocarbonate is from the recovery of Na₂CS₃, as one of the secondary products in the manufacturing process of cellulose xanthate. The chemical structure is shown in Figure 1. An excess of carbon disulfide and sodium hydroxide are used in the process for manufacturing cellulose xanthate and combine to produce Na₂CS₃, Na₂CO₃, and water.

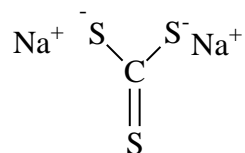


Figure 1. Chemical Structure of Sodium Triothiocarbonate(Na₂CS₃)

Regarding the use of thrithiocarbonate to remove heavy metal ions, it must be added to the heavy metal-contaminated liquid in an amount sufficient for reaction with substantially all of the heavy metals in the liquid, and there avoid any excess of trithiocarbonate. The heavy metal ions are then precipitated as the corresponding sulfides.

Combined method approach involves the use of Sodium Trithiocarbonate and Hydroxide precipitation. In this route, lime or caustic is added to reach the pH where the minimum solubility of the metal(s) hydroxide is formed; the supernatant water is treated in another clarifier or passed through a sand filter. At this point, a Sodium Trithiocarbonate product is added to form a pin floc for liquid/solids separation. This will sequester those metals remaining in solution after the hydroxide precipitation step.

A modification of the above approach is the simultaneous use of hydroxide source and Sodium Trithiocarbonate in a one step. The metal hydroxide formation will capture a significant portion

of the metals in solution, while the Sodium Trithiocarbonate captures the remaining metals unreacted with the hydroxide. This method may be required when a second polishing clarifier or filter is not available.

The "general rule" of 10 ppm Sodium Trithiocarbonate treatment for every 1 ppm metal in the waste stream is only a guideline for a starting point. The most successful jar testing is to bracket a range of dosages from low to high. It is recommended to more accurately determine the performance of the Sodium Trithiocarbonate, run a series of jar tests with dosages at 5, 10, 20, 50 and 100 ppm to start with. You can then narrow this range down depending on what the pin flocs look like, settling characteristics and resulting turbidity. The only way to fully know the treatment effects is to have an analysis done on the supernatant (ICP-MS¹). We can get a good feel for which is the most likely dosage to meet your needs by visual observations. Strongly complexed or chelated metals may require acidification followed by neutralization to the metals' minimum solubility along with addition of the Sodium Trithiocarbonate.

3.2 Adsorption-Based Processes

Adsorption is a surface phenomenon that is characterized by the concentration of a chemical species (adsorbate) from its vapor phase or from a solution onto or near the surfaces or pores of a solid (adsorbent). This surface excess occurs in general when the attractive energy of a substance with the solid surface (i.e., the adhesive work) is greater than the cohesive energy of the substance itself. The adsorptive uptake is amplified if the solid material has a high surface area. If the adsorption occurs by London-van der Waals forces between the solid and adsorbate, it is called physical adsorption. If the forces leading to adsorption are related to chemical bonding forces, the adsorption is referred to as chemisorption.

For a substance adsorbed onto a previously unoccupied solid surface or its pore space, the amount adsorbed is proportional to the solid mass, and is dependent on temperature (T), the surface mass equilibrium partial pressure of the vapor, (P), and the nature of both, adsorbate and adsorbent. The adsorbed quantity per unit mass of the adsorbent ("Q"), which is specific for the pair adsorbate/adsorbent, is then only a function of adsorbate concentration ("C") when

¹ ICP-MS- Inductively Coupled Plasma Mass Spectrometry

adsorption occurs from a liquid phase at a fixed temperature. The relation between Q and C at a given temperature is called the adsorption isotherm. Q is an important design variable because it will dictate, for a given adsorbate concentration to be removed from solution, how much adsorbent is necessary.

$$\text{Mass of adsorbent needed (kg)} = \text{Mass of adsorbate to be removed (kg)} / Q \text{ (kg/kg)} \quad (3.2-1)$$

Adsorption isotherms must be obtained for each specific system adsorbate/adsorbent, either by laboratory or pilot scale experiments. The isotherm may be represented graphically or through adsorption models. The model mostly used in engineering is the Freundlich equation:

$$Q = KC^n \quad (3.2-2)$$

Where Q is the amount adsorbed in mg of adsorbate per g of adsorbent (for example) and C is given in mg of adsorbate per gram of solution. K has complex units $(\text{mg/g})/(\text{mg/g})^{1/n}$. In the special case when “ n ” is equal to unity, the isotherm is said to be linear.

3.2.1 Adsorbent Materials

The main mechanisms by which metals adsorb to solids are cation exchange, physisorption, and surface complexation reactions. Cation exchange occurs mainly when the solid contains Sodium attached to chemical groups at its surface; Sodium is very ionic in water and may be readily displaced by other metals. Physisorption results usually from van der Waals forces caused by electronic clouds around metallic atoms. Surface complexation occurs in soils and similar solids, due to the presence of active groups such as oxo-hydroxides and active sites caused by isomorphic substitution.

Activated carbon is an adsorbent that is widely used in water treatment, at advanced wastewater treatment, and the treatment of certain organic industrial wastewater, because it adsorbs a wide variety of organic compounds and is cost-effective. In water treatment, it is used to remove compounds that cause objectionable taste, odor or color. It is generally used in granular form in batch, column, or fluidized bed operation. Occasionally activated carbon is used in powdered form and is not recovered for regeneration.

Great interest has been directed to the use of alternative materials for metal removal applications related to wastewater treatment, given the limitations in process costs. The use of activated carbon, although efficient, is not cost effective. The solid waste materials that have been mostly considered as feasible options have been soils, tire chips, and sludge. The experience with adsorption of metals in soils is interesting for water treatment plants since the sludge generated in the sludge handling system consists mostly of soils removed from the raw water.

3.2.1.a. Non -conventional Adsorbents: Waste Tire Crumb Rubber

Crumb rubber is composed of a complex mixture of elastomers like polyisoprene, polybutadiene and styrene-butadiene. Crumb rubber also consists of curatives (sulfur and peroxide), cure system-activators (stearic acid), fillers and reinforcing agents (carbon black, fibers, etc.), process oils, plasticizers, and additives (antioxidants, antiozonants). The most commonly used rubber matrix is the co-polymer styrene-butadiene (SBR) or a blend of natural rubber and SBR. On a rubber-composition point of view the major components of tires are rubber vulcanized with sulfur (1.1%), stearic acid (1.2%), ZnO (1.9%), extender oil (1.9%), and carbon black (31.0%) (Amari et al., 1999). 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 organic and inorganic compounds from aqueous and gaseous effluents, a fact that makes viable the removal of target species through sorption/adsorption mechanisms, posed of a complex mixture of elastomers like polyisoprene, polybutadiene and styrene-butadiene, according to Alamo (2006).

Crumb rubber has been investigated as a potential adsorbent for metals contained in several effluents such as landfill leachate and mine drainage. A series of tests were conducted to investigate the fate of heavy metals and gasoline components in a simulated landfill, one cell containing a 30 cm thick clay liner and a leachate collection layer containing tire chips, and another similar cell without tire chips. Arsenic, selenium, mercury, barium, and lead concentrations were lower while zinc concentration was higher in the cell containing tire chips compared to the one without tire-chips. In another study, the effectiveness of used tire rubber for immobilizing Hg(II) in a contaminated soil was evaluated using batch extraction and field

rainwater leaching tests. Hg(II) concentration in the initial rainwater leachate was reduced from 84 ppb for untreated soil to 1.2 ppb for the rubber-treated soil. Batch extraction and adsorption results indicated that the rubber had high adsorption capacity for Hg(II) when pH values were between 2 and 8.

Guanasekara et al. (2000) 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% removal of naphthalene from an initial concentration of 15 ug/L. Results suggested that rubber particles had greater affinity for naphthalene than toluene. A black powder of crumb rubber with particles sizes of 220 and 280 μm were used. This powder has more superficial area, however, it can cause problems due to its small size and difficulty of recovery, according to Alamo (2006).

Variations in size and possible differences in the surface between samples could be obtained using manual shredding of rubber. These differences can affect the sorption process by changing the quantity of pores. However, crumb rubber was demonstrated to be an effective medium for removing metals from aqueous solutions. The Zinc contained in tires is released to solution, increasing its content in the liquid and requiring additional Zinc removal downstream.

3.2.1.b. Non-conventional Adsorbents: Silica-based Sludge

Adsorption of metals to distinct sludge types have been conducted with positive results. Adsorption capacity depends on the composition of the sludge and on the metal species. Most work has been conducted with wastewater sludge, which has a high organic content. In the case of sludge generated in water treatment plants, the components depend on solid matter in the raw water, and on chemicals added during the treatment process, consisting mostly of soils and coagulants that bonded to the raw water solids. Several soils are known to exhibit adsorption capacity.

Davis and Cornwell (1998) investigated the behavior of heavy metals accumulating in soils treated with urban sludge. Metal sorption during transport in the soils was evaluated by means of breakthrough curves obtained via the soil column leaching test. Tests showed that the amount of heavy metals retained in the soil increases when the soil is treated with sludge both in situ and in

laboratory; the order of selectivity ($\text{Pb} > \text{Cu} > \text{Zn} > \text{Ni}$) remains similar for the two types of matrix.

In the work by Metcalf and Eddy (2003), the applicability of ground water sludge (GWS), a waste material from a ground water treatment plant, as a potential absorbent for heavy metals was experimentally analyzed. The metals tested were Ni, Cd, and Zn. The potential for metal adsorption was indicated by the presence of 4% of Fe_2O_3 in the GWS composition. The batch adsorption experiment indicated that Ni, Cd, and Zn were undetectable concentrations adsorbed using 4000 mg/L of the absorbent at a contact time of 24 hours.

Although limited work has been conducted on the use of water treatment sludge to adsorb metals, it should be investigated as an option to remove metals in the liquids generated by the sludge handling systems of water treatment plants, given the low cost associated with obtaining the materials, which are generated in the plant itself.

3.3 Reverse Osmosis

Osmosis is defined as the spontaneous transport of a solvent from a dilute solution to a concentrated solution across semipermeable membrane that impedes passage of the solute across, but allows the solvent to flow (American Water Works Association, AWWA, 1990).

Reverse Osmosis consists of separating a solvent, such as water, from a saline by the use of a semipermeable membrane and hydrostatic pressure. Also this process can remove heavy metals. As applied to metal-finishing wastewater, the solute is the metal and the solvent is pure water. Worldwide, Reverse Osmosis is used primarily for desalination. It is also, used for the removal of dissolved constituents from wastewater remaining after microfiltration. The membranes exclude ions, but require high pressures to produce the deionized water. The pore size is between $0.0001 - 0.001 \mu\text{m}$ and operating pressure between $150 - 500 \text{ psig}$ (Environmental Protection Agency, EPA, 2002). Reverse Osmosis reduced other constituent like COD, TSS, TDS, $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, PO_4 , SO_4 , and Cl. Some disadvantages for Reverse Osmosis are high cost, requires residuals handling and disposal, low performance in surface water, and biofouling problems.

Reverse osmosis systems have plenty of advantages. They are friendly to the environment, as they do not produce or use any harmful chemicals during the process. These systems also require a minimal amount of power. Reverse osmosis systems work well in home filtration systems because they are typically small in size.

Taste of the purified water is another distinct advantage. Reverse osmosis removes dissolved minerals and other contaminants that cause water to smell unpleasant, taste poorly and take on unusual colors. Removal of dissolved minerals, metals and other particles benefits plumbing systems. There is nothing in the water to corrode pipes or collect as sediment.

Reverse osmosis treatments require an enormous amount of water. Such systems typically return as little as 5 to 15 percent of the water pushed through the system, which means it also takes a long time to properly treat the water. What's left then exits the system as wastewater. This amount of wastewater can burden home septic systems. Water entering the reverse osmosis system should also be free of bacteria. While reverse osmosis systems do remove nearly all microorganisms, the risk of contamination through tiny leaks or deteriorating parts is prevented.

3.4 Nanofiltration

Nanofiltration is defined as relatively recent membrane filtration process used most often with low total dissolved solids water such as surface water and fresh groundwater, with the purpose of softening and removal of disinfection by-product precursors such as natural organic matter and synthetic organic matter.

Nanofiltration is recommended for the removal of heavy metals, but it is a very expensive process. This process has the capability to reject particles as small as 0.001 μm and operating pressure between 75 – 250 psig (Weber, 1972). nanofiltration is used for the removal of selected dissolved constituents from wastewater. Also, nanofiltration can remove bacteria and viruses. The type of membrane used in nanofiltration process is in a spiral-wound configuration. The main advantage is a production of high water quality. The only disadvantages using nanofiltration is a biofouling problem. Biofouling is the deposition and accumulation of biological constituents contained in the influent water on the surface of the membrane.

The advantage of nanofiltration is that it is an effective method of treating water that cannot be treated using conventional treatment methods. A disadvantage concerning nanofiltration is that it removes a number of healthy minerals from water, in addition to the harmful minerals and particles. The removal of these minerals, including calcium and magnesium, can actually make water unhealthy, especially for people with inadequate diets and people who live in hot climates, as water can provide these necessary minerals. The addition of calcium and magnesium, as described above, can resolve these concerns.

3.5 Electrodialysis, ED

Electrodialysis is defined as a process by which ionized materials dissolved in a liquid, such as the anions and cations of dissolved salts, are moved across a membrane by the application of an electric field, separating them from liquids or ions of opposite charge.

The Electrodialysis process can be used for heavy metals removal. In the Electrodialysis process, ionic components of a solution are separated through the use of semipermeable ion – selective membranes. Application of an electrical potential between the two electrodes causes an electric current to pass through the solution, which in turn causes a migration of cations toward the negative electrode and a migration of anions toward the positive electrode. Water is pumped through the membranes, which are separated by spacers and assembled into stacks.

Usually the electrodialysis membrane is porous, sheetlike, and made of synthetic ion exchange resin. Dissolved solids or heavy metals removal vary with the wastewater temperature, amounts of electrical current passed, type and amounts of ions, wastewater flow rates and number and configurations of stages.

The electrodialysis process may be operated in either a continuous or a batch mode. A portion of the concentrate stream is recycled to maintain nearly equal flow rates and pressures on both sides of each membrane. Electrodialysis process requires pre-treatment processes like activated carbon, chemical precipitation and multimedia filtration to reduce fouling. One application using electrodialysis, is the electroextraction methodology where heavy metals from diluted solutions was achieved by continuous electro permutation combining ion exchanges resins and membranes. Finally, electrodialysis can separate a waste influent containing 1000-5000 mg/l

inorganic salts into a dilute effluent that contains 100-500 mg/L salts (Environmental Protection Agency, EPA, 2007). Some disadvantages are high power requirements, variable current density, plugging, and equipment limitations.

Some advantages of electrodialysis are:

- When brackish water is desalted by ED system, the product water needs only limited pre-treatment. Typically only chlorination for disinfection is required.
- Because ED system removes only ionized species, it is particularly suitable for separating non-ionized from ionized components.
- Osmotic pressure is not a factor in ED system, so the pressure can be used for concentrating salt solutions to 20% or higher.

Some disadvantages are:

- Organic matter, colloids and SiO_2 are not removed by ED system.
- Feed water pre-treatment is necessary to prevent ED stacks fouling.
- Elaborate controls are required, and keeping them at optimum condition can be difficult.
- Selection of materials of construction for membranes and stack is important to ensure compatibility with the feed stream.

3.6 Ion Exchange

Ion Exchange is a process in which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. Ion Exchange has been used in wastewater applications for the removal of nitrogen, heavy metals, and total dissolved solids. High metal concentrations also can be found in leachate from landfills and stormwater runoff, for which ion exchange can be effectively applied.

The economic feasibility of using Ion Exchange processes for metal removal greatly improves when the process is used for the removal and recovery of valuable metals. Otherwise, the process is very expensive. Materials used for the exchange of metals include zeolites, weak and strong

anion and cation resins, chelating resins, and microbial and plant biomass. Resins are typically spherical in shape and range from 20-40 mesh (0.8 to 0.4 mm) (Lester et al., 1983).

Other materials used as ion-exchange resins are represented by several types of polymers; that is composed of a large number of bonded molecules (American Water Works Association, AWWA, 1990). Ion Exchange process is highly pH-dependent and upon selectivity coefficient. Cationic and Anionic resins prefer some metals over others. These resins prefer ions of higher valence, small solvated volume and ions with greater ability to polarize (Otero et al., 2008); for example, the selectivity coefficient for Zinc, Copper, and Lead are 3.5, 3.8, and 9.9, respectively (Environmental Protection Agency, EPA, 2002). Ion Exchange is more likely to remove Lead, but less likely to remove Zinc.

Most metals bind better at higher pH, due to less competition from protons for adsorption sites. The presence of oxidants, particles, solvent, and polymers may affect the performance of Ion Exchange resins (Environmental Protection Agency, EPA, 2002).

Some advantages of the ion exchange route are:

- Removes dissolved inorganics effectively
- Regenerable (service deionization)
- Relatively inexpensive initial capital investment

In turn, some disadvantages are:

- Does not effectively remove particles, pyrogens or bacteria
- DI (Deionization) beds can generate resin particles and culture bacteria
- High operating costs over long-term

3.7 Biological Removal Process

Metal removal in biological treatment processes is achieved mainly by adsorption.

Microorganisms combine with metals and adsorb them to the cell surfaces because of

interactions between the metal ions and the negatively charged microbial surfaces (Environmental Protection Agency, EPA, 2002). Also, metals can be absorbed by protein materials in the biological cell. The removal of metals in biological processes fit adsorption characteristics of the Freundlich Isotherm Model. The ranges of metals removal are between 50-98 percent (EnvironmentalProtection Agency, EPA, 2002).

4 TECHNICAL BACKGROUND

4.1 Miradero Water Treatment Plant Description

Miradero Water Treatment Plant is the principal source of potable water that supply to west region of Puerto Rico mostly to the cities of Mayagüez, Añasco, Hormigueros, Rincón, Moca, and Cabo Rojo. The facility receives raw waters from Rio Grande de Añasco and Cañas rivers. The influent is treated with an aluminum chlorhydrate solution (GC 850) that acts as a primary coagulant and gaseous chlorine before entering the flocculation and sedimentation process. The supernatant (overflow) solution passes through bed-type filters (anthracite and sand beds). Finally, waters receive disinfection using gaseous chlorine and storage in a 2.0 MG tank, then distributed to several towns mentioned above. The Plant has a design capacity to treat 20 MGD. This plant is located in the West Region of the island according with U.S.G:S coordinates, the latitude $18^{\circ} 13' 42''$ N and $67^{\circ} 08' 29''$ (Mayagüez, P.R.). The specific location is in road PR 108 km 3.0.

In the Figure 2, the location of the facility are shown.



Figure 2. Location of the Miradero Water Treatment Plant in western Puerto Rico

4.2 Water Treatment Process Description

The water treatment plant is equipped with a conventional treatment system containing coagulation, settling, and filtration operations. Figure 3 presents an aerial photo with the plant's components.

Sludge is removed from the settling operation and is generated during filter backwash. Filter backwash operations occur once a day for each filter unit, generating approximately 240,000 gallons of backwash wastewaters.

The Miradero WTP is equipped with a Sludge Handling System (SHS). Sludge from either settling or filter backwash flow to the thickener, which works as a holding or equalization tank. The thickening operation separates the incoming sludge into a more concentrated bottom stream that is pumped to the drying beds, whenever the torque on the mixing system reaches the limit value. Three 750 gpm pumps are used for feeding the drying beds from the thickener #1.

The supernatant stream from the thickener #1 is pumped to thickener #2 by two 450 gpm centrifugal pumps. The clarifier receives supernatant from the thickener, and is designed to control turbidity in the liquids to be discharged. Note that since the thickener works as an equalization tank, the quality of its supernatant is not homogeneous and compliance cannot be assured at all times, making necessary the use of the clarifier. Supernatant from the clarifier is discharged to the Pitillos Creek and is subject to NPDES permit requirements. Sludge collected in the thickener #2 is returned to the thickener #1.

The vacuum assisted drying beds (VADB) receive the bottom flow from the thickener #1. Three beds are available and, therefore, one bed is filled a day on the average process. Vacuum is provided by three pumps. The solids from drying are collected on a daily basis and stored for disposal in a landfill. The liquid extracted from the beds is returned to the thickener. No disinfection of discharged liquids is conducted prior to the discharge.

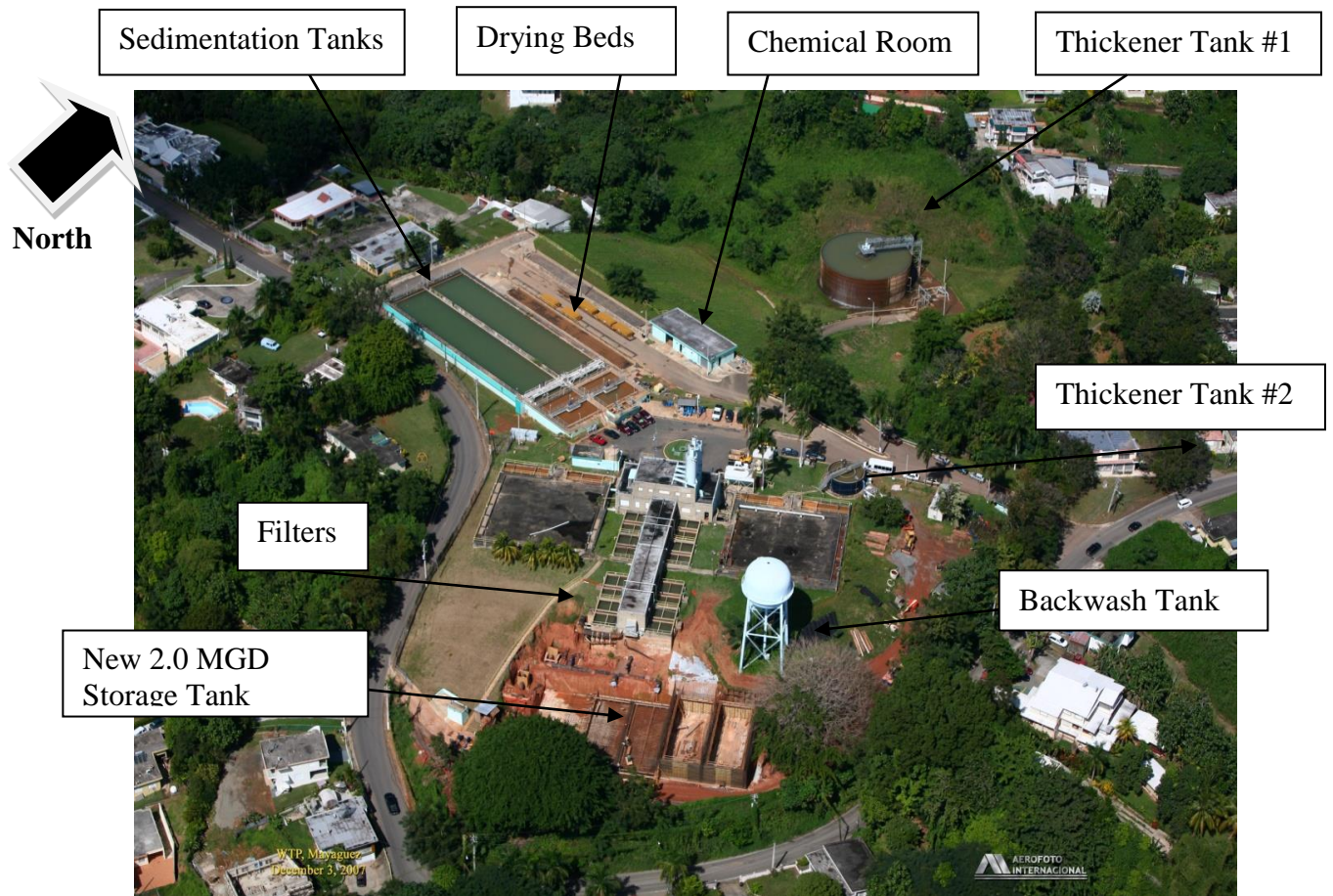


Figure 3. Miradero Water Treatment Plant aerial photo

Liquids discharged from the SHS at the Miradero WTP have presented excessive values of Zinc, Lead, and Copper in the past. The SHS, as currently implemented, has no capabilities to remove metals, and additional processing is required to address such limitation. The regulations included in NPDES allow maximum concentrations of 1.8 ppb, 8.0 ppb and 50 ppb for Lead, Copper, and Zinc, respectively. Figure 4 shows the actual Miradero Plant Sludge Handling Flow-sheet

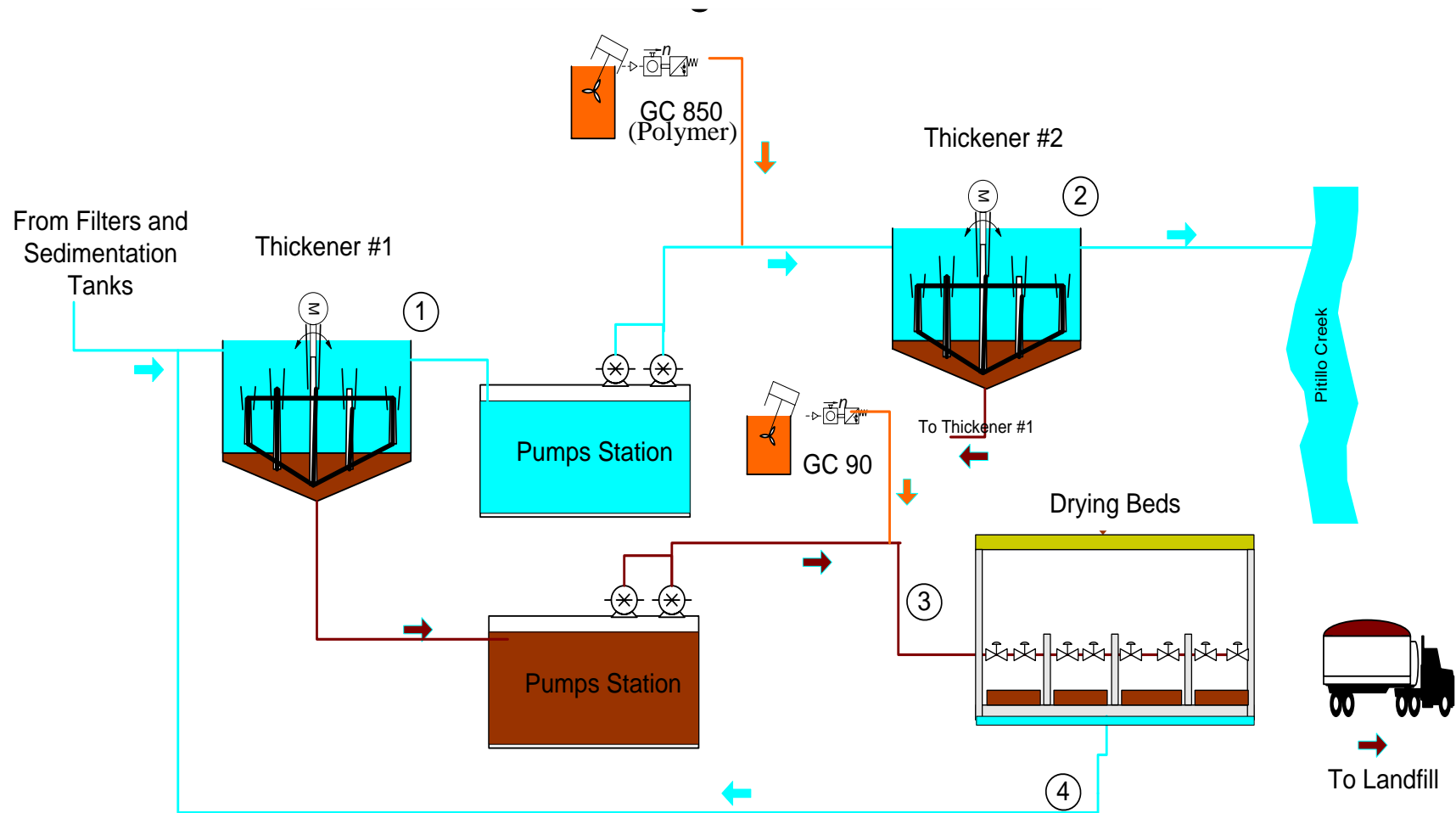


Figure 4. Actual Miradero Plant: Sludge Handling Flow-sheet

4.2.1 Sludge Treatment System Characteristics

4.2.1.a Thickener

The thickener receives backwash wastewater from the filtration units and sludge from the Sludge Treatment System clarifier. It may also receive sludge from the sedimentation tanks during cleaning operations.

The main dimensions and parameters of the thickener:

- Diameter: 90 ft
- Height: 28 ft
- Volume: 1.3 MG
- Average Inflow: 275,000 gpd (backwash only)
- Settling area: 6,291 ft²
- Average Retention time: 5 days
- Overflow rate: 0.24 ft/h
- Capacity of pumps to discharge supernatant: 450 gpm
- Time to discharge the volume of supernatant generated in one day of operation: 12 hours

The thickener presented on Figure 5, discharges sludge to the dryings beds and supernatant to the clarifier. The sedimentation tanks are cleaned for period of three months, generating 1.23 MG of sludge for the four smaller sedimentation tanks and 3 MG for the bigger ones.



Figure 5. Miradero Water Treatment Plant Thickener

4.2 .1.b Thickener #2

The thickener #2 receives supernatant from the thickener #1. The main dimensions and parameters of the thickener #2 are:

- Diameter: 31 ft
- Height: 12 ft
- Volume: 58,000 gallons
- Average inflow: 240,000 gpd
- Average Retention time: 5.8 hours
- Settling area: 755 ft²
- Overflow rate (based on daily inflow): 2.03 ft/h
- Overflow rate based on pumped flow: 4.78 ft/h

The thickener #2 discharge sludge back to the thickener #1 and supernatant to discharge point in Pitillos creek. Figure 6 shows Miradero WTP clarifier.



Figure 6. Miradero Water Treatment Plant Clarifier

4.2.1.c Drying Beds

The Sludge Treatment System is equipped with three vacuum assisted drying beds units, for a total of 2,656 ft². Each drying beds may receive the equivalent of 12 inches of dewatered sludge per cycle. The main dimensions and parameters of the drying beds are:

- Average inflow: 25,000 gpd
- Total bed surface area (3 beds): 2,656 ft²
- Drying Cycle: 3 days

Dewatered sludge is mechanically removed and stored in a 20 yd³ container for disposal. Leachate from drying beds return to the Thickener. The Figure 7 show the Miradero WTP Drying Beds.



Figure 7. Miradero Water Treatment Plant Drying Beds

4.3 Metal Concentrations Discharge

The Miradero Water Treatment Plant has NPDES permit that allows discharging all washwater from the Sedimentation Tank and Filters to the Pitillos Creek. The studied data have a ten years period. Before 2001, the Plant discharges the washwater without treatment to remove sludge. After 2001, PRASA built the sludge treatment using a Drying Bed Process. The conventional sludge treatment system consists in remove suspended solids from the washwater using physical process. The process does not have the capability to remove heavy metals. Tables 3 and 4 show the average concentrations of heavy metals between 1998 and 2008, respectively. The main reason in the difference between heavy metals concentrations was the operation of the Sludge System. For example, the average concentration for Copper was between 21.53 $\mu\text{g/l}$ and 14.6 $\mu\text{g/l}$. However, the heavy metals never reached the required concentration (10 $\mu\text{g/l}$), according with the NPDES permit using the existing process.

Table 3. NPDES Concentration Discharge for Copper, Lead, and Zinc with Existing Process (1998)

Heavy Metals	Existing Average Concentrations (µg/L)	Regulated Concentrations (µg/L)	New Regulated Concentrations (µg/L)
Copper (Cu)	155.27	10	8
Lead (Pb)	21.53	2.6	1.8
Zinc (Zn)	108.52	50	50

Source: Environmental Protection Agency [52]

Table 4. NPDES Concentration Discharge for Copper, Lead, and Zinc at June 2008

Heavy Metals	New Average Concentrations Until June 2008 (µg/L)	Regulated Concentrations (µg/L)	New Regulated Concentrations (µg/L)
Copper (Cu)	114	10	8
Lead (Pb)	14.6	2.6	1.8
Zinc (Zn)	74.5	50	50

Source: Environmental Protection Agency [52]

5 EXPERIMENTAL

5.1 Materials

5.1.1 Chemical Reagents

The properties of the chemical reagents are described as follows: Argon Gas, 99.998% Purity was obtained from Linde Gas. Lead Standard 1000ppm was obtained from Leeman Labs, Inc. The following reagents were obtained from Fisher Scientific: CaCO_3 , (CAS # 1317-65-3, 99 % purity); Cadmium Standard 1000ppm, (99 % purity, CAS # 7440-43-9); Calcium Standard 1000ppm (99% purity, CAS # 471-34-1); $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, CAS # 10022-68-1 (99% purity); Copper Standard 1000ppm (CAS# 7440-50-8, 99% purity); $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (CAS # 7758-99-8, 99% purity, Distilled-Deionized (17.8-18 M Ω); HCl trace metal grade (ACS certified, CAS # 7647-01-0); HNO_3 (trace metal grade, ACS certified, Manganese Standard 1000ppm (CAS # 7439-96-5); Magnesium Standard 1000ppm (CAS # 13446-18-9); Mg (magnesium polished limes); NaOH (sodium hydroxide, analytical grade); NIST Standard Reference Material, trace elements in natural waters 1640; $\text{Pb}(\text{NO}_3)_2$, (CAS # 10099-74-8); pH buffers; Potassium Phosphate Monobasic-Sodium Hydroxide Buffer (CAS #7778-77-0 pH 7.00); Potassium Biphthalate Buffer (CAS 877-24-7 pH 4.00); Potassium carbonate, borate-potassium hydroxide buffer (CAS# 1310-58-3, pH 10.00); Zinc Standard 1000ppm (CAS # 7440-66-6).

5.2 Adsorbents

5.2.1 Sludge

On November 6, 2008 eight sludge samples (@ 1kg/sample) were obtained from one of the Drying Beds. As shown in Figure 5.1, the eight samples were taken along the Drying Beds with separate distance between samples of 32 feet. In the left side of the Figure 5.1, the dimensions of the Drying Beds are indicated as length of 164 feet by 16 feet with and 1.25 foot of thickness. All samples were taken to the laboratory where the sample were analyzed for moisture content, density, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) as shown in figure 10, Toxicity Characteristics Leaching Procedure (TCPL), and Sorption Test.

The sampling procedures for dried sludge samples consist of weigh one gram of dried sludge, then transferred to a beaker and add 10 ml (1:4) HCl and 4 ml (1:1) HNO₃ in a hot plate heated at 95° C for three hours. Afterward, the sample is allowed to cool and transferred to a 100 ml Volumetric Flask. Finally, after 24 hours, 10 ml of the sample was taken and dilute with distilled deionized water.



Figure 8. Sludge samples in the Drying Beds

The dried sludge were subjected to acidic digestion and analyzed for metals contents. The major metals concentrations were Iron (Fe), Aluminum (Al), Magnesium (Mg), and Calcium (Ca). In minor concentration were found Zinc (Zn), Vanadium (V), Copper (Cu), and Niquel (Ni). The moisture percent of the sludge founded was 59.9 percent and with the density of 2.6.

Sludge has a capability to absorb metals in solution form. The main reason is the presence of silica (SiO₂) in the sludge characterization. Also the XRD analysis of the powders revealed the presence of silica as major component. Other components in a crystalline phase are:

- AlFeO₃ – Aluminum Iron Oxide
- Al₂ SiO₅ – Sillimanite
- Fe₂O₃ – Hematite
- FeO(OH) – Goethite
- MgP₄O₁₁ – Magnesium Phosphate
- CaCuV₂O₇ – Calcium Copper Vanadium Oxide

The image in Figure 9 shows a Scanning Electron Microscope (SEM) image of the above described dried sludge. SEM can provide information about sample morphology and composition (when EDX is part of the system). As observed, the solids consist of aggregated colloids below 1 micrometer in size.

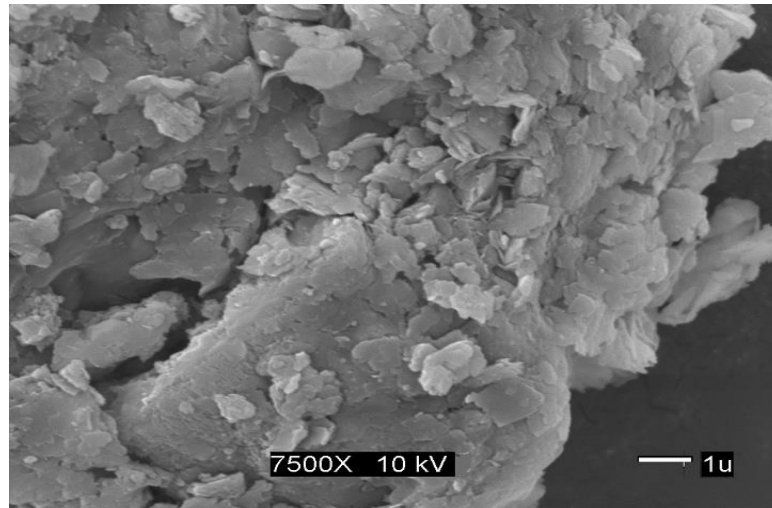


Figure 9. Dewatered sludge produced at Miradero Facility

Figure 10 shows the X ray diffraction (XRD) pattern for the dewatered sludge sampled at the Drying Beds. Silica was the major component in the sample.

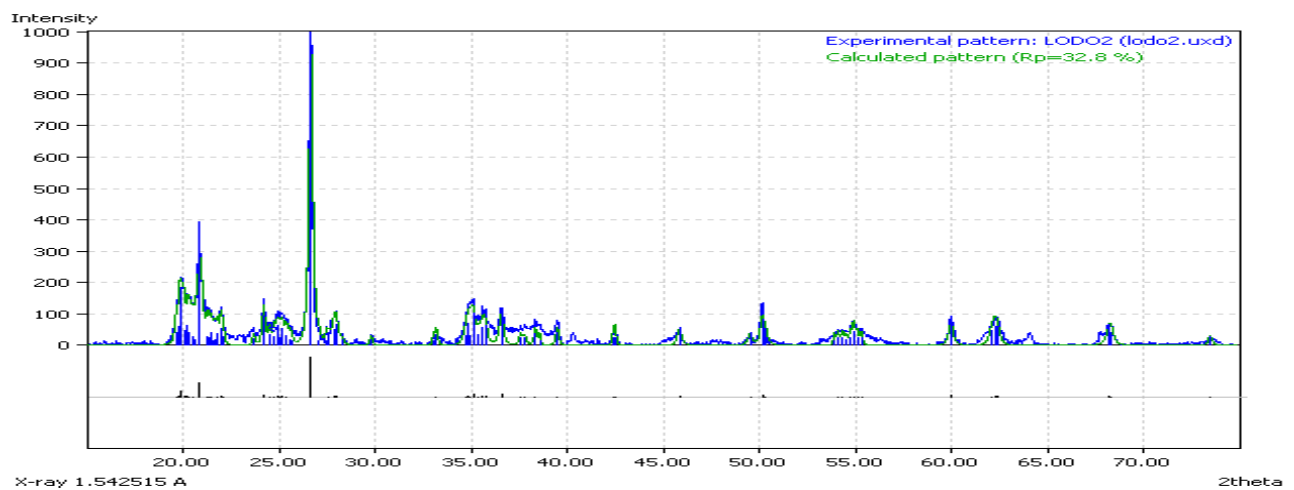


Figure 10. XRD spectrum of dewatered sludge

5.2.2 Tire waste tire crumb rubber (WTCR)

Crumb rubber is the result after shredding tires, separation of metals and fiber, and pulverizing of the clean rubber into different size. 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. Crumb rubber particles mesh 14-20 exhibit different sizes between 1.5 to 4.0 mm. The average size is 2.45 mm of diameter and the superficial area was roughly estimated at 18.86 mm^2 . The average weight of tire crumb rubber was 1.82 mg and the specific surface area was $10.36 \text{ mm}^2/\text{mg}$ or $0.1036 \text{ m}^2/\text{g}$. The waste tire crumb rubber (WTCR) was kindly provided by REMA, a Puerto Rican rubber recycling industry located in Caguas. The WTCR used was washed with distilled-deionized water for a period of time of 24 hours in a water shaker bath at a velocity of 200 cycles per minute. The concentration of the rubber during the washing period was 200g per liter of water. At the end of the washing period, the rubber was filtered and let dry at ambient temperature prior to use.

5.3 Characterization Techniques for the Adsorption Tests

Inductive Coupled Plasma-Mass Spectroscopy (ICP-MS) was used in this project for the quantitative evaluation of the sorption and desorption experiments. ICP-MS has multi-elemental capabilities, good sensitivity, high precision, accuracy, wide dynamic range, and cost effectiveness. US EPA method 200.9 is an ICP-MS method used for the determination of heavy metals including Cu, Pb, and Zn in aqueous solutions. The main features and applicability of each characterization techniques are briefly described as follows.

5.3.1 ICP-MS

Inductively Coupled Plasma- Mass Spectrophotometer (ICP-MS) from Agilent Technologies, model 7500ce was used to determine the metals concentrations in both analyses for analytical and real samples. Figure 11 shows ICP-MS basic components.

The Plasma is an ionized gas, usually argon, which is sustained by a radio frequency (RF) generator. The RF generator applies an electric force through a copper coil that as consequence ionizes the argon gas onto Ar^+ ions and electrons (e^-). The argon gas is selected among others because is the noble gas found in more abundance in the atmosphere and has a low ionization energy (15.68 eV) relative with other noble gases with less atomic mass. As consequence, it is cheaper and easier to ionize than other noble gases. In the plasma, the temperature can reach 10,000 K and it is responsible to excite and ionize the atoms.

As mentioned before, the RF generator supplies the energy to sustain the plasma. It produces an electromagnetic high frequency field in the induction coil that ranges 1-1.2 kV, at a frequency of 40.68 (27.12 for the ICP-MS) MHz. The efficiency of a conventional generator is low, on an average of 50% and the rest of energy must be removed by cooling water or air. The induction coil, which generally is made of copper, is exposed to several stress and must be cooled with distilled water recirculating continuously and uniformly.

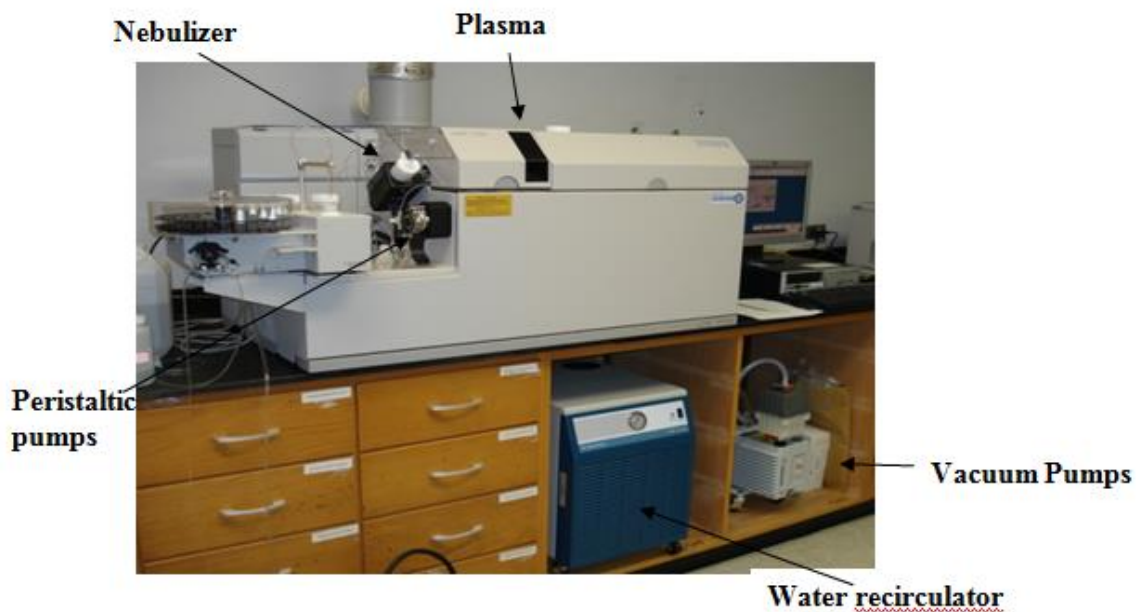


Figure 11. ICP-MS basic components

The nebulizer is part of the sample introduction system. Its name comes from the Latin word “nebula” that means spray, which describes very well its main function which is to convert the liquid sample into a fine spray. The fine droplets can be easily dried, and then the atoms can be

excited or ionized on the plasma. There are two basic types of nebulizers pneumatic and ultrasonic. The first one uses the carrier flow gas to create a pressure zone that breaks the solution onto fine droplets. The last one is used in our ICP-MS instrumentation because requires a low flow that is suitable for the introduction into the high sensitive MS detector. Instead, the ultrasonic nebulizer uses ultrasonic frequency on a small vibrating plate that helps in the conversion of the liquid solution onto a fine spray. The advantage of the ultrasonic nebulizer versus the pneumatic is that can raise the sensitivity of the analysis up to ten times. The disadvantage is the limited applications, it is useful for trace metal analysis and low dissolved matter content samples.

The Nebulizer Chamber is the part of the instrument design to guide the droplets toward the plasma by the carrier gas flow. Two basic types of chamber are generally used: the Scott and the cyclonic chamber. The Scott design chamber consist of two concentric tubes, where the inner one is smallest in dimension, typically 3 cm in diameter, where the finest droplets of the solution are transported through the torch by the carrier gas flow; the greater droplets are impacted in the walls of the chamber and then go to waste. The cyclonic chamber design uses centrifugal forces to separate the spray fine droplets. The main advantage of this type of chamber is that increases the sensitivity of the analysis, and as consequence the limits of detection are also improved. An extra accessory is used for ICP-MS system which consists of a Peltier cooler that sustain a desire temperature (2°C aqueous samples, -5°C organic samples) of the spray chamber allowing a more stable signal. The Peristaltic Pump is used to help in the introduction of the liquid samples to the plasma. The pressure of the tubes against the pump must be adequate to avoid poor reproducibility. Also, the flow of the pump must be optimized. Generally, the analyte emission signal increases when the flow is increased up to a point, and at higher flows the sensitivity tends to drop.

After the ions are formed in the plasma, they enter into the vacuum interface zone prior to their entrance into the optics of the equipment. The optics of our MS consists of two parts; in the first stage the ions pass through an Einzel lens and then to an Omega lens. This allows to focus the ion beam and does not permit the passage of neutral species or photons to the quadrupole. The quadrupole mass analyzer consists of four metal rods adjusted at diverse voltages. The voltage

changes such as only the desired mass to charge ratio (m/z) ions passed to the detector; all other masses collide with the rods and as consequence are removed from the system. The entire mass range (2-260 amu) can be scanned in 10 milliseconds. After passing the mass filter, the ions reached the electron multiplier (EM). The EM detector multiplies the electrons as they collide with the dynodes present as the part of the design. The EM can be operated in a pulse mode or analogue mode, depending if used for low or high concentrations. The ICP-MS system is suitable for trace metals analysis and can read concentrations as low as part per trillion (ppt).

5.3.2 X-Ray Diffractometry

X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction. Single-crystal X-ray diffraction is a technique used to solve the complete structure of crystalline materials, ranging from simple inorganic solids to complex macromolecules, such as proteins.

Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds. Powder diffraction is also a common method for determining strains in crystalline materials. An effect of the finite crystallite sizes is seen as a broadening of the peaks in an X-ray diffraction.

Thin film diffraction and grazing incidence X-ray diffraction may be used to characterize the crystallographic structure and preferred orientation of substrate-anchored thin films.

5.3.3 Electron Microscopy

An electron microscope is a type of microscope that uses a particle beam of electrons to illuminate the specimen and produce a magnified image. Electron microscopes (EM) have a greater resolving power than a light-powered optical microscope, because electrons have

wavelengths about 100,000 times shorter than visible light (photons), and can achieve better than 50 pm resolution and magnifications of up to about 10,000,000x, whereas ordinary, non-confocal light microscopes are limited by diffraction to about 200 nm resolution and useful magnifications below 2000x.

The electron microscope uses electrostatic and electromagnetic "lenses" to control the electron beam and focus it to form an image. These lenses are analogous to, but different from the glass lenses of an optical microscope that forms a magnified image by focusing light on or through the specimen. In transmission, the electron beam is first diffracted by the specimen, and then, the electron microscope "lenses" re-focus the beam into a Fourier-transformed image of the diffraction pattern for the selected area of investigation..

The advantages of electron microscopy over X-ray crystallography are that the specimen need not be a single crystal or even a polycrystalline powder, and also that the Fourier transform reconstruction of the object's magnified structure occurs physically and thus avoids the need for solving the phase problem faced by the X-ray crystallographers after obtaining their X-ray diffraction patterns of a single crystal or polycrystalline powder. The transmission electron microscopes major 'disadvantage' is the need for extremely thin sections of the specimens, typically less than 100 nanometers.

5.4 Experimental Procedures

The following parameters were evaluated in batch equilibrium sorption experiments: concentration of hazardous species, pH, and sorbent concentration. All experiments were carried out at laboratory room temperature conditions (20°C) and the samples were preserved using EPA Standard procedures. Synthetic solutions bearing Cu, Pb, and Zn species were prepared in distilled water at the same concentration (highest and lowest levels) reported by Puerto Rico Aqueduct and Sewer Authority (PRASA). Discharged Monitoring Report (1998-2006). The solution pH was the same as the value measured in the actual final discharge samples. Whenever needed, pH was adjusted by suitable amounts of NaOH or HNO₃. Prepared multi-ionic solutions were then contacted with granular crumb rubber in Erlenmeyer flasks immersed in temperature controlled water bath shaker and mechanical stirrers. After determining the pH of the solution at

the end of the contact period, the samples were filtered through membrane filters and submitted for quantitative analysis by ICP-MS techniques. The kinetic experiments work determined the equilibrium uptake, sorption rates, and removal efficiency.

5.4.1 TCLP Test of the dewatered sludges

The Toxicity Characteristics Leaching Procedure (TCLP test) is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. In this case the TCLP test is performed to verify the mobility for some metals in the dried sludge sample.

The flowchart of Figure 12 summarizes the TCLP procedure. Five grams of dried sludge sample were suspended in water and stirred for 5 minutes. The pH was measured; if the pH was less than 5, then it was used as extraction fluid. If pH was more than 5, then HCL was added and heated for ten minutes and while being stirred. Use another 5 grams of dried sludge and added 40 ml of extraction fluid (acid acetic) and 64.3 ml of NaOH and diluted in one liter solution.. Finally mix the sample at 31 rpm for a period of 20 hours and fixed temperature of 22° C. ICP-OS was used to measure the concentration of ionic species in the extracting solution. The results showed that Cobalt has 100 percent of mobility, Zinc has almost half the mobility, Copper and Lead have very low mobility, while Vanadium showed no mobility.

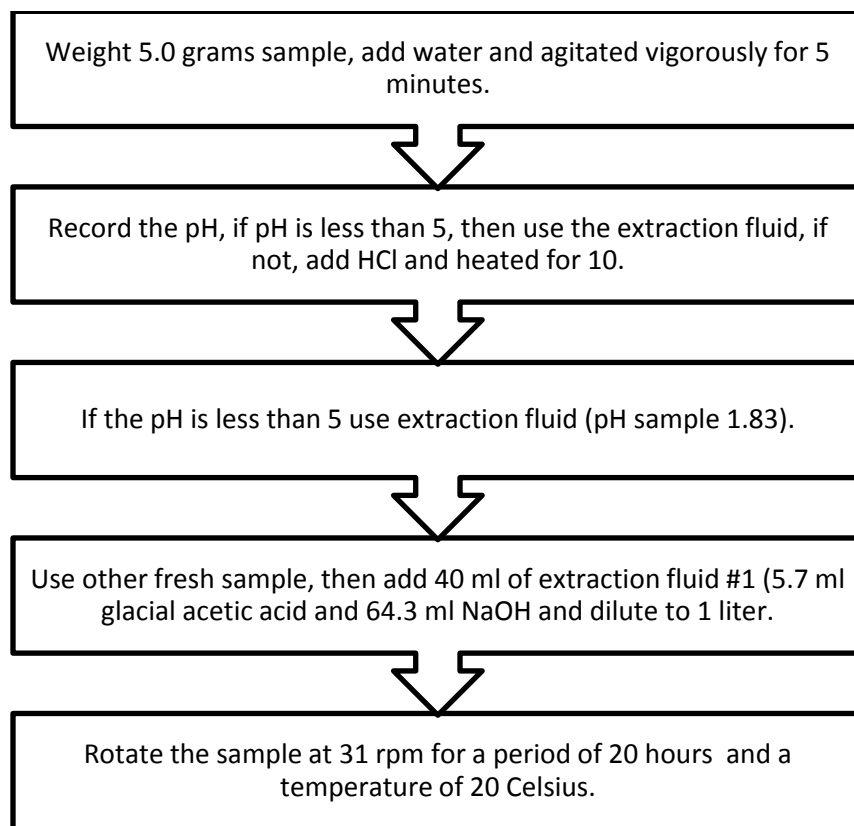


Figure 12. Flowchart procedures for TCPL analysis

5.4.2 Waste Tire Crumb Rubber Chemical Stability Test

Release of metals ions from crumb rubber will limit its applicability as a clean sorbent, because it can be a source of contamination. In order to evaluate this possibility, 10 g/L aqueous solutions of crumb rubber at pH 1.5, 3.0, 6.0, and 9.0 were stirred for 24 hours. The pH of these solutions was adjusted adding HNO_3 10% v/v or NaOH 10% w/v. Solution samples were withdrawn at the end of the contact period, acidified with 2.0% of HNO_3 and submitted for copper, cadmium, arsenic, zinc, lead, and chromium analyses by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The analytical conditions and standard procedures were realized following the EPA 200.7 rev 5.0 method. All analyzes were run by duplicate.

5.4.3 Sorption Tests In-single schemes

5.4.3.a Sorption Tests Using Crumb rubber as sorbent

The concentration of the rubber in the sorption studies was 10 or 15 g of tire crumb rubber per liter of solution, depending on the time to reach equilibrium for each metal ions. Concentrations of 100-1000 ppb of the cations of Zn(II), Cu(II), and Pb(II) were prepared from the following soluble salts: ZnSO₄, CuSO₄·5H₂O, and Pb(NO₃)₂ in distilled-deionized water. The pH was adjusted with nitric acid trace metal grade or sodium hydroxide of analytical grade. The toxic metals solutions were prepared on volumetric flasks of 100.00 mL and then placed in plastic sealed bottles of 120.0 mL capacity to prevent water evaporation. All solutions were prepared in duplicate and placed on a shaker bath (200 cycles per minute) or magnetic stirrer (260 rpm) at a 298 K temperature.

Aliquots of the metal solutions were taken at 0, 3, 6, 20, 24 hours and acidified with nitric acid trace metal grade in order to preserve the samples for further analysis. Samples were stored in sealed centrifuge tubes for ICP-MS analysis. All analyses were validated using quality control solutions such as matrix spikes (± 30 % maximum permitted error), check standards (± 20 % maximum error), and standards reference materials ($\pm 20\%$ max. error). The method used for the experimental analysis was EPA 200.8 Rev 5.4. Some of the evaluated parameters, as pH, mixed solutions, and concentration of the toxic metals, were changed in order to optimize the sorption capability parameters. The experiments were made on batch solutions because is less expensive, and easier to control than a continuous flow system. Although, is recommended a continuous flow system if more than 10,000 gallons of water needed treatment.



**Figure 13. Crumb rubber at different mesh sizes
(Mesh 30 above the cent and mesh 14-20 below the coin)**

Adsorption tests evaluated the effect of using both sizes of crumb rubber. First the tire rubber was placed in shaker bath with deionized water at pH 6 for 24 hours. After shaker bath with deionized water, the tire rubber was placed again in the shaker bath with acidic solution at pH 1.5 at 24 hours. The tire rubber was placed in magnetic stirrer at 770 revolutions per minute with deionized water for 24 hours at 50 °C. After the washed for 24 hours at 50 °C, the tire rubber was placed again in magnetic stirrer, the same procedure, but the temperature increased to 60°C.

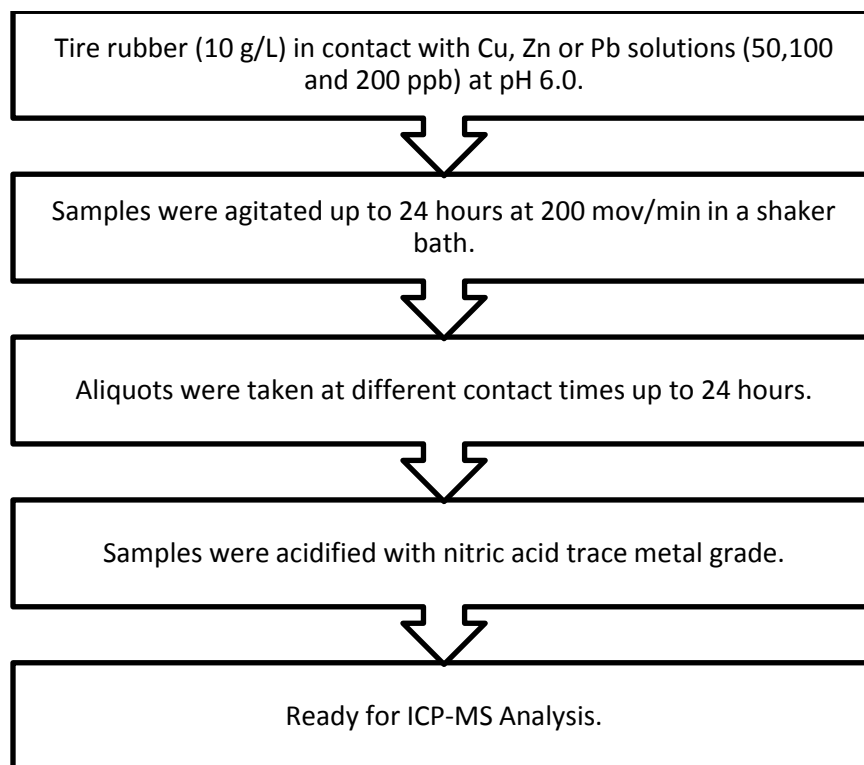


Figure 14. Flowchart for tire rubber samples preparation procedure for ICP-MS analysis

Finally the tire rubber was placed again in the magnetic stirrer with a basic solution (0.5 M of NaOH) at 60°C for 24 hours. After all washed with acidic and basic solution and passed the 24 hours period the tire rubber was filtered. The tire rubber dried at room temperature, and then it was ready for use it as sorbent.

5.4.3.b Sorption Tests Using Dewatered sludge as sorbent

In the case of dried sludge at a concentration of 10-20 g per liter of solution, the dried sludge was placed in contact with 100 mL of 100 or 200 ppb of Cu, Pb or Zn solutions. Previous studies show a better uptake at pH 8.0 and we used it as a guideline. Each sample was run in duplicate. Aliquots were taken at different contact times, acidified with nitric acid trace metal grade and later subjected to ICP-MS analysis. As mentioned before, the majors metals concentration found in the dried sludge were: Fe, Al, Mg and Ca. In minor concentration were found: Zn, V, Cu, Cr, Ni and Co.

5.4.3.c Chemical Precipitation Coagulation using Sodium Trithiocarbonate and Aluminum Chlorohydrate

The dosage of chemical precipitant, Sodium Trithiocarbonate, was selected according to the manufacturer's protocol. For this purpose, a synthetic aqueous solution of 1 ppm of each Cu, Pb and Zn was used in these experiments.

The following figure shows the procedure using chemical precipitation.

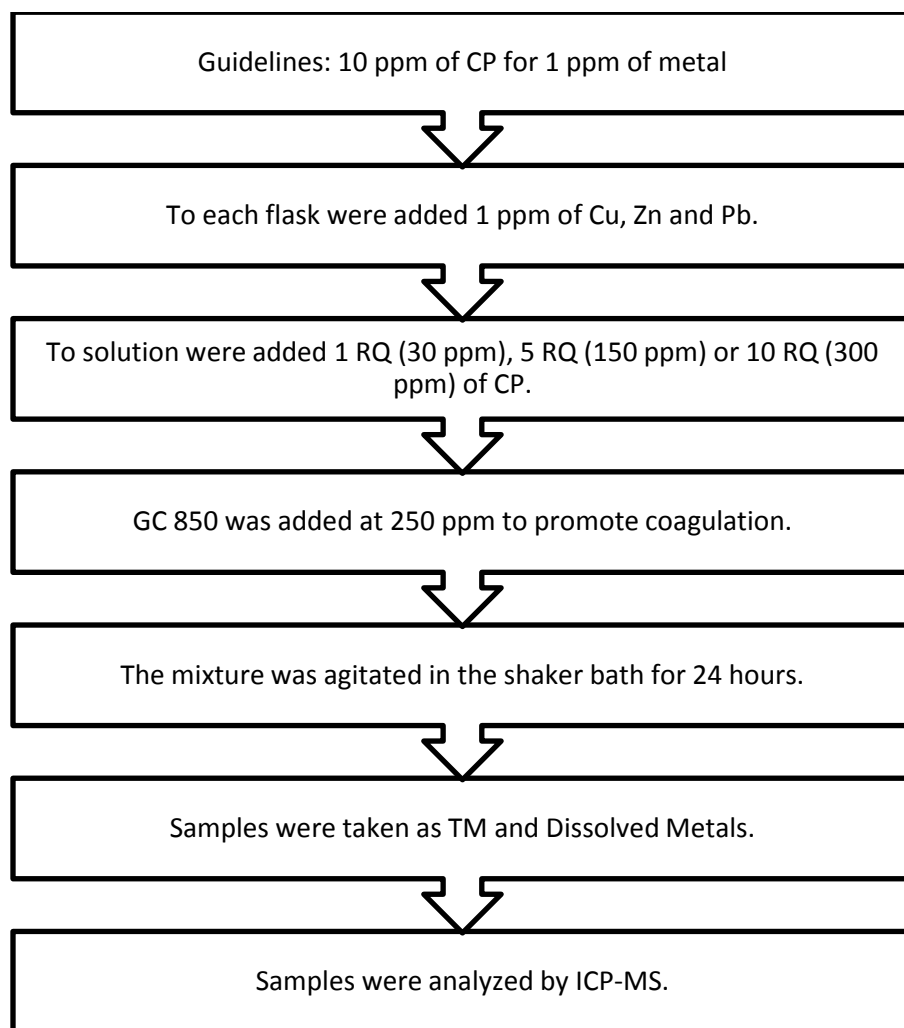


Figure 15. Flowchart for chemical precipitant and coagulant for heavy metals removal

All ions generated after dissolving the Al-salt in water will neutralize the surface charge of the suspended colloids making them amenable to aggregation and subsequent settling. The Al-chlorohydrate salt was used in addition to the chemical precipitant in order to promote the settling

of produced colloidal metal sulfides. The experimental work considered different concentrations of the Al-salt (30, 150 and 350ppm). In all experiments an excess of 0 ppm of GC 850 was added to promote coagulation of produced solids. The mixture of the chemical precipitant and the coagulant was contacted with the metal solution at pH 8 containing Cu, Pb and Zn (1ppm) or 24 hours in a shaker unit at room temperature. Experiments were run by duplicate and samples were withdrawn at different times and analyzed for dissolved metals by ICP-MS.

5.4.4 Sorption Tests using Combined Schemes

The combined use of crumb rubber (mesh 30), sludge and chemical precipitant were also evaluated as an attempt to decrease targeted Cu, Pb and Zn ions concentration down below the environmental regulations. Accordingly, the following three-schemes were evaluated. The next step consisted on mixing tire rubber and dried sludge as sorbent at different heavy metals concentrations. First, different ratio concentration of dried sludge and tire rubber mesh 30 were mixed with 200 ppb Cu, Zn, and Pb in water at pH 8.0. The ratio concentrations were 1:1 (dried sludge and tire rubber), 2:1(dried sludge and tire rubber) and 5:1 (dried sludge and tire rubber). The mixing solution was put it in shaker bath for 24 hours. Finally, the samples were taken and the heavy metals concentration determined by ICP-MS. The scheme is represented in the next figure 16.

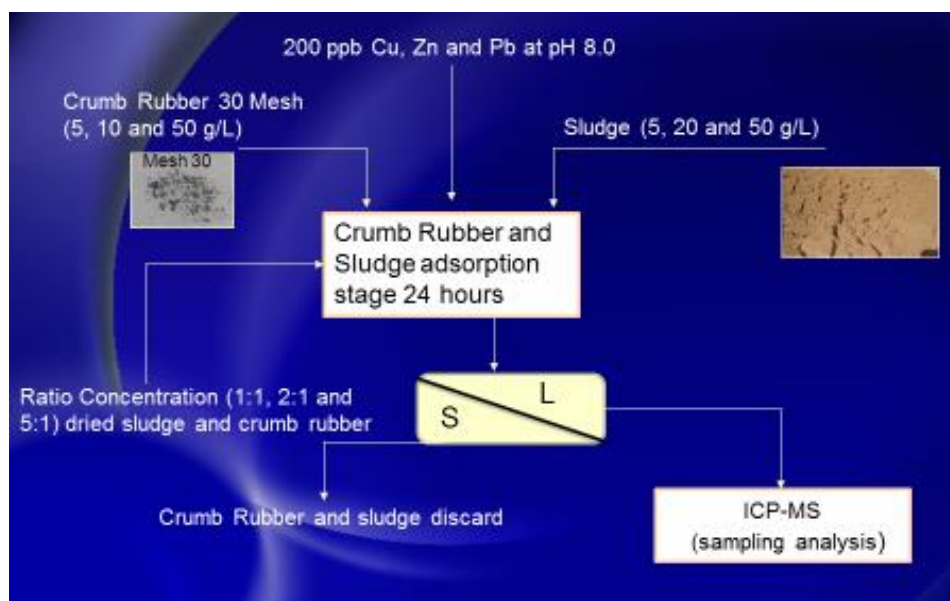


Figure 16. Flowchart for Sorption Test using combined schemes

5.4.4.a Scheme-1: Crumb rubber followed by dewatered sludge

The first method used rubber, dried sludge and chemical precipitation at different concentration. Initially, 100 ppb of heavy metals concentrations rubber was mixed with the heavy metals solution at different concentration (10 and 20 g/L) at pH 6.0. After mixing process, the samples were put in the shaker machine for 24 hours. The rubber was removed and discarded. After the liquid and solid separation, the liquid portion was mixed with sludge at different concentration (10g/L and 20g/L) or with chemical precipitant at different concentration at pH 8.0 for 24 hours. Finally the samples were taken. Figure 17 and figure 18 shown the flowchart using this step mechanism

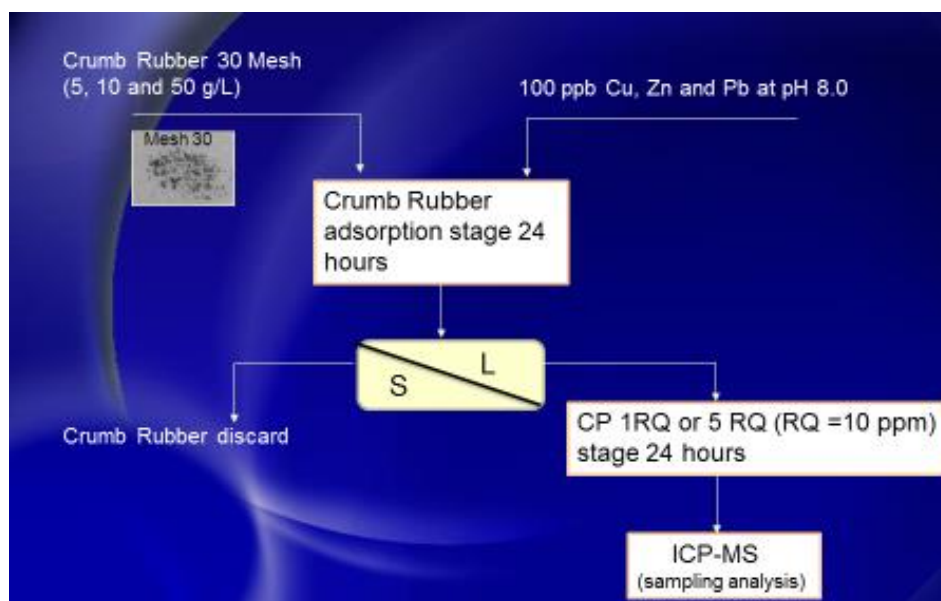


Figure 17. Flowchart using crumb rubber and chemical precipitant

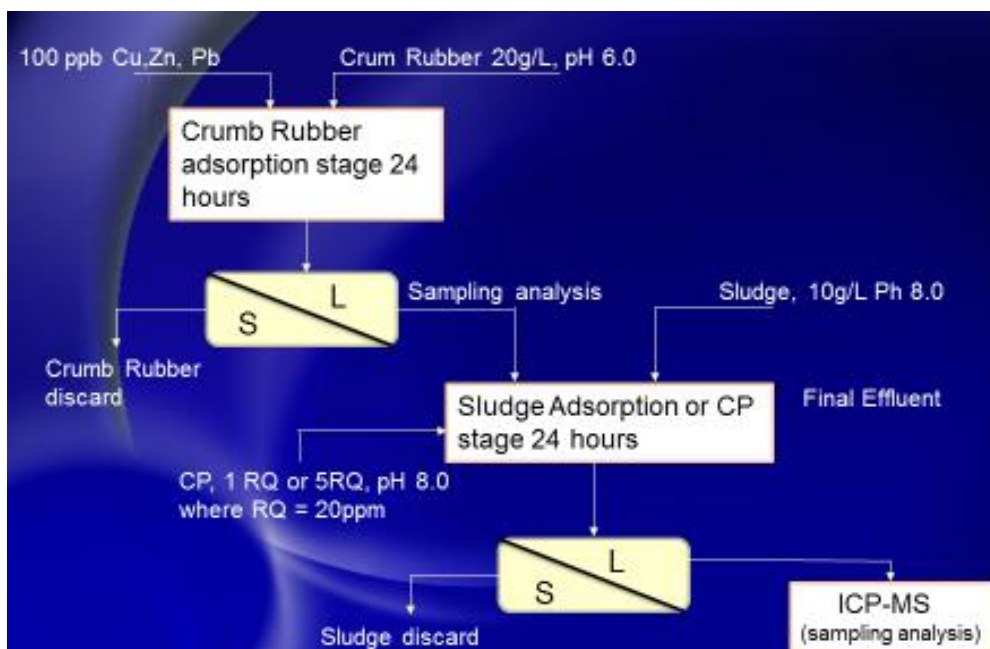


Figure 18. Flowchart using crumb rubber, dewatered sludge or chemical precipitant

5.4.4.b Scheme-2: Crumb rubber and chemical precipitant

As mentioned before, the samples started with initial concentration of 100 ppb for each studied heavy metals. In this method, the samples were mixed with rubber at different concentrations, then the samples were mixed chemical precipitant at different concentration. In figure 19 show the experimental procedure using crumb rubber and chemical precipitant. The next chapter, showed the results using this mechanism and compare with the others mechanism.

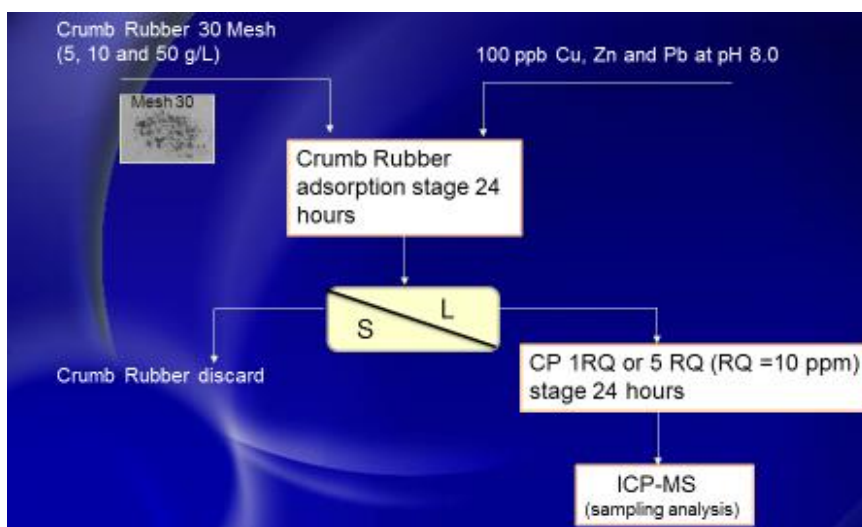


Figure 19. Flowchart using processes crumb rubber and chemical precipitant

5.4.4.c Scheme 3: Crumb rubber followed by dewatered sludge and chemical precipitant

In the third method all the components were mixed. The difference between the first method and this method is the reaction time period. In this case, the rubber was mixed with the samples for 24 hour period and then the samples were mixed with sludge and chemical precipitant at the same time for 24 hour period. First, the synthetic samples initially with 100 ppb for each heavy metals. In this case, the rubber concentration was set with 20g/L at pH 6.0. The samples and the rubber were mixed in a shaker for 24 hours, then the rubber was discarded and the liquid portion was subjected with sludge concentration of 10g/L and chemical precipitant at different concentration at the same time. The liquid portion was mixed for 24 hours at pH 8.0. Finally the sludge was discarded and the samples were taken for analysis purposes. Figure 20 shows the flowchart process using this mechanism.

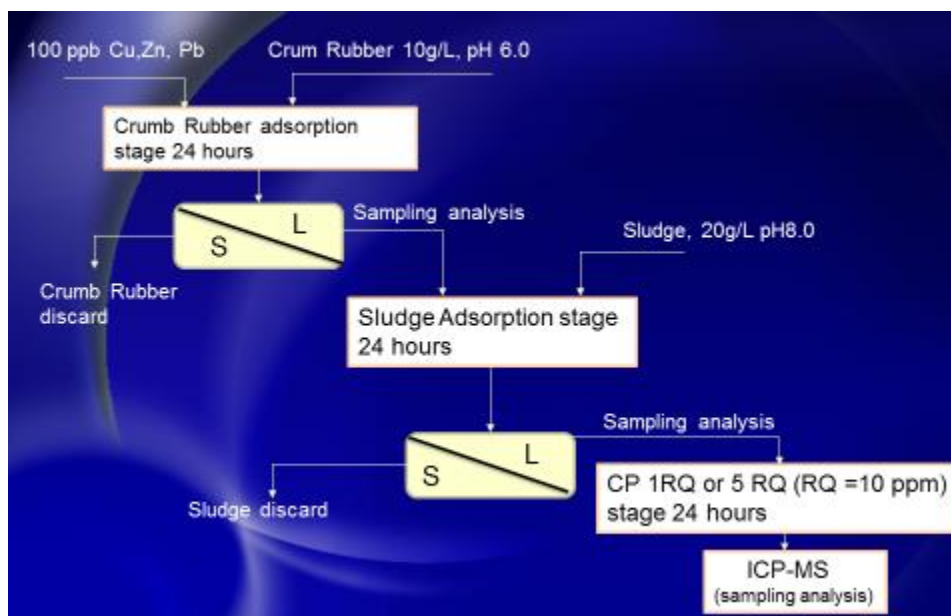


Figure 20. Step Mechanism using rubber, dried sludge and chemical precipitant

The final step mechanism using synthetic samples includes rubber, dried sludge, and chemical precipitant over a 24-hour period for each component. The initial concentrations of the samples were 100 ppb for each heavy metal. The samples were mixed with 10 g/L of rubber concentration in the shaker

for 24 hours period at pH 6.0. The rubber was discarded and the samples were taken. The reason to take a sample in this part is to verify the rubber performance to decrease the heavy metal concentration. Then the samples were subjected to dried sludge with 20 g/L at pH 8.0 for another 24 hours. The samples were taken and the sludge was discarded. Finally the samples (liquid portion) were mixed with chemical precipitant using different concentration (1RQ and 5 RQ) for another 24 hours at pH 8.0. The samples were taken for analysis purposes. Figure 20 showed the flowchart in this method. The results are discussed in the next chapter.

5.4.4.d Scheme : Dewatered sludge and chemical precipitant with coagulant

In the scheme using dewatered sludge and chemical precipitant with coagulant, the first step was contact 10 g/L of sludge with 100 ppb solution of Pb, Cu, and Zn at pH 8.0. After 24 hours period, the samples were separated where the sludge were discard and the supernatant was in contact with 10 ppm of chemical precipitant and coagulant (GC 850) for 24 hours period. Finally the precipitant discarded and the supernatant was analyzed. In figure 21 show the flowchart. The results were discussed in the next chapter.

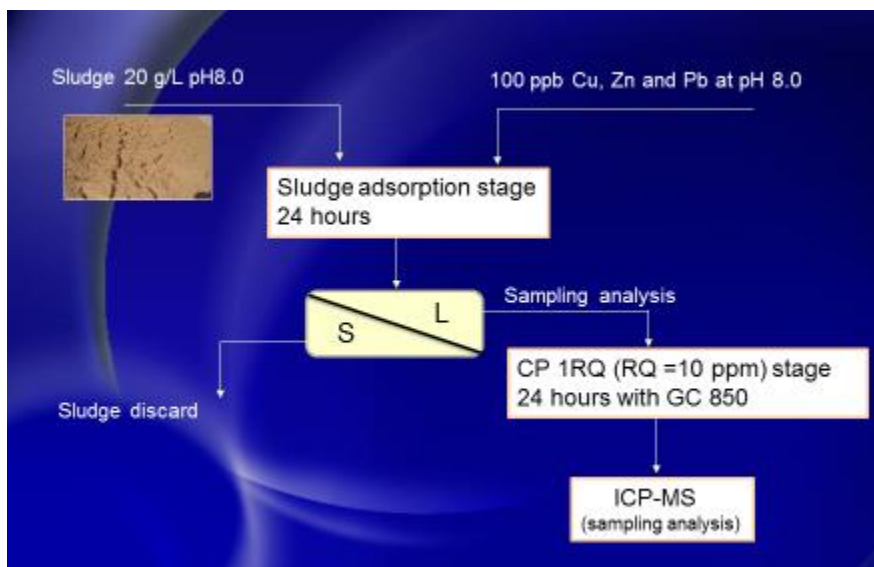


Figure 21. Step Mechanism using dried sludge and chemical precipitant with coagulant

5.4.4.e Scheme : Dewatered sludge and chemical precipitant

This scheme used the same procedure as mentioned in the last section, the only change in the process was the coagulant. The samples were in contact first with sludge as first stage for 24 hours period and then the supernatant was in contact with chemical precipitant at different concentrations. The samples were analyzed. In the figure 22 show the flowchart. The results were discussed in the next chapter.

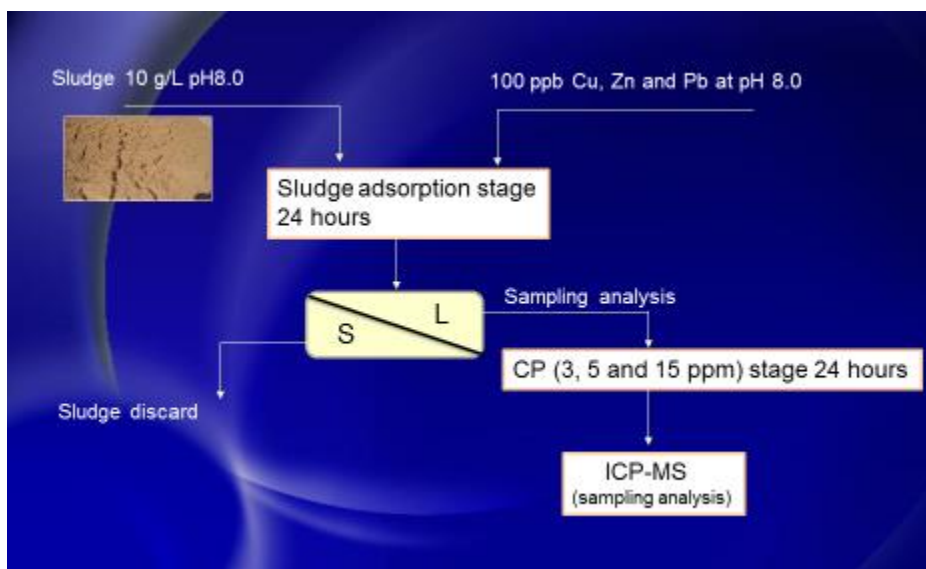


Figure 22. Step Mechanism using dried sludge and chemical precipitant

5.5 Sorption tests using actual water samples

After laboratory tests, using synthetic samples and obtaining the best method to remove metals we proceed to perform real sample at Miradero Water Treatment Plant. The results of the better method for metals removal is described in Chapter 6.

Three sampling points in the sludge process system were identified to take the real samples. The sampling points chosen had to show different sample characteristics due to existing plant process. Samples were collected at different times of the day during three days during the last week of November 2008. The time of sampling was: 8:00 am, 12:00 pm and 4:00 pm. Samples were taken duplicated as recommended by EPA 200.7 Method for Sampling and Determination of Heavy Metals. They were collected in a plastic bottle, identified and taken to Environmental

Nanotechnology and Remediation Research Laboratory at the University of Puerto Rico at Mayaguez. Samples were preserved with nitric acid HNO_3 and pH 2 as described in EPA 200.7 method. The samples can be validated up to six months later after collecting them. A total of 18 samples per day and their blanks for process control were collected on the field. Blanks were opened in the sampling place to atmosphere for the field conditions. Figure 23 describes a sludge process diagram and sampling points of Miradero Water Treatment Plant.

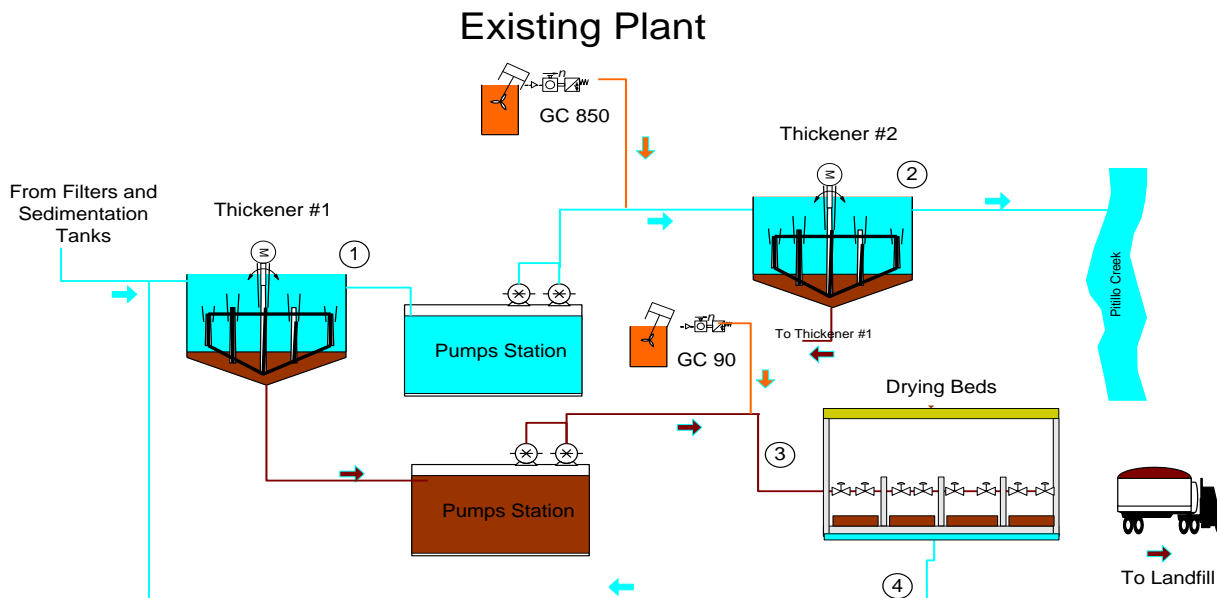


Figure 23. Sludge process diagram and sampling points of Miradero Water Treatment Plant

The Figures 23 and 24 show sampling point 1 that was located at the Thickener #1. At this point, the solid phase has been separated from the liquid phase of the wash water that comes from the filters and the sedimentation tanks of the plant. The sample collected was obtained from the liquid phase of this process. These clarified waters are sent to the second Thickener tank.



Figure 23. Thickener #1 and sampling point #1



Figure 24. Pumps from Thickener #1 and samples collection #1

The second sampling point was the polymer injection point from the sludge process system. At this point, the GC 850 and the clarified water from the Thickener #1 were mixed. In the normal plant process, at this injection point the suspended solids are removed to comply with the discharge as described in Plant NPDES permit. Three times a day, duplicate samples were collected at this point. Figure 25 shows sampling point number 2.



Figure 25. Sampling point #2 and polymer addition for suspended solid removal

Last sampling point is at Second Thickener exit. This point is also known as Sampling Point 001 of the NPDES permit. At this point, regulatory agencies, takes representative samples and compare results with NPDES permit.

The sample collected was the clarified water that passed through the Thickener #2. The Thickener #2 provides the water containing polymer, the retention time required for these particles can settle and be removed. Sludge is removed in this tank and does to the drying beds and the clarified water goes to the discharge point 001. Like the other sampling points were sampled three times a day and a duplicate. Figure 26 illustrates the Thickener #2 and the point of sample collection. Samples were taken in duplicate three times a day.



Figure 26. Thickener #2 and Discharge Point 001

5.5.1 Samples preservation

Three samples were taken at different times at each sampling point. These three samples were then mixed up to have one-day representative sample. The samples were placed in plastic containers and labeled depending on the sampling location and time and transported to the analysis laboratory. EPA procedure 800.5 related to the handling of heavy metals water samples, was used to handle these samples. After adjusting pH, the samples were placed in a 150 mL container and then in a 5 mL volumetric flask. An 2.5 mL aliquot was taken from the flask, and replaced with 2.5 mL of Nitric Acid (HNO_3), thus preserving the metal in solution and avoid any contamination. After acid addition, the sample was placed in a plastic test tube with a capacity of 15 mL. The procedure recommended plastic to prevent metal to adhere to another surface like the glass. Sample aliquots were analyzed for heavy metals concentration of each sampling point by using ICP-OS. Turbidity and pH was also measured in each sample.

6 RESULTS AND DISCUSSION

6.1 Sorption Tests Using Tire Crumb Rubber

Tire crumb rubber as sorbent was more efficient to removing two heavy metals: Copper (Cu) and Lead (Pb). As shown in Figure 27, the removal of those heavy metals varied between 95% and 98% using tire rubber mesh 30 water washed at pH 6.0 and at a concentration of 10 g/L. The initial concentration of both Cu and Pb solutions were 50 ppb.

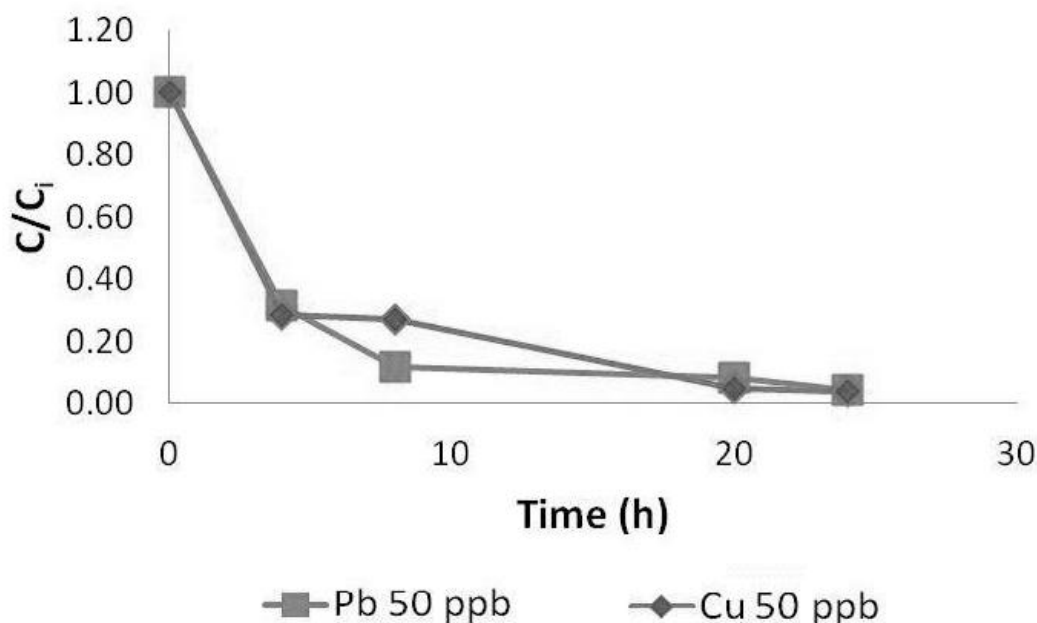


Figure 27. Pb and Cu sorption as a function of contact time using tire rubber as sorbent

Figure 27 shows the Pb sorption results but using crumb rubber at different mesh sizes. On a general basis, both sizes of crumb rubber were conducive to similar removal capacity and contact times. It may be an indicative of a strong chemical affinity between the carbon black particles in the rubber and the dissolved Pb species in water; accordingly an adsorption-based process can be suggested.

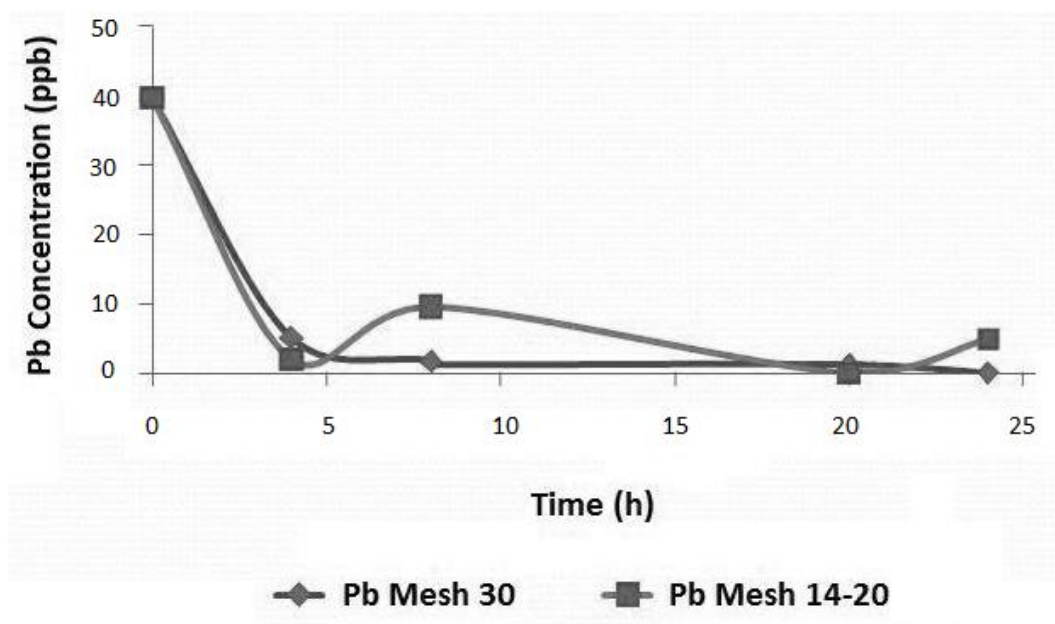


Figure 2818. Pb sorption behavior using tire rubber mesh 30 and 14-20

The results of the Cu sorption (initial concentration 180 ppb) by crumb rubber mesh 14-20- and 30 are shown in Figure 29. Both sizes of crumb rubber particles are capable of removing Cu species; however, it becomes evident that smaller sizes favored a faster adsorption. It can be expected on basis of the higher availability of adsorption (ie, carbon black nanoparticles) in smaller rubber particle sizes in contact with heavy metals. Crumb rubber has carbon black component, this component has a good adsorption capabilities due carbon chemistry. On this basis, mesh 30 was selected as the optimum size of the crumb rubber for the subsequent experimental work.

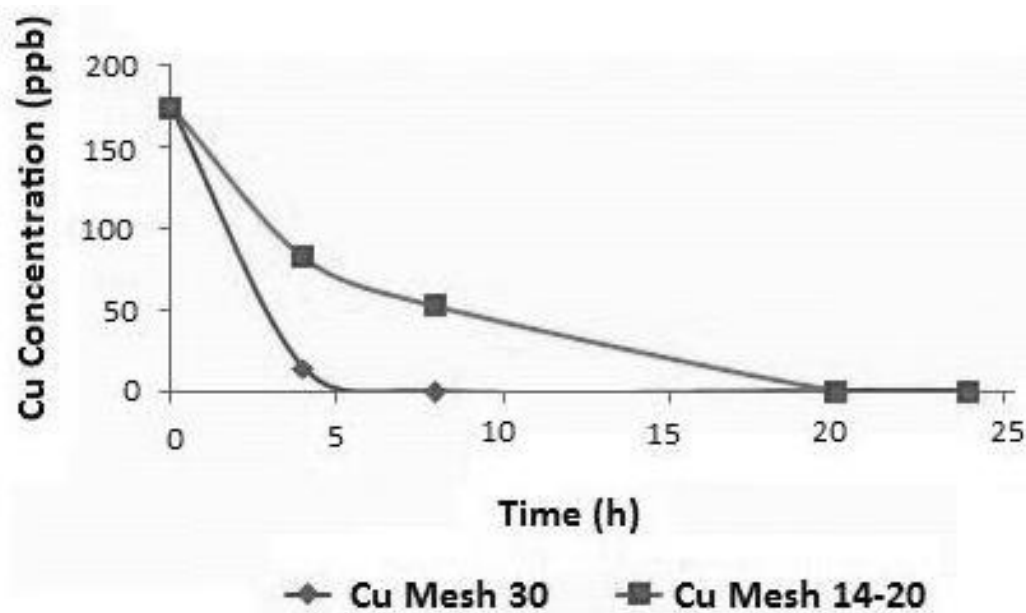


Figure 2919. Cu Sorption behavior using tire rubber as sorbent at 298 K, 10 g/L and pH 6.0

Based on the fact that waste tire crumb rubber contains Zn as ZnO in its composition, the release of this species to water was assessed. Figure 30 shows the variation in the concentration of dissolved Zn as a function of the contact time of crumb rubber in water at pH 6; the continuous release of Zn became evident, although still small (in the part per billion order). A concentration of Zn of 1000 ppb was found after a contact time as long as 24 hours. Initially with none concentration of Zinc, the maximum concentration of Zinc was around 1100 ppb. The drop at the end of the 24 hours-contact could be related to hydrolysis of Zn species and subsequent precipitation due to changes for pH. On this basis, different routes were evaluated to remove Zn from the crumb rubber prior to its use in the adsorption stage. The next step was washing the tire rubber with acidic solution. If tire rubber is used as an alternative of heavy metals removal, is necessary to add additional cleaning mechanisms for the tire before using it as sorbent. That will mean an increase in operational costs.

Figure 30 shows the Zn concentration release using tire rubber mesh 30 as sorbent. The graph shows how the tire rubber started releasing Zn concentration in the solution. However, the tire rubber showed different behavior, if the tire rubber was washed in acidic solution.

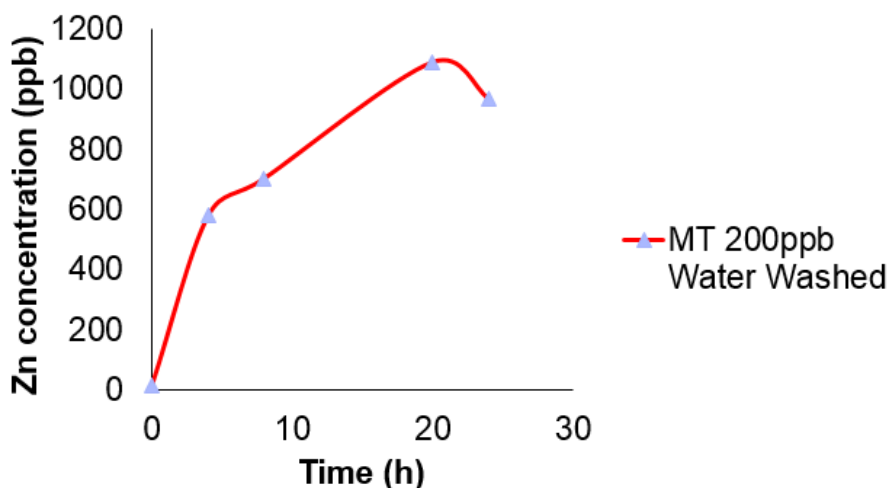


Figure 30. Concentration of Zn release from tire rubber at pH 6.0

The tire rubber can be used as sorbent for heavy metal species, but it becomes necessary to remove initial Zn (from ZnO used in manufacture of tires) because tire rubber release Zn. In order to find the best option that decrease the release of Zn, tire rubber was subjected to different types of wash.

Figure 31 shows the performance of tire rubber releasing Zinc when is washed with different solutions. This graph shows Zinc release at different tire rubber washed using an initial concentration of 200 ppb of total dissolved metals. In the graph, the line with the triangle symbol shows the higher release of Zn concentration using the tire rubber as sorbent washed with deionized water with pH 6. The line with the diamond symbol shows some decrease in Zn concentration release, using tire rubber as sorbent at pH 1.5. The release of Zinc decreased when the pH was below 6. Finally, when the tire rubber was washed with acidic or basic solution the releasing of Zinc was almost ineligible. The best performance was observed when the tire rubber was washed with basic solution.

In conclusion, the tire rubber was capable to remove Zinc concentration as sorbent, if at the beginning of the process the tire rubber is washed, preferably with basic solution.

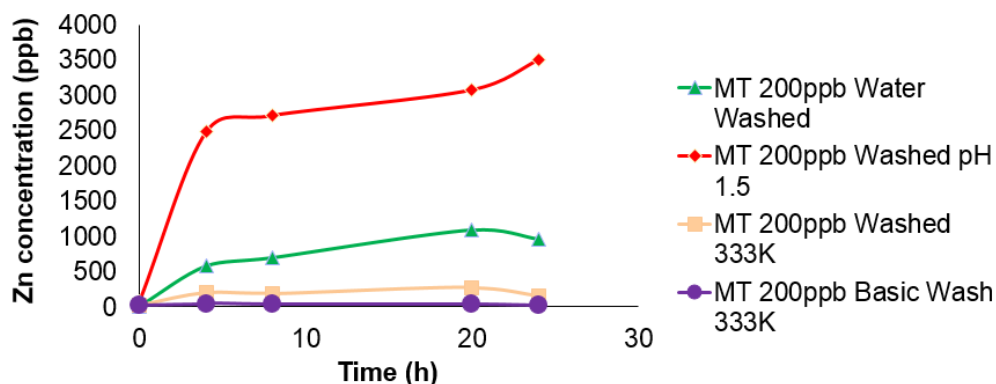


Figure 31. Concentration of Zinc release at tire rubber wash 10 g/L solution subjected to total metals (MT) concentration of 200 ppb at initial pH 6.0

After the tire rubber was washed with basic solution, it was used as sorbent for others heavy metals. Table 5 shows the heavy metals removal efficiency for Copper and Lead using the tire rubber at different water washed conditions. The removal efficiency is above 90 percent for both heavy metals.

Table 5. Comparison between the removal efficiency of Cu and Pb using crumb rubber as sorbent previously washed under acidic conditions at different temperatures

MT 200 ppb (10 g/L, pH 6.0)	Cu Concentration (ppb)	Cu Removal (%)	Pb Concentration (ppb)	Pb Removal (%)	SD
Washed 50 °C	3.39	98	3.64	98	.25
Washed 50 °C	3.56	98	3.81	98	.27
Washed 60 °C	13.16	93	10.77	94	40.3

6.2 Sorption tests using dewatered sludge

As suggested by the results shown in Figures 32-34, the capability of sludge to remove lead, copper, and zinc species was evident. Figure 32 shows the variation in Pb concentration with contact time at three different initial concentrations of the metal species. The average removal efficiency was as high as 74% using dried sludge as sorbent at pH 8.0 and after 24 hours of

contact. This adsorption capability of the dried sludge is attributed to the presence of silica (SiO_2) as the major component in the sludge; the adsorption capacity of silica, and other mineral oxides, has been demonstrated elsewhere. The formation of Si-Metal surface complexes can explain the removal of lead species from the water samples.

Although the removal of Pb using dried sludge was verified, the terminal concentration is still high and do not reach the required concentrations of the NPDES for the Miradero Water treatment Plant. The terminal Pb concentration was as low as 13 ppm, from starting 50 ppb-Pb solutions, whereas the compliance concentration for Lead is 1.8 ppb according from EPA discharge permit for Miradero Water Treatment Plant.

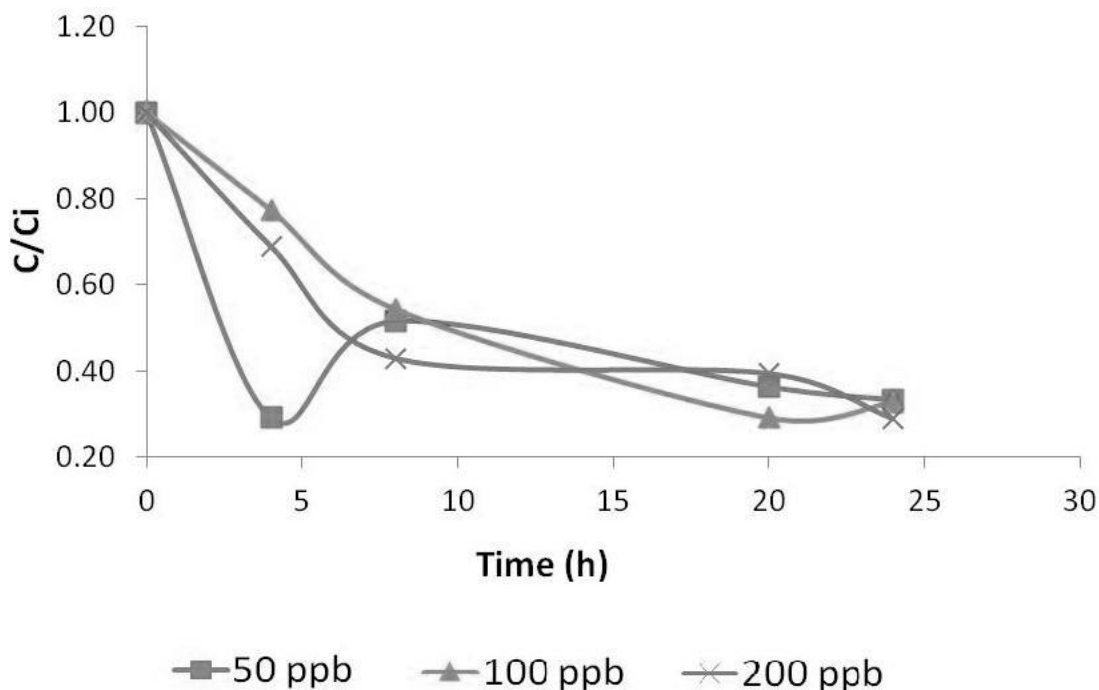


Figure 32. Sorption behavior of Pb using dried sludge at pH 8.0 and 10 g/L

Figure 33 shows the variation in the Cu concentration with contact time in presence of dried sludge. The average removal efficiency was very high and averaged 95% and the corresponding terminal concentration was 2.5-10 ppm Cu range; in this case, the use of dried slugged was capable of complying with the regulation for Cu (8.0 ppb) for starting solutions containing 50

ppb or 100 ppb of Cu. After 20 hours, the dried sludge released Cu, some explanation could be that the adsorption capability exhausted.

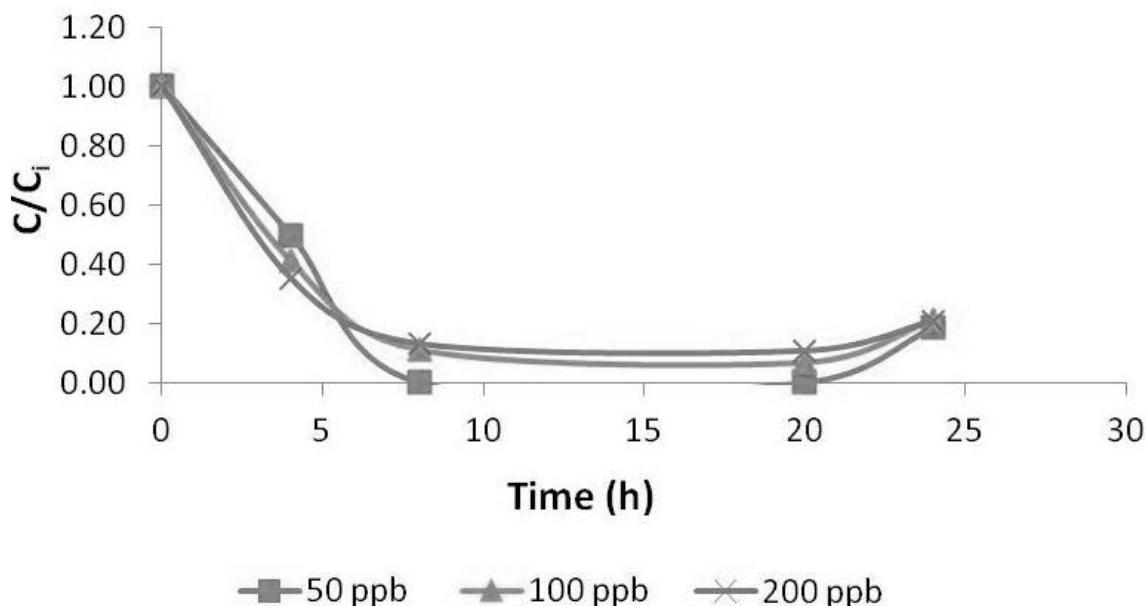


Figure 33. Sorption behavior of Cu using dried sludge

The removal of Zn by using the dried sludge was also attempted. For this purpose, Zn solutions with starting concentrations in the 50-200 ppb range were contacted with dried sludge (10 g/L). Also in this case, the dried sludge was capable of removing Zn species (Figure 34). The corresponding removal efficiency varied from 70% to 88% for terminal concentrations of Zn in the 60-68 ppb range. For compliance purposes, the use of dried sludge made possible to comply with the discharge regulatory permit for Miradero Water Treatment Plant.

Based on the above results, it is evident that both crumb rubber and dried sludge exhibited suitable adsorption capabilities for the heavy metal species of our interest. The adsorption capability of the crumb rubber is attributed to the presence of carbon black in the tire rubber. Carbon black as any other carbonaceous solid exhibits strong affinity for dissolved metal ions. In turn, the large contents of SiO_2 , and minor amounts of other iron oxides, can explain the availability of adsorption sites for the metal species. However, both adsorbents also exhibit

some limitations; crumb rubber is an effective adsorbent for Cu and Pb but it releases Zn whereas dried sludge can effectively remove only Cu and Zn.

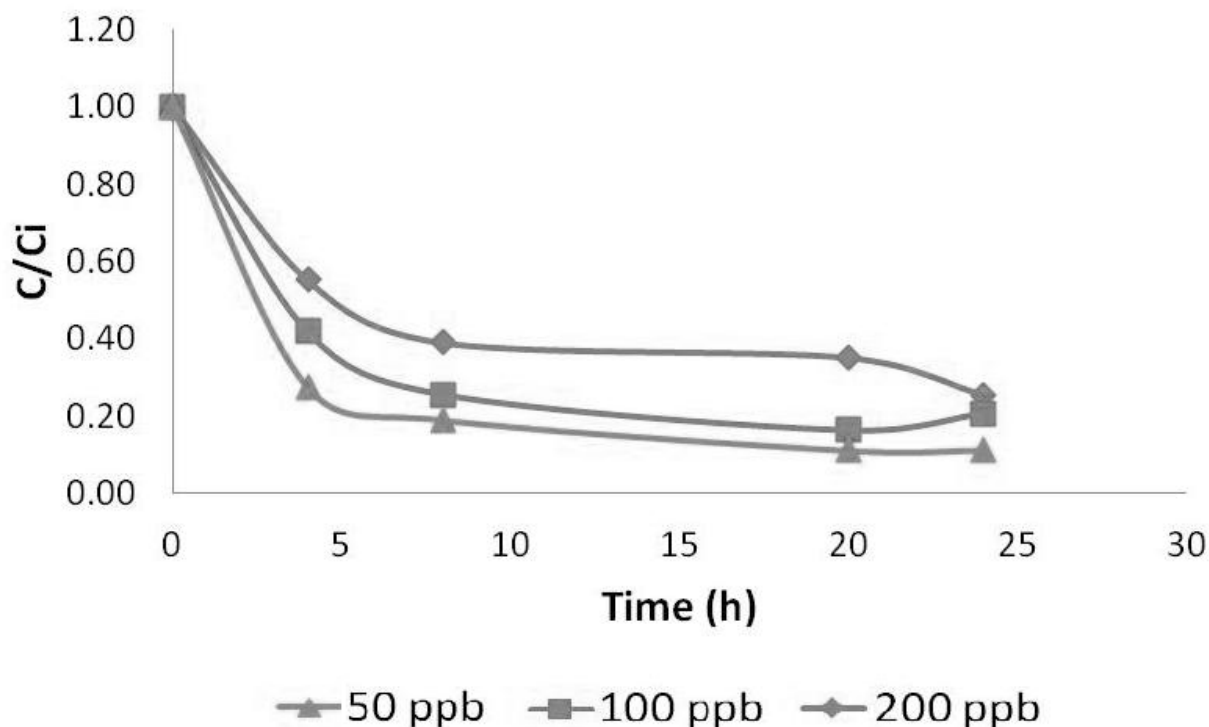


Figure 34. Sorption behavior of Zn using sludge at pH 8.0

6.3 Sorption tests using mixtures of crumb rubber and sludge

Based on the above results, the removal of heavy metal ions was evaluated in presence of crumb rubber-sludge mixtures. As Figure 35 shows, no improvement was obtained in the removal of Cu and Pb after using crumb rubber and dried sludges in a 1/1 weight ratio for a total 10 g/L of concentration. The concentration of Cu and Pb were fixed at 100 ppb each. The removal efficiency of Cu and Pb were 70% (15 ppb in final solution) and 50% (25 ppb in final solution), respectively. These terminal concentrations are above the NPDES regulation.

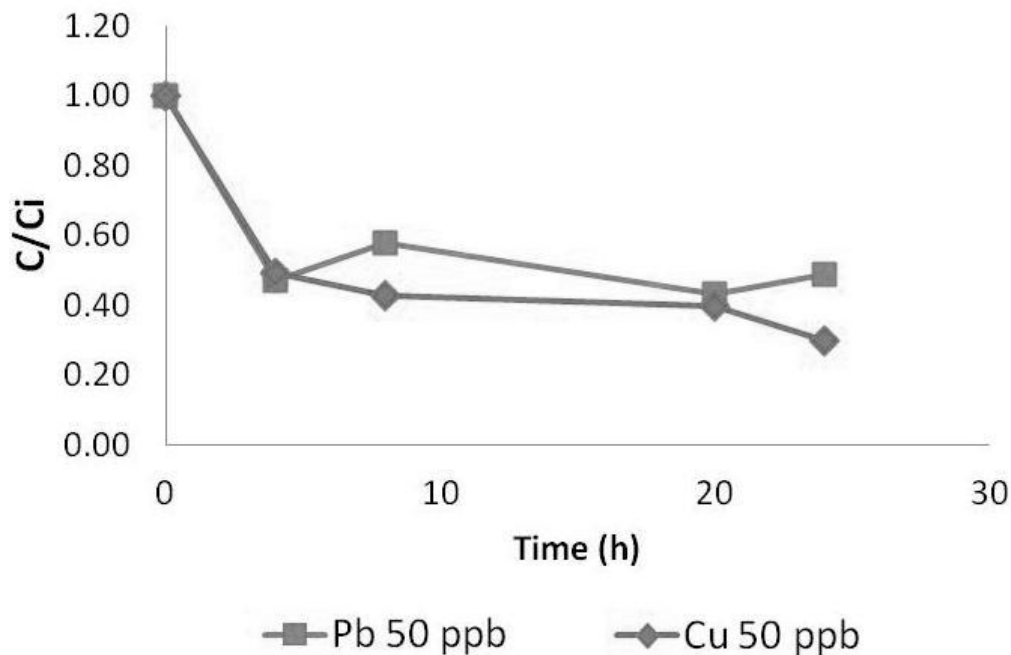


Figure 35. Pb and Cu sorption as a function of contact time using 5 g/L of each, dried sludge and tire rubber, and pH 8.0

The adsorption capacity was also evaluated at different crumb rubber/sludge w/w ratios. The results are summarized in Table 6. The best results observed were using a tire rubber and dried sludge weight ratio of 1:10. The corresponding removal efficiencies were 93% for Pb (3.7 ppb of terminal concentration) and 48% for Cu (26 ppb of terminal concentration). However, the solution reported 100 ppb of Zn that should have been released out from the crumb rubber matrix. The 1/10 mixture of crumb rubber and dried sludge demonstrated enhanced capabilities to remove heavy metals species; however, the main drawback was the release of Zn species from rubber matrix.

Figure 35 shows the results in concentration removal for both heavy metals for 24 hours of contact. The results did not show any improvement in concentration removal for both metals. The concentration removal were 76% and 57% for Copper (Cu) and Lead (Pb), respectively.

Table 6. Copper and Lead removal at different crumb rubber/sludge w/w ratios.

The initial concentrations of Cu and Pb were 100 ppb as total metals.

	Cu terminal concentration (ppb)	% Removal Cu	Pb terminal concentration (ppb)	% Removal Pb
1:1 Rubber: Sludge	26.0	48	38.8	22
1:2 Rubber:Sludge	29.7	40	29.1	42
1:10 Rubber:Sludge	33.1	34	3.7	93

As observed in figure 36, the main concern associated to the use of crumb rubber, alone or in mixtures, relies on the release of Zn species. Zn released less concentration at different rubber/sludge weight ratios used in the adsorption tests. Although released Zn from the crumb rubber could have been adsorbed by the dried sludge, the results suggest that this removal was not enough, to prevent the solution get enriched in Zn and make the process fail, to comply with the NPDES requirement.

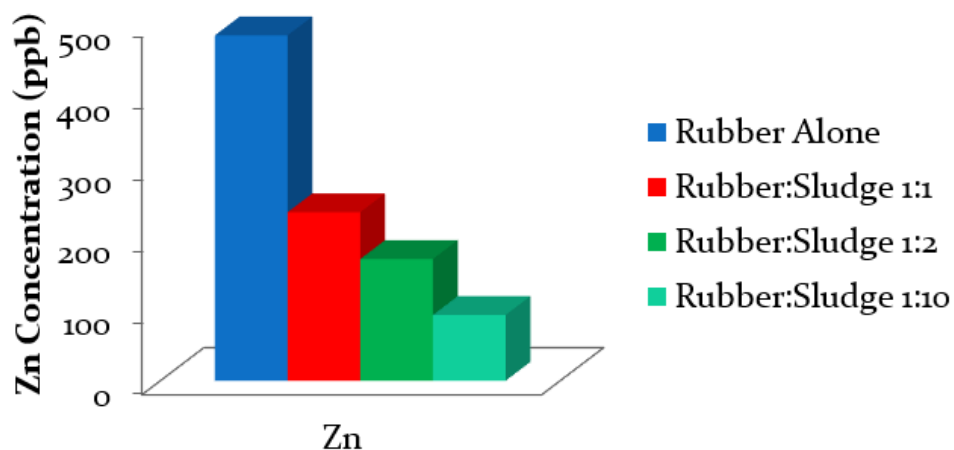


Figure 36. Concentration of Zn released at different crumb rubber/dried sludge weight ratio

6.4 Sorption tests in presence of sodium trithiocarbonate and aluminum chlorohydrate (GC 850)

The removal of heavy metals was also attempted by chemical precipitation. In this case, the use of coagulant becomes indispensable to promote the aggregation of colloidal particles (metal hydroxides) and facilitate the solid/liquid separation stage. On this basis, the chemical treatment of the metal solutions with trithiocarbonate (alkaline precipitant) and the aluminum salt (GC 850, as coagulant) allowed the efficient removal of Cu and Zn but not Pb. The use of trithiocarbonate would favor the formation of colloidal hydroxide particles in aqueous phase. The initial concentration for the chemical precipitant was 10 ppm and coagulant was 1 mg/L, respectively, which is the dosage recommended by the manufacturer. Table 7 shows the corresponding results of the removal of heavy metal species using the combined use of the chemical precipitant and GC 850. The removal of Cu and Pb was as high as 92-94% whereas a 85% of Zn removal was attained. NPDES compliance for Cu (8 ppb) and Zn (50 ppb) was achieved using chemical precipitation; however, it was not the case for Pb (1.8 ppb). It is important to mention that the initial concentration of heavy metal ions used in these experiments was 100 ppb. In comparison with historical data at the Miradero Facility these concentrations were high.

Table 7. Heavy metals terminal concentration after using chemical precipitant and coagulant at different concentrations (Initial concentrations for Pb, Cu, and Zn were 100ppb)

CP added	Cu terminal concentration (ppb)	Cu Removal (%)	Pb terminal concentration (ppb)	Pb Removal (%)	Zn terminal concentration (ppb)	Zn Removal (%)
1 RQ* (10 ppm)	31.6	68.4	15.1	85	35.4	64.6
5RQ* (50 ppm)	6.6	94	7.9	92	14.3	85.7
10RQ*(100 ppm)	9.6	90	16.9	83	30.0	70

*RQ = recommended quantity

Chemical Precipitant: 1 RQ = 10 ppm and Coagulant GC 850 = 1ppm

Based on the above overall experimental work, a combined scheme to remove all heavy metal species (Cu, Pb, and Zn) down to the NPDES limits will be proposed. The proposed combined schemes are discussed in the following sections.

6.5 Combined schemes and process flow sheet development

Two approaches were evaluated: (i) using crumb rubber and sludge at the same time; (ii) using crumb rubber and chemical precipitation in two stages; (iii) using crumb rubber, sludge and chemical precipitation, or (iv) using sludge with chemical precipitation in presence of GC-850.

6.5.1 Scheme 1: Heavy metals removal using crumb rubber and dried sludge treatment

The initial concentration of Cu, Zn, and Pb was fixed at 100 ppb in all tests. These solutions were first contacted with 10 g/L of crumb rubber and dried sludge at different concentrations. Table 8 summarizes the corresponding results. The use of crumb rubber and dried sludge at the same individual concentrations (10g/L) was conducive to the removal of 74% Cu, 92% Pb, and 73% Zn. It is interesting to notice that although the crumb rubber would have released Zn into solutions, its concentration went down in the second stage due to its adsorption by the dried sludge. These results confirmed our previous expectations. Besides, although the NPDES for Zn was in the first condition the removal percent was from 51 to 74% which complies with the NPDES limitation for Zinc was in compliance, it was not the case for Cu and Pb. In the second test, the concentration of crumb rubber was kept constant while doubling the amount of dried sludge. Although the removal of the three species was also attained, the NPDES limitations for Cu and Pb were not achieved. A similar trend was observed in the third case, when both crumb rubber and dried sludge concentrations were duplicated.

Table 8. Terminal concentrations and removal of heavy metal ions using a two-steps process: crumb rubber (CR) + dried sludge (DS). (Initial concentration were 100ppb)

Metal	10g/L CR + 10g/L DS Terminal concentration (ppb)	% Removal	10g/L CR + 20g/L DS Terminal concentration (ppb)	% Removal	20g/L CR + 20g/L DS Terminal concentration (ppb)	% Removal
Cu	26.4	74	25.3	75	18.6	81
Pb	8.9	92	2.8	97	5.4	95
Zn	27.5	73	49.0	51	41.0	59

6.5.2 Scheme 2: Heavy metals removal using tire rubber followed by chemical precipitation with trithiocarbonate

The heavy metal solution (100 ppb of Cu, Pb, or Zn) was first contacted with crumb rubber (20 g/L) and, after filtration, with a 20 ppm-solution of the chemical precipitant as recommended by the manufacturer. The chemical precipitant dose was increased up to 5 times the recommended quantity (RQ).

As Table 9 shows, the removal of Cu and Pb were far better (89% and 97.5%, respectively) than for Zn (only 30%). It can be again attributed to the contribution of the crumb rubber to the enhancement in Zn concentration during the first stage. Despite of the high removal efficiencies the high levels of the terminal concentration of all metal species are still above the NPDES requirements. The increase in the concentration of the chemical precipitant up to 100 ppm (5 times the recommended concentration) caused the rise in the removal efficiency (58.3% for Zn, 99% for Pb and 92% for Cu) and subsequently, contributed to the decrease of the corresponding terminal concentrations. The drop in the terminal concentrations were very close to those required by the NPDES. The results suggest the combined effect of adsorption by crumb rubber and subsequent precipitation of residual metal concentrations, including the Zn released from the crumb rubber, as hydroxides. The pH was maintained at 8.5.

Table 9. Heavy metals removal using crumb rubber + Chemical Precipitation at two doses of the precipitant (Initial concentration = 100ppb)

Metal	Terminal concentration (ppb) 20g/L CR-1RQ (20ppm)	% Removal	Terminal concentration (ppb) 20g/L CR-5RQ (100ppm)	% Removal
Cu	11.0	89	8.2	92
Pb	2.5	97.5	1.2	99
Zn	70.0	30	41.7	58.3

*RQ = 10 ppm

6.5.3 Scheme 3: use of tire rubber, followed by dried sludge and chemical precipitation

In this scheme the metal solutions were first contacted with crumb rubber in presence of the chemical precipitant followed by filtration and subsequent treatment of the solutions with dried sludge.

In these tests, the concentration of crumb rubber and dried sludge were 20 g/L and 10 g/L, respectively. The concentration of the chemical precipitant (trithiocarbonate) was increased from 20 ppm up to 100 ppm. Initial concentrations of Cu, Pb, and Zn were 100ppb. Table 10 shows the corresponding results. Although the removal capacity of crumb rubber and dried sludge was confirmed for Pb and Cu and the corresponding terminal concentrations did not comply with NPDES regulation. It was interesting to realize that the removal efficiency for Zn was higher than in scheme 2 (69% – 79 %); it can be attributed to the combined effect of Zn hydroxide precipitation and subsequent adsorption of remaining dissolved Zn species by the dried sludge. It was expected an almost complete removal of the metal species since optimum conditions were selected: adsorption of Cu and Pb by crumb rubber, hydroxide precipitation of Zn dissolved species and ultimate adsorption of residual dissolved species by dried sludge; one probable explanation could be related to the failure in removing colloidal precipitates (too small to be recovered by conventional solid-liquid separation techniques) formed during the contact time. Accordingly, the evaluation of a combined scheme but including the presence of coagulant GC-850 is justified.

Table 10. Terminal heavy metals concentrations and removal efficiencies using scheme 3: crumb rubber followed by chemical precipitation followed by dried sludge. The pH was 8.5 and the initial concentration of metal ions 100 ppb.

Metal	Terminal concentration (ppb) 20g/L CR + 1RQ (20ppm) + 10g/L DS	% Removal	Terminal Concentration (ppb) 20g/L CR + 5RQ (100ppm) + 10g/L DS	% Removal
Cu	12.6	87.4	9.1	91
Pb	2.8	97	3.5	96.5
Zn	30.9	69.1	20.7	79.3

Based on the above trends, we wanted to evaluate the removal efficiency under more extreme conditions. For this purpose, the dried sludge concentration was increased up to 20g/L as an attempt to remove all residual amounts of dissolved metal species. The corresponding results are shown in Table 11. The expectations were satisfied; the removal of those three metal ions was 88% (Zn), 99% (Pb) and 92% (Cu). The corresponding minimum terminal concentrations were 11.3 ppm, 0.6 ppm and 8.0 ppm, respectively. Evidently the presence of the dried sludge should be responsible for the adsorption of any residual amount of Zn, Cu and Pb after the crumb rubber adsorption and chemical precipitation stages (at pH 8.5). All results are in excellent compliance with the NPDES regulation for the Miradero Facility.

Based on the above results, the best scheme for removal of heavy metals was determined. The optimum scheme considers the use of 20 g/L of sludge and the optimal dose (10 mg/L) of trithiocarbonate precipitant.

Table 11. Heavy metals removal using crumb rubber followed by dried sludge and followed by chemical precipitant with initial concentration of 100 ppb of heavy metals

Metal	Terminal Concentration (ppb) 10g/L CR + 20g/L DS + 1RQ (10ppm)	% Removal	Terminal Concentration (ppb) 10g/L CR + 20g/L DS + 5RQ (50ppm)	% Removal	NPDES Compliance Concentrations (ppb)
Cu	8.4	91.6	8.0	92	8
Pb	0.6	99	0.7	99	1.8
Zn	11.3	89	12.1	88	50

6.5.4 Scheme 4: Dried sludge followed by chemical precipitation

6.5.4. a. Effect of the presence of coagulant GC-850

In order to understand the specific effect of the coagulant, another scheme was devised including adsorption by dried sludge in presence of the precipitant and GC polymer 850. The initial concentration was of 100 ppb for each heavy metal studied. The first step was to use 20 g/L of sludge and the pH was maintained at 8.5. Table 12 shows the results. The removal of zinc was in compliance with the NPDES, but for Pb and Cu, it was not achieved. The most important information coming out from these tests was the promoting effect of the coagulant in the removal efficiency of Zn; it is apparent that colloidal Zn hydroxide particles could be better settled down after coagulating them. Figure 37 evidenced that most of the removal took place during the earlier contact times (around 2 hours in this case); the removal preference followed the order Pb>Zn>Cu.

Table 12. Final heavy metals concentration using sludge followed by chemical precipitation with or without coagulant (GC-850)

Sludge 20g/L pH 8.5	Terminal concentration (ppb) Cu	% Removal Cu	Terminal concentration (ppb) Pb	% Removal Pb	Terminal concentration (ppb) Zn	% Removal Zn
With GC850	38.1	61	3.6	96	28.4	71.6
Without GC850	32.05	68	9.9	90	13.4	86

GC 850 concentration = 10ppm

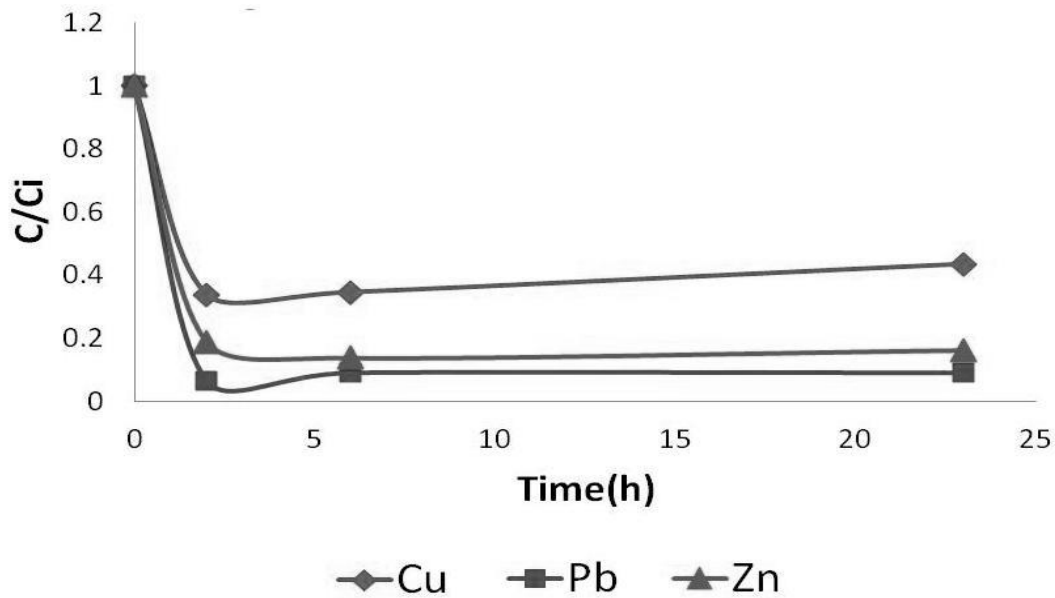


Figure 20. Normalized variation of the concentration of metal species as a function of contact time using 20g/L of dried sludge and 10 mg/L of trithiocarnionate. The initial metal concentration was 100 ppb in each case

6.5.4.b.Effect of the concentration of the chemical precipitant (trithiocarbonate)

In these 2-steps experiments, the initial metal solutions were contacted with the chemical precipitant, the produced solids removed by filtration and the residual solution contacted with the dried sludge. The concentrations used were 10 g/L sludge. The pH was kept at 8.5 and the contact time was 48 hours. Table 13 summarizes the metal concentrations in the solutions after the first step (contact of metal solutions with trithiocarbonate at different concentrations). The removal efficiency values were very high and varied between 86 to 99%. The final concentrations were 2.7 ppb for Cu (NPDES permit 8.0 ppb), 1.7 ppb for Pb (NPDES permit 1.8 ppb) and 4.8 ppb for Zn (NPDES permit 50 ppb). Accordingly, the simplicity of this scheme (dried sludge followed by chemical precipitation) and its capability to generate final effluents that comply with NPDES regulations allow us to select this route as the final treatment scheme for the treatment of the effluents generated at the Miradero facility plant.

Table 13. Removal efficiency and terminal concentrations of metal species after first step: chemical precipitation with trithiocarbonate with initial concentrations of 100 ppb

10g/L sludge + X CP*	Final Concentration (ppb) Cu	% Removal 1st step Cu	Final concentration (ppb) Pb	% Removal 1st step Pb	Final Concentration (ppb) Zn	% Removal 1st step Zn
3 ppm	7.9	92	2.4	98	16.7	83.3
5 ppm	11.4	89	1.2	99	N/A	N/A
15 ppm	8.4	92	1.8	98	13.5	86.5

*X CP – concentration of trithiocarbonate. The pH was kept constant at 8.5

After reached the optimum dosage of chemical precipitant (3ppm), in the next table 14, showed the scheme results where the concentration of dried sludge increase to 20 g/L and keep the dosage of 3 ppm of chemical precipitant with initial concentration of heavy metals were 100 ppb. The results showed the removal efficiency for all heavy metals was over 95 percent and comply with the NPDES permit for Miradero Water Treatment Plant.

Table 14. Removal efficiency and terminal concentrations of metal species after second step: adsorption by dried sludge (10 g/l). The concentration of trithiocarbonate was 3 mg/L with 100ppb of initial concentrations

Metal	Terminal Concentration (ppb)	% Removal 2 nd step	NPDES Compliance Concentrations (ppb)
Cu	2.7	97.3	8
Pb	1.7	98.3	1.8
Zn	4.8	95.2	50

On the above basis, the proposed scheme for the treatment of the effluents generated at the Miradero facility can be represented by Figure 38.

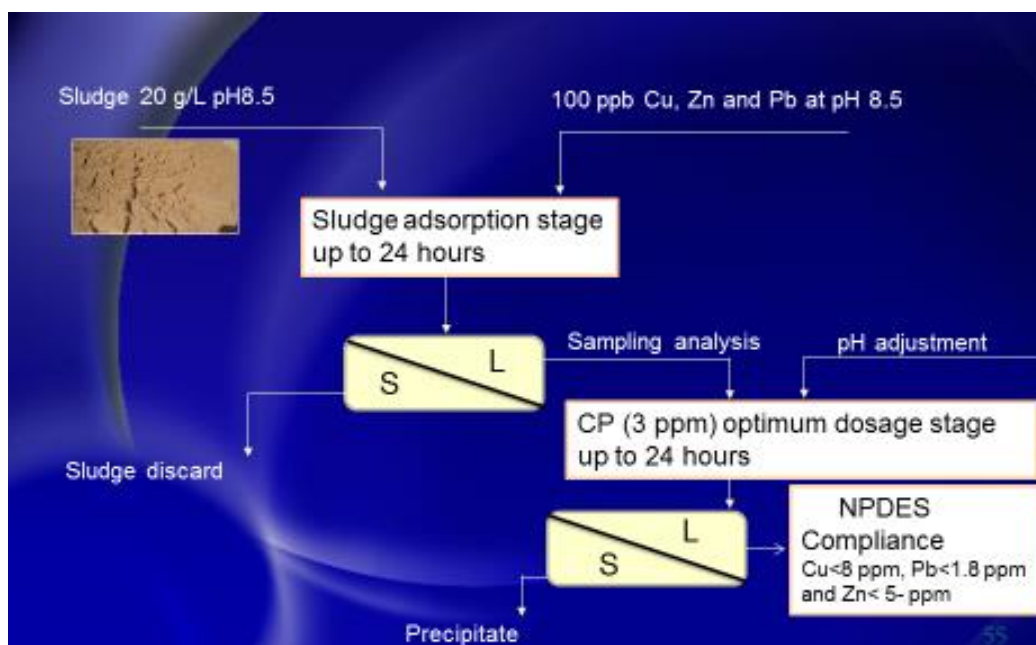


Figure 38. Tentative flow sheet for the removal of heavy metal ions from the effluent generated at the Miradero facility plant

6.6 Heavy metals removal using actual samples

The selected process was used to treat actual samples taken at the Miradero plant. The locations of the sampling points were described in Chapter 3. The sampling procedure followed the protocol according to EPA 300.7 procedure for sampling and preservation of samples for heavy metals analyses. Table 15 shows the pH and turbidity values for each one of the actual water

samples. Samples #1, #2 and #3 were taken at Thickener #1, polymer injection point, and at the exit of Thickener #2, respectively. The samples were taken on November 2008.

Table 15. pH and turbidity in actual water samples

Sample	pH	Turbidity (NTU)
1	6.49	44.61
2	6.75	39.13
3	6.76	21.07
Blank	7.03	0.04

Blank was deionized water

The corresponding elemental analyses of each sample are shown in Table 16. The ICP-OS analyses revealed the presence of Cu and Zn. No Pb was detected in the collected samples. The concentration of Zn (4.7 and 5.7 ppb) was below of what is required by the NPDES (50 ppb). The samples did contain Cu at concentrations above the NPDES regulation; the highest Cu concentration (28.9pppb) was found in sample # 3, which indicates that this species accumulated in the sludge handling step. Tables 16 and 17 show the results found in total and dissolved metals, respectively.

Table 16. Total Heavy metals concentration in actual samples from Miradero treatment plant

Concentration (ppb)	Blank	Sample 1	Sample 2	Sample 3
Cu	1.04	12.2	12.1	28.9
Pb	ND	ND	ND	ND
Zn	ND	4.7	0.00	5.7

ND: Not detected

Table 17. Dissolved heavy metals concentration from actual samples from Miradero treatment plant

Concentration, ppm	Blank	Sample 1	Sample 2	Sample 3
Cu	0.87	4.33	5.98	6.64
Pb	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00

Sample #3 was treated by following the flowsheet described earlier for a contact time of 48 hours (contact with the dried sludge) and chemical precipitation during two hours.

7 CONCLUSIONS

Miradero Filtration Plant has struggled for years with its discharge permit, especially with the compliance of the heavy metals parameters. After considering several methods of removal, it was demonstrated that it is possible to decrease the concentration of heavy metals, without the need for advanced technology like reverse osmosis or other technologies.

The combination of various mechanisms as crumb rubber, sludge and chemical precipitation reduces the heavy metal concentration to levels necessary for compliance with the Discharge Permit for the Plant. The sludge decreases the concentration of heavy metals with a contact time between 1 to 3 hours. The main reason that the sludge removes these concentrations of heavy metals is due to the kinetic characteristics of the sludge where large amounts of silicates are present and those silicates have large absorption characteristics. However, it is necessary to apply a dose of chemical precipitant and polymer coagulant to remove the remaining concentration in solution. It is equally necessary have a contact time with the chemical precipitant to remove heavy metals by coagulation and sedimentation methods. This will depend on the initial concentration of heavy metals that the plant receives during that period of time.

It was also shown that the crumb rubber has excellent absorption characteristics and has a capacity of heavy metal removal average of 85%. In this project, Zinc was one of the heavy metals to be removed and crumb rubber caused an increase in the concentration of this metal, due to a release of that metal from the rubber. However other alternatives such as washing the crumb rubber with acids was considered, but that would represent an additional expense to the sludge handling process in the filter plant and it would add new material to be disposed off at the end of the process

Sometimes if the concentration of heavy metals is close to the compliance parameters, process may only require one dose of the chemical precipitant to remove the concentration necessary to comply with NPDES. It has been shown that chemical precipitation removes over 88% of the total average concentration without the need for another mechanism.

However, our final recommendation is to use both mechanisms and thus ensuring compliance with the NPDES. This will require a continuous monitoring at sludge input system and personnel in charge will take the final decision how to proceed with the removal of heavy metals.

The final application using these mechanisms can be incorporated in the sludge management system of Miradero Filtration Plant with the construction of a tank that can form a fixed sludge blanket and force the flow to pass right through the sludge blanket. Currently there are several tanks like these and in many cases is known as Helicon, since they are cone shaped. After the flow passes through this special tank, it will require a precipitating chemical injection; this would be done by a tap on the start line of this tank cone and before the entry of final Thickener. The last tank would bring the contact time required for the chemical precipitant and coagulant, which is already part of the processing system of the existing plant, to remove the heavy metal concentration required. Finally, we would continue with the existing process at Miradero filtration plant. In the next chapter the recommended layout using these processes is shown.

The capital investment for these improvements is around 1.5 to 2.5 million dollars. This is due to the large amount of sludge produced in this facility. The plant produces 20 MGD of potable water. If this type of problem is found in a facility that produces less than 1.0 MGD of sludge, the capital investment to solve this problem would be lower than 10% of the production capacity of the facility.

There are different ways that one could obtain financing for this project, but it can be justified as this would mean constant compliance with discharge permit, which in turn would eliminate any fines or penalties that the facility, is subjected to.

Finally, it was demonstrated that is not necessary to implement advanced technology for the removal of heavy metals and with the correct process control, compliance with the NPDES could be achieved.

8 RECOMENDATIONS

As explained in previous chapters, it is possible to remove heavy metals before discharging clarified water from the sludge handling system to the point of discharge. Therefore, the recommended infrastructure is based on an injection point where the chemical precipitant can be added and a system that can create a sludge blanket for the removal of heavy metals by an absorption method.

However, it is recommended that there be continuous monitoring of the sludge handling system, since in many cases will only be necessary to apply the chemical precipitant or just use the sludge blanket tank. All depends on the initial concentration of heavy metals in the thickener tank at Miradero Filtration Plant.

It is recommended to use the chemical precipitant injection proposed after the tank that produces the sludge blanket. In this case we recommend a tank known as Helicons. These tanks have the ability to create a blanket of sludge that absorbs the concentration of heavy metals and lowers it. The turbidity at the discharge outlet can be reduced as it removes a large amount of suspended solids in the clarified water from the thickener #1.

Therefore, the infrastructure necessary would be a Helicons tank with a minimum capacity of 1.3 MGD. This capacity is the maximum flow that can be send from the existing pumps of thickener tank #1. This tank would be located between the thickener tank #1, the existing injection point, and the Thickener #2. In the next section a layout of the proposed infrastructure is illustrated. It is important to mention that a hydraulic study of the existing infrastructures are needed to determine if the system works by gravity or if there is any need for additional pumping station.

The additional injection point would be after this new proposed tank and the chemical could be placed in the existing chemicals room used in the plant. There is no need for an additional building for storage. The spares injection equipment available at the plant can be used. In both systems it is necessary the installation of pipes for the interconnection with the existing processes.

After the application at the new injection point, the water is sent to the existing thickener tank #2. Nowadays, the tank has a retention time of 3 hours, this depending on the flow entering the tank; we understand that this time is sufficient to achieve the removal of heavy metals. The removal mainly occurs over a period of one hour and then the interaction between the chemical precipitant and the sample remains constant.

These systems of Helicons tanks do not require continuous maintenance, but it is important to monitor the concentrations of heavy metals in the sludge blanket. At some point it will be require the removal of the sludge, since the absorption capacity will reach its limit and could affect the discharge parameters as required by the NPDES permit. However, if the operation of Helicons tanks is managed as an efficiency process, where sludge removes constantly, the adsorption capability of sludge increase.

The sludge that does not have any more absorption capacity can be disposed at the drying beds available at the filtration plant and then taken to the Ponce landfill. The sludge produced and disposed in Ponce landfill is not consider a toxic sludge, because the concentration removal of heavy metals are low (ppb). Figures 39 and 40 illustrate a Helicon tank currently used in other facilities of the Water and Sewer Authority, but used with another purpose.



Figure 39. Helicons Tanks at side view profile



Figure 40 Top view of Helicons Tanks

8.1 Proposed Configuration at Plant site

Figure 41 illustrates the proposed configuration which includes the Helicon tank and the proposed injection point. The figure illustrates the Helicon tank and then a pump station to transfer treated waters to the final thickener. This is a proposed configuration, but this will depend on a study of the hydraulic system and the existing elevations of the site. When necessary to remove the sludge blanket, it can be sent directly to Drying Beds, the latter would be the best option. The diagram illustrates the injection of the polymer, the chemical precipitant and, if necessary, application of lime for pH adjustment. It is important to maintain the pH around 8.0 for best results in the removal or decrease of the concentration of heavy metals. This configuration is very simple and requires only a tap on the existing pipe. The chemicals can be stored in the existing building which controls the Sludge Management.

During the monitoring process is recommended to find the optimal polymer dose and chemical precipitant using the Jar Test. This test is widely known and is required by regulatory agencies to obtain the optimal dose of precipitating agents.

This type of layout compared to other processes to remove heavy metals, such as reverse osmosis, or Ion Exchange electrodialysis, is very simple and easy to operate. Finally we recommend an operation and maintenance manual for the new systems to process control and lengthen the lifespan of these new processes. Constantly monitoring the system will permit the achievement of compliance as required according to the NPDES Discharge Permit.

8.2 Cost estimate

Table 18 illustrates the estimated cost of the infrastructure used as the base layout. This type of work does not require infrastructure of specialized companies. The most expensive equipment is the Helicon tank due to the type of material, usually made of Stainless Steel. The cost of operation is affected by the addition of another chemical precipitant and the need to have certain amount stored as spare to maintain performance and compliance to process required.

Table 18. Cost Estimate for Sludge System for heavy metals removal

Description	Unit Cost	Quantity	Final Cost
Helicon Tanks	ea	1	\$750,000.00
Piping	ls	1	\$50,000.00
Surveying	ls	1	\$15,000.00
Earthwork	ls	1	\$75,000.00
Electricity	ls	1	\$30,000.00
Valves and accessories	ls	1	\$50,000.00
Instrumentation	ls	1	\$30,000.00
Start up and Training	ls	1	\$15,000.00
Operation cost	month	1	\$8,000.00
Design Fees	ls	1	\$85,000.00
Subtotal			\$1,108,000.00
25% contingencies			\$277,000.00
TOTAL			\$1,385,000.00

Funding for this type of work is feasible identifying federal funds, since these improvements produce full compliance with the Discharge Permit Filters Plant Miradero. This analysis of cost does not include the necessary improvements, as the expansion of the sludge handling system, which cannot handle the sludge that is currently generated throughout the facility.

Finally, it was shown that there are less complex mechanisms and more cost effective methods for the removal of heavy metals, which is not only a problem exclusively at this facility, but also at others PRASA facilities.

9 REFERENCES

Ahamed, Maqsood; Mohd. Kaleem; Javed Siddiqui. *Clinical Nutrition*. **2007**, Volume 26, Issue 4, 400-408.

Alamo, Luis. *Use of Recycled Crumb Rubber to Remove Organic Pollutants from Aqueous Solutions*. **2006**.

Alamo-Nole, L.; O. Perales-Perez; F.R. Roman. *Journal of Hazardous Materials*. **2010**, 1-5.

Altas, Levent; Hanife Büyükgüngör. *Journal of Hazardous Materials*. **2008**, Volume 153, Issues 1-2, 462-469.

Amari, T, Themelis NJ, Wernick IK, 1999; Resources Recovery from used rubber tires, Resources Policy (25)

American Society Civil Engineering, WEF and APHS. *Standard Methods for the Examination of Water and Wastewater*. New York: McGraw-Hill, 2001.

American Water Works Association. *Water Quality and Treatment*. Fourth. Ed. New York: McGraw-Hill, Inc, 1990.

Ayoub, G. M. F; Merhebi. *Advances in Environmental Research*. **2002**, Volume 6, Issue 3, 277-28.

Calisir, F.; F.R. Roman; L. Alamo; O. Perales; M. Arocha; S. Akman. *Desalination*. **2009**, Vol. 249, 515-518.

Cenens, Chantal; Ilse Y. Smets; Vincent G. Ryckaert; Jan F. Van Impe. *Water Research*. **2000**, Volume 34, Issue 9, 2525-2534.

Davis, Mackenzie L. and David A. Cornwell. *Introduction to Environmental Engineering*. Third. Ed. New York: McGraw-Hill, Inc, 1998.

DC Adriano; NS Bolan; J Vangronsveld; WW Wenzel. *Heavy Metals*. Elsevier, SC, USA, 2004.

Driscoll, Fletcher G. *Groundwater and Wells*. Second. Ed. St. Paul, MN: US Filter/Johnson Screens, 1995.

Environmental and Engineering Services CPS. *Evaluation of the Puerto Rico Aqueduct and Sewer Authority's Miradero Water Treatment Plant Mayaguez-PWS ID PR0003283. Sludge Handling System Evaluation*. November 2009.

Environmental Protection Agency. *Clean Water Act Requirements*. Section B.
http://www.epa.gov/dfe/pubs/pwb/tech_rep/fedregs/regsectb.htm. Accessed on June 2008.

Environmental Protection Agency. (2007). *Frontera Creek*. Recuperado el 7 de octubre de 2007 del, <http://www.epa.gov/region2/superfund/npl/0202550c.pdf>

Environmental Protection Agency. (2002). *Juncos Landfill*. Recuperado el 7 de octubre de 2007 del, <http://www.epa.gov/Region2/superfund/npl/0202511c.pdf>

Food and Agriculture Organization of the United Nations. *Wastewater Treatment*.
<http://www.fao.org/docrep/t0551e/t0551e05.htm>. Accessed on June 2008.

Fundación Eroski. (2008). *Metales pesados: toda una amenaza*. La revista del consumidor de hoy. Recuperado el 17 de octubre de 2007 del, <http://revista.consumer.es/web/es/20010301/medioambiente/>

García-Lestón, Julia; Josefina Méndez; Eduardo Pásaro; Blanca Laffon. *Environment International*. **2010**, Volume 36, Issue 6, August Pages 623-636.

G Blanchard; M Maunaye; G Martin. *Water Research*. Volume 18, Issue 12, 1984, Pages 1501-1507.

G.M. Gadd. *Heavy Metal Pollutants: Environmental and Biotechnological Aspects*. Third Ed. Scotland, 2009.

Ghosh, Prabir; Amar Nath Samanta; Subhabrata Ray. *Desalination*. **2011**, Volume 266, Issues 1-3, 213-217.

Guanasekara, A., Donovan J., and Xing, B, A, "Ground Discard Tire Remove Naphtalene, Toluene, and Mercury from water". *Chemosphere*, 41, 1155. 2000.

Hoffmann, Gaby. *Veterinary Clinics of North America: Small Animal Practice*. **2009**, Volume 39, Issue 3, 489-511.

Kaindl, Nikolaus; Ulf Tillman; Christian H. Möbius. *Water Science and Technology*. **1999**, Volume 40, Issues 11-12, 231-239.

Kawamura, Susumu. *Integrated Design and Operations of Water Treatment Facilities*. Second. Ed. Canada: John Wiley & Son, Inc, 2000.

Lagos, G.E. L.C.; Maggi, D. Peters; F. Reveco. *Science of The Total Environment*. **1999**, Volume 239, Issues 1-3, 49-70.

Lehtinen, Karl-Johan ; Gunnar Klingstedt. *Aquatic Toxicology*. **1983**, Volume 3, Issue 2, 93-102.

Lester, J.N.; R.M. Sterrit and P.W.W. Kirk. *Significance and behaviour of heavy metals in waste water treatment processes II. Sludge treatment and disposal*. First Edition. London: Imperial College, 1983.

Liao, P.H.; Y. Gao; K.V. Lo. *Biomass and Bioenergy*. **1993**, Volume 4, Issue 5, 365-371.

Lindbergh, Michael R. *Civil Engineering Reference Manual*. Eight. Ed. Belmont, CA: Professional Publications, Inc, 2001.

Liu, Haizhou; Kenneth D. Schonberger; Gregory V. Korshin; John F. Ferguson; Paul Meyerhofer; Erik Desormeaux; Heidi Luckenbach. *Water Research*. **2010**, Volume 44, Issue 14, 4057-4066.

Lockitch, Gillian. *Clinical Biochemistry*. **1993**, Volume 26, Issue 5, 371-381.

Matlock, Matthew; M., Brock; S. Howerton; David A. Atwood. *Water Research*. **2002**, Volume 36, Issue 19, 4757-4764.

Meier, Johannes; Thomas Melin; Ludger H. Eilers. *Desalination*. **2002**, Volume 146, Issues 1-3, 361-366.

Metcalf and Eddy. *Wastewater Engineering Treatment and Reuse*. Fourth. Ed. New York: McGraw-Hill, 2003.

Meyer, Pamela A.; Mary Jean Brown; Henry Falk. *Mutation Research/Reviews in Mutation Research*. **2008**, Volume 659, Issues 1-2, 166-175.

Nolan, C.V.; Z.A. Shaikh. *Toxicology*. **1992**, Volume 73, Issue 2, 127-146.

O'Reilly, A.J. *Process Safety and Environmental Protection*. **2000**, Volume 78, Issue 6, 454-464.

Otero, M.; F. Rozada; A. Morán; L.F. Calvo; A.I. García. *Desalination*. **2008**, Vol. 239, 46-57.

Oueslati, W. H; Ben Rhaïem; A. Ben Haj Amara. *Desalination*. **2011**, Volume 271, Issues 1-3, 139-149.

Parthasarathy, N.; J. Buffle. *Water Research*. **1985**, Volume 19, Issue 1, 25-36.

Peavy, Howard S, Donald R. Rowe and George Tchobanoglous. *Water Resources and Environmental Engineering*. New York: McGraw-Hill, 1985.

Qemi International. <http://www.qemi.com>. Accessed on June 2008.

Quaiyoom, Shah. *Trithiocarbonate Metal Precipitant for Metal Removal in Wastewater Treatment and Metal Recovery*. Qemi International. April 2003.

Rautenbach R.; K. Vossenkaul; T. Linn; T. Katz. *Desalination*. **1997**, Volume 108, Issues 1-3, 247-253.

Razali, M.; Y.Q. Zhao; M. Bruen. *Separation and Purification Technology*. **2007**, Volume 55, Issue 3, 300-306.

Reynolds, Tom R. and Richards Paul A. *Unit Operations and Processes in Environmental Engineering*. Second. Ed. Boston, MA: PWS Publishing Company, 1996.

SW 846 EPA Methods. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Revision 2. Washington, DC: December 1996.

Verrelli, David I.; David R. Dixon; Peter J. Scales. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **2009**, Volume 348, Issues 1-3, 14-23.

Verrelli, David I.; David R. Dixon; Peter J. Scales. *Water Research*. **2010**, Volume 44, Issue 5, 1542-1552.

Wang, Wei; Lizhong Zhu. *Journal of Hazardous Materials*. **2010**, Volume 174, Issues 1-3, 40-46.

Weber, Walter J. *PhysicoChemical Processes for Water Quality Control*. Canada: John Wiley & Sons, Inc, 1972.

Winner, Robert W. *Water Research*. **1985**, Volume 19, Issue 4, 449-455.

APPENDICES

APPENDIX A. MASS BALANCE

On 2009, the Environmental and Engineering services CPS, made a report [10] that described the analysis performed on the sludge handling system in the Miradero Treatment Plant (PWSID # PR0003283) in Mayagüez, Puerto Rico. This work was presented as requested by the Puerto Rico Aqueduct and Sewage Authority at Miradero filtration plant. There are several methods of sludge handling system, which varies the flow of mass and retention time in each process. The following explains in detail the different scenarios, but it was found that currently lacks the capacity to remove the sludge generated at the plant, when the settlers and filters are washed.

As reported by plant personnel, each of the eight granular filtration units in the water treatment process spends around 34,200 gallons of water per backwash, totaling an average of 273,600 gallons per day. This corresponds to 1.2 % of the raw water intake, within the typical range of 1% to 5 % (Tchobanoglous, 2005 d).

Backwash water flows directly from the filters to the thickener by gravity. Under normal operating conditions, it is assumed that all solids entering the plant are removed in the clarifiers on a daily basis, including those resulting from raw water turbidity and from coagulant and flocculant addition. This assumption is good because all streams flow to the thickener and are mixed before flowing downstream. Therefore, it is assumed that backwash only contributes to the amount of liquid flowing through the system; the corresponding solids are assumed to be removed in the settling tanks.

For the scenario in which settling and flocculation tanks are washed on a monthly basis, the backwash wastewater is assumed to contain 1,000 mg/L of suspended solids, the maximum reported in the literature (Tchobanoglous, 2005 d).

As reported by plant personnel, sludge is not removed on a daily basis from settling tanks at the Miradero WTP. Therefore, two scenarios will be developed for the SHS evaluation; one considering daily removal of sludge from settling tanks, and a second considering periodic washing operations.

Distinct ways are proposed to estimate these two components (AWWA, 2005; Kawamura,2000). A combination of these methods was used to generate an average model specific for coagulation by polymers (practiced at the Miradero WTP), where it is assumed that 1 g of dry sludge is generated per g of polymer added to the system, plus 1.25 g of dry sludge per m³ of water per NTU of turbidity removed from the raw water, yielding:

$$S(kg/dayTSS) = \frac{QT}{100} + (P_1 + P_2) \frac{Q}{100}$$

Where:

Q = flow rate in m³/day

T = turbidity of raw water in NTU

P₁ = concentration of primary polymer in the water in g/m³

P₂ = concentration of secondary polymer in the water in g/m³

The results for the estimates of solids and sludge volume generation as a function of raw water turbidity are shown in the next table, where solids generated by raw water turbidity (Turbidity column) and addition of coagulants (Polymer column) are calculated separately as a function of raw water turbidity.

For periods of peak sludge generation, corresponding to the 90th percentile raw water turbidity (917 NTU) the dry solids contribution from settling to the SHS would be 104,228 kg/day. Assuming sludge with a solids concentration of 10 kg/ m³, the daily volume of settling sludge generated would be 5,211 m³.

Considering the first scenario in which sludge is removed from the settling tanks on a daily basis and using the 90th percentile raw water turbidity to calculate the solids load to the SHS (peak periods), the following amounts of sludge would flow from the treatment process into the Thickener:

- Volumetric Flow Rates:
 - Backwash wastewater: 1,034 m³/day
 - Sludge from settling tanks: 5,211 m³/day

- Return from beds: 3,000 m³/day
- Total: 9,245 m³/day
- Solids Load: 104,228 kg/day
- Solids Concentration: 11 kg/m³

Table A.1 Raw Turbidity and sludge volume generation

Turbidity	Solids, kg/day dry			Settling Sludge		Total Sludge
	Turbidity	Polymer	Total	gal/day	m3/day	m3/day
10	1,029	8,228	9,257	122,440	463	1,497
50	5,143	8,228	13,371	176,858	669	1,703
100	10,285	9,874	20,159	266,648	1,008	2,042
200	20,570	9,874	30,444	402,693	1,522	2,556
267	27,413	9,874	37,286	493,207	1,864	2,899
500	51,425	9,874	61,299	810,828	3,065	4,099
917	94,355	9,874	104,228	1,378,680	5,211	6,246
1,200	123,420	9,874	133,294	1,763,143	6,665	7,699
1,600	164,560	9,874	174,434	2,307,323	8,722	9,756
2,000	205,700	9,874	215,574	2,851,503	10,779	11,813
4,000	411,400	9,874	421,274	5,572,402	21,064	22,098

Backwash wastewater flows are as reported by plant personnel; solids load is based on raw water turbidity for peak conditions and polymer consumption; sludge from settling tanks is based on daily solids load and a solids concentration of 10 kg/m³. Return from beds is calculated based on sludge treatment needs and not on capacity of beds available.

When only backwash wastewater is discharged to the SHS, a scenario that occurs at the Miradero WTP during days in which no tank washing operations are conducted, the following amounts of sludge would flow to the SHS Holding Tank:

- Backwash Wastewater Flow: 1,034 m³/day
- Maximum Solids Concentration: 1 kg/m³
- Solids Load: 1,034 kg/day

If washing operations are conducted, then the following additional flows would enter the SHS during such operations. It is assumed that washing operations are conducted in one 8 hour period.

- Volume of water to drain one settling tank: 3,745 m³ per wash
- Volume of water to drain one flocculation tank: 511 m³ per wash
- Volume of water to wash (hose) both tanks (+25%): 1,064 m³ per wash
- Total volume of sludge generated per washing operation: 5,320 m³
- Total Solids removed from one settling tank: 187,235 kg

Total Solids removed from one settling tank, accumulated between washing operations, is calculated based on average solids concentration of 50 kg/m³ in the sludge removed, which is typical for compacted sludge. The sludge becomes more compact when periods between washing operations increase.

Under SHS operating conditions considering daily discharge of sludge from both settling tanks and backwash operations, the thickener would produce a supernatant after decanting, which might be discharged to point 001, and a bottom sludge which would be transferred to the drying beds.

The thickener available at the Miradero WTP operates in a batch mode, and must be evaluated as such, taking into consideration the downtimes for decanting and discharge. The cycle adopted for the evaluation considers 18 hours a day for filling operations (sludge and backwash wastewater), 4 hours for decanting and 2 hours for discharge. No effluents may enter the thickener during the decanting and discharge periods. The discharge to the clarifier may start from the top port available for pump suction after 1 hour of decanting, and finish by the end of the decanting period (3 hours total). The discharge of sludge to the beds would be conducted in the 2 hour period after decanting is finished.

The quantities to be used for evaluation of the first scenario (daily sludge discharge from settling tanks) are presented below:

- Total sludge: 9,245 m³/day
- Total solids rate: 104,228 kg/day
- Average solids concentration: 11.3 kg/m³

The main evaluation parameter for holding tanks is the retention time, which characterizes the ability of the tank to receive all streams required, to equalize them, and to transfer them down stream at a constant rate. Note that the thickener at the Miradero WTP operates also as a holding tank, and retention time must be evaluated. A reference value of one day of retention capacity is used in the evaluation, as explained in section 2.1.

- Tank volume: 4,974 m³
- Retention time: 12.9 h
- Rating for the retention time: 186 %

The retention time calculated for the conditions assumed is 12.9 h or 54 % of the reference value of one day, which is limited for good SHS process control. The thickener must operate two batches a day to reduce the risk of overflowing during peak raw water turbidity periods. In such case each of the two cycles would consist of 6 hours of filling operations and six hours of downtime for decanting and discharge, thus reducing the total period in which the thickener may receive effluents from the water treatment process to two six hour periods a day. The actual decanting time may be measured during operation and reduced if adequate sludge concentration is achieved in a shorter decanting period, thus decreasing downtime.

Figure 6.14 presents the thickener retention time as a function of daily average raw water turbidity for the thickener at the Miradero WTP. As observed, when daily average raw water turbidity exceeds 660 NTU, the retention time in the thickener drops below 24 hours, and the operation strategy has to be changed to two batches a day. The probability of such raw water turbidity event is 21.8 % or 80 days in one year.

Adequate operation of the thickener depends also on adequate pumping capacity for the discharges required. The pumps available to discharge the thickener are:

- Sludge pumps: 3 x 750 gpm or 340 m³ in a two hour period for one pump and 680 m³ if two pumps are used
- Supernatant pumps: 2 x 450 gpm or 306 m³ in a three hour period for one pump operating

The pumping capacity available for thickener discharge is limited. The capacity is limited even for processing backwash wastewater alone, since approximately 1,034 m³ are generated in a day. To operate under peak sludge generation periods the pumping capacity would need expansion:

Required pumping capacity:

- Sludge: 5,300 gpm for two hours operation a day or 2,650 gpm per pump (if three pumps are available)
- Top effluent: 7,000 gpm for three hours operation a day (if two pumps are available)

To be able to pump the required amounts of liquid and sludge generated in a day when peak conditions occur, the sludge pumps currently available would need to operate 21 hours per day, and the liquid pumps for 47 hour per day, further illustrating pumping limitations.

Considering the second scenario, of periodic washing operations of flocculation and settling tanks, the calculation is performed first for the days when no tank washing is conducted. In this case only backwash wastewater is generated:

- Backwash flow: 1,034 m³/day
- Settling sludge: 0 m³/day
- Liquids returned from the drying beds: 260 m³/day
- Total solids load: 1,034 kg/day
- Average solids concentration (worst case): 1 kg/m³
- Tank volume: 4,974 m³
- Retention time: 3.5 days

- Rating for the retention time: 23 %

For this operation scenario, the capacity of the thickener is adequate to equalize flows. Still the downtime of 6 hours would be necessary to decant and discharge, but such operations would occur each 3 days approximately. The limitation for pumping sludge and liquids from the thickener would still persist, given the limited time available for discharge.

Therefore, the thickener can equalize the backwash wastewater generated on a daily basis, for days in which no washing operations are conducted, but thickener discharge is limited by pumping capacity.

In days in which washing operations are conducted, additional loads of sludge would enter the thickener, as follows:

- Sludge from washing: 5,319 m³/day
- Liquids returned from the drying beds: 3,000 m³/day
- Total Liquids: 9,613 m³/day
- Total solids rate: 187,235 kg in one day (at 50 kg/m³ for a volume of sludge equivalent to the whole volume of the settling tank).
- Total (including backwash): 188,269 kg/day
- Average solids concentration (including all effluents): 20.1 kg/m³
- Tank volume: 4,974 m³
- Retention time: 0.52 days = 12.4 hours
- Rating for the retention time: 193 %

Therefore, the thickener is limited to handle tank washing effluents. Volumes of sludge generated during such operations exceed the volume of the thickener. In addition, washing operations cannot be stopped for 6 hours to allow intermediate decanting and discharge, and the volume of sludge that must enter the thickener under this scenario far exceeds the volume of the tank, causing overflows (> 4,000 m³ in a day).

To complete thickener capacity evaluation, the solids load per unit surface area must also be calculated. Note that the overflow rate is not evaluated for batch thickeners because they operate by decanting and not by overflow. For the operation scenario contemplating regular daily removal of sludge from settling tanks:

- Thickener Settling Area = 744 m^2
- Solids load to thickener = $140 \text{ kg/m}^2/\text{day}$
- Rating for Solids Load: 280 %

The results indicate that under this proposed scenario the thickener does not have adequate capacity to handle the solids it receives during a day of operation, for one batch a day, since the solids load is well above the reference value adopted for the evaluation ($50 \text{ kg/m}^2/\text{day}$). To handle all solids the thickener would need three downtimes a day for decanting and discharge, for a total of 18 hours a day, which would leave only 6 hours a day for all backwash and sludge discharges from the treatment process, which is limited for handling 8 filter units.

Figure A.1 shows how daily average raw water turbidity affects the solids load to the thickener. The Figure A.2 illustrates that limit solids load would be reached when daily average raw water turbidity exceeds 260 NTU, which can occur 50% of the time (average daily turbidity = 267 NTU) at the Miradero WTP.

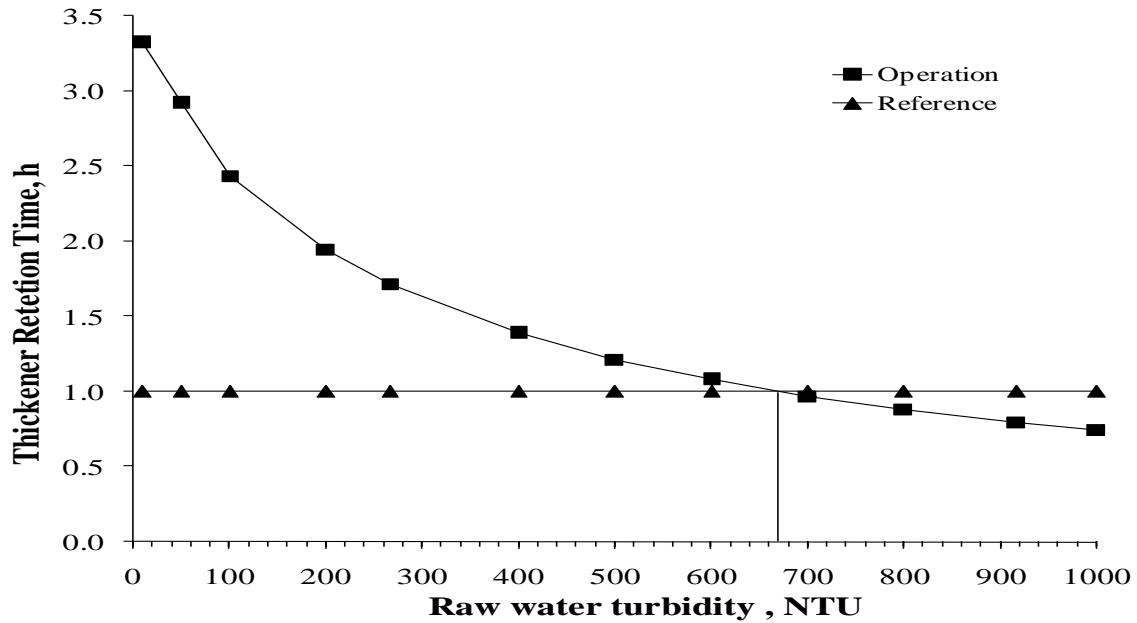


Figure A.1 Potential Graph for Thickener Retention Time[10]

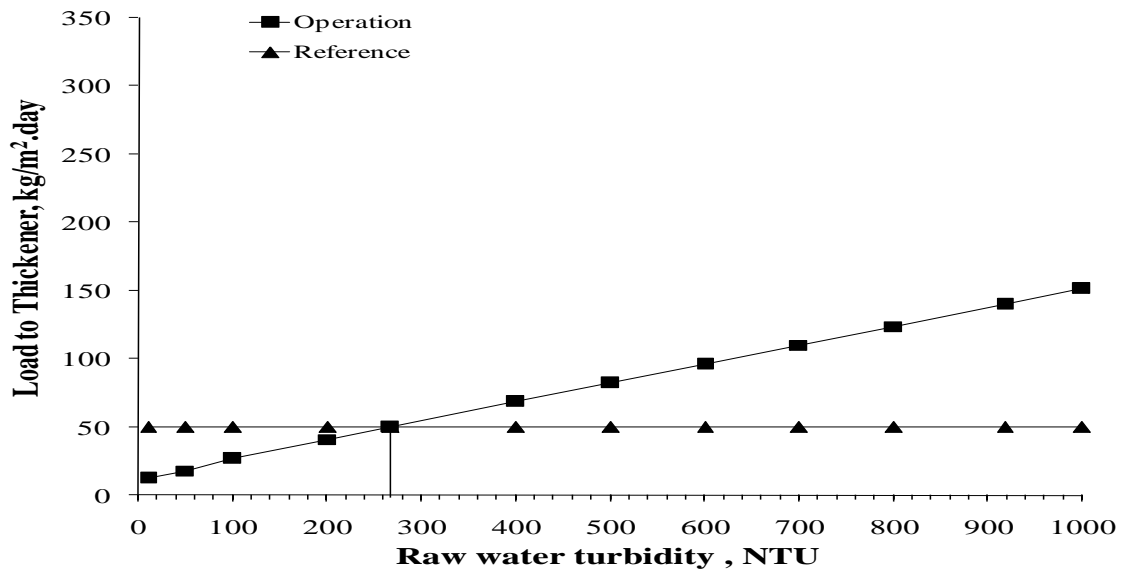


Figure A.2 Potential Graph for Thickener Solids Load [10]

Considering the second scenario, of periodic washing operations of flocculation and settling tanks, the calculation is performed first for the days when no tank washing is conducted. In this case only backwash wastewater is generated:

- Total solids load: 1,034 kg/day
- Solids load to thickener = $1.74 \text{ kg/m}^2/\text{day}$
 - Rating for Solids Load: 3.5 %

The Thickener at the Miradero WTP has adequate capacity to handle backwash wastewater alone, as demonstrated above, since the solids load to be handled would be smaller than the reference values considered. However, during days in which washing operations are conducted, the following additional solids load would flow to the system:

- Solids Flows from washing operation: 187,235 kg/day
- Solids load to thickener = $252 \text{ kg/m}^2/\text{day}$
 - Rating for Solids Load: 504 %

The results indicate that under this proposed scenario the Thickener capacity is limited to handle all solids removed during washing operations, which amount to 5 times the thickener daily capacity.

The clarifier receives decanted liquids from the thickener and overflows a clarified effluent for discharge from the plant. The main parameters for the clarifier are its overflow rate, since it was designed for continuous operation, and the solids load per unit surface area. The analysis is conducted for discharge to the clarifier on a 24 hour period, which is the maximum discharge period possible.

For the first scenario, contemplating daily discharge of sludge and backwash wastewater during peak conditions, the operating conditions for the clarifier will be the following:

- Flow rate of liquids in: $5,771 \text{ m}^3/\text{day}$
- Flow of solids in: 577 kg/day (100 mg/L TSS)
- Overflow Rate: 3.4 m/h
 - Rating: 340%
- Solids Load: $8 \text{ kg/m}^2/\text{day}$

- Rating: Adequate

The capacity of the clarifier is limited for peak conditions, because the overflow rate would be excessive. This would increase if discharges to the clarifier are conducted in daily periods shorter than 24 h, as necessary if operating with only one batch thickener. Figure A.3 shows how the flow of liquids to the clarifier varies with raw water turbidity. It is clear that clarifier capacity is reached when daily average raw water turbidity reaches 40 NTU. This turbidity may happen 71% of the time, or 258 days in one year. This limitation is aggravated due to the fact that the clarifier must be fed in a period of three hours a day for the configuration available, rather than in 24 hours as used in the evaluation, increasing considerably the overflow rate the clarifier is subjected to.

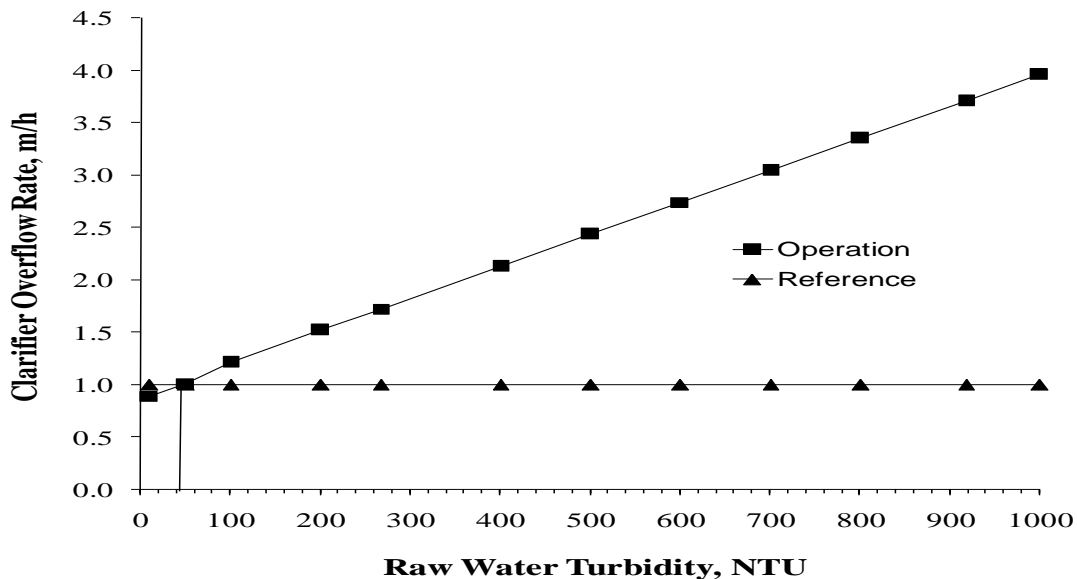


Figure A.3 Potential Curve for Clarifier Overflow Rate [10]

The SHS is equipped with three vacuum assisted drying bed units with bed areas of 217 m² each, for a total of 652 m². Each drying bed may receive a solids load limited to 72 kg/m². The potential capacity for the drying beds is first evaluated for daily sludge generation from settling tanks together with backwash wastewater.

- Reference Solids Load = 72 kg/m²
- Surface area per bed = 217 m²
- Dry Solids capacity per fill = 15,648 kg

- Dry Solids load to drying beds = 104.228 kg/fill
- Potential = Actual load/Capacity = 666 %

The capacity of the Drying Beds is limited for the peak operating conditions considered (daily raw water turbidity of 917 NTU), when both backwash wastewater and daily settling sludge are processed by the SHS. This limitation is also encountered during periods when tank washing operations are conducted, since the solids load to the system are even higher. For the periods when only backwash wastewater is processed by the SHS, the capacity of the Drying Beds is sufficient, with a rating of 8.3%.

Figure A.4 shows how the capacity rating for the drying beds is affected by raw water turbidity. The maximum capacity of the beds is reached when raw water turbidity exceeds 70 NTU. The probability of this turbidity being exceeded at the Miradero WTP is 65 %, approximately, indicating that the available drying bed capacity would be insufficient 2/3 of the time, for daily discharge of settled sludge. Again, the beds are also limited to handle tank washing operations.

Figure A.5 represents a diagram illustrating the mass balance of the existing system.

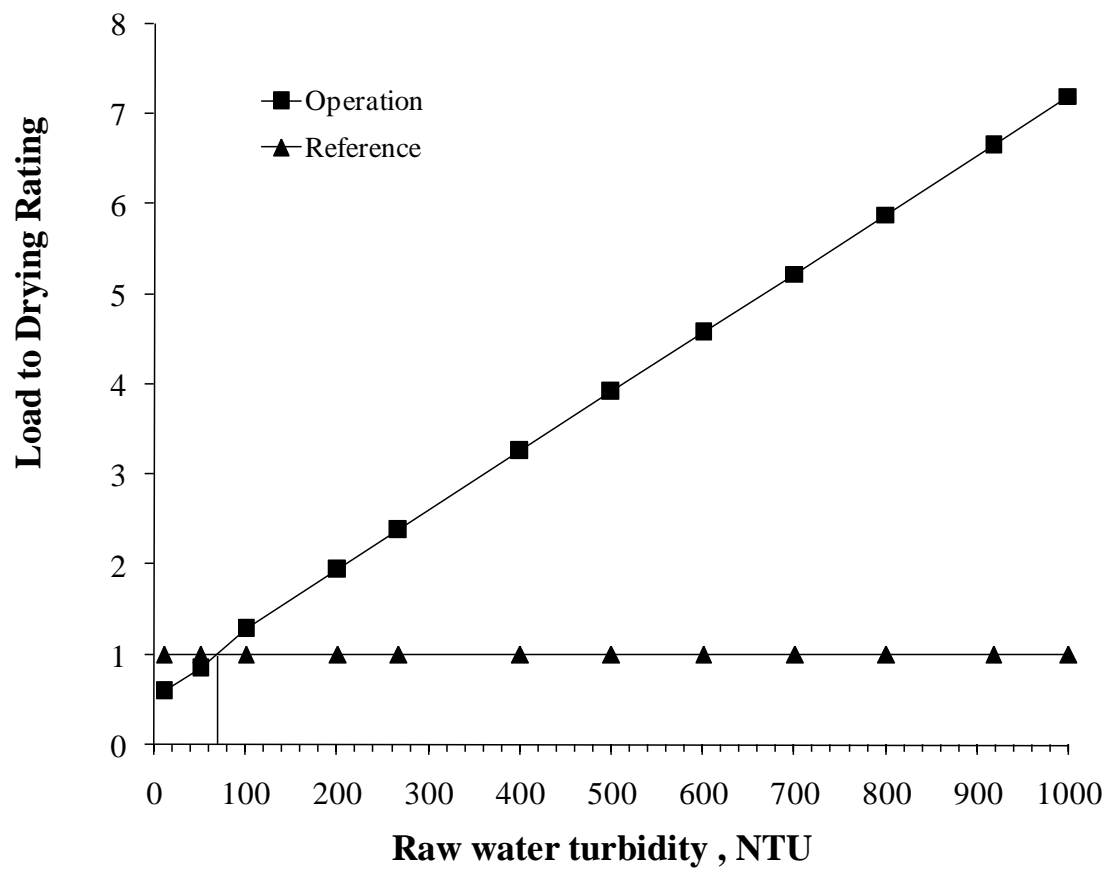


Figure A.4 Potential Curve for Drying Bed Solids Load [10]

Mass Balance for Existing Sludge System

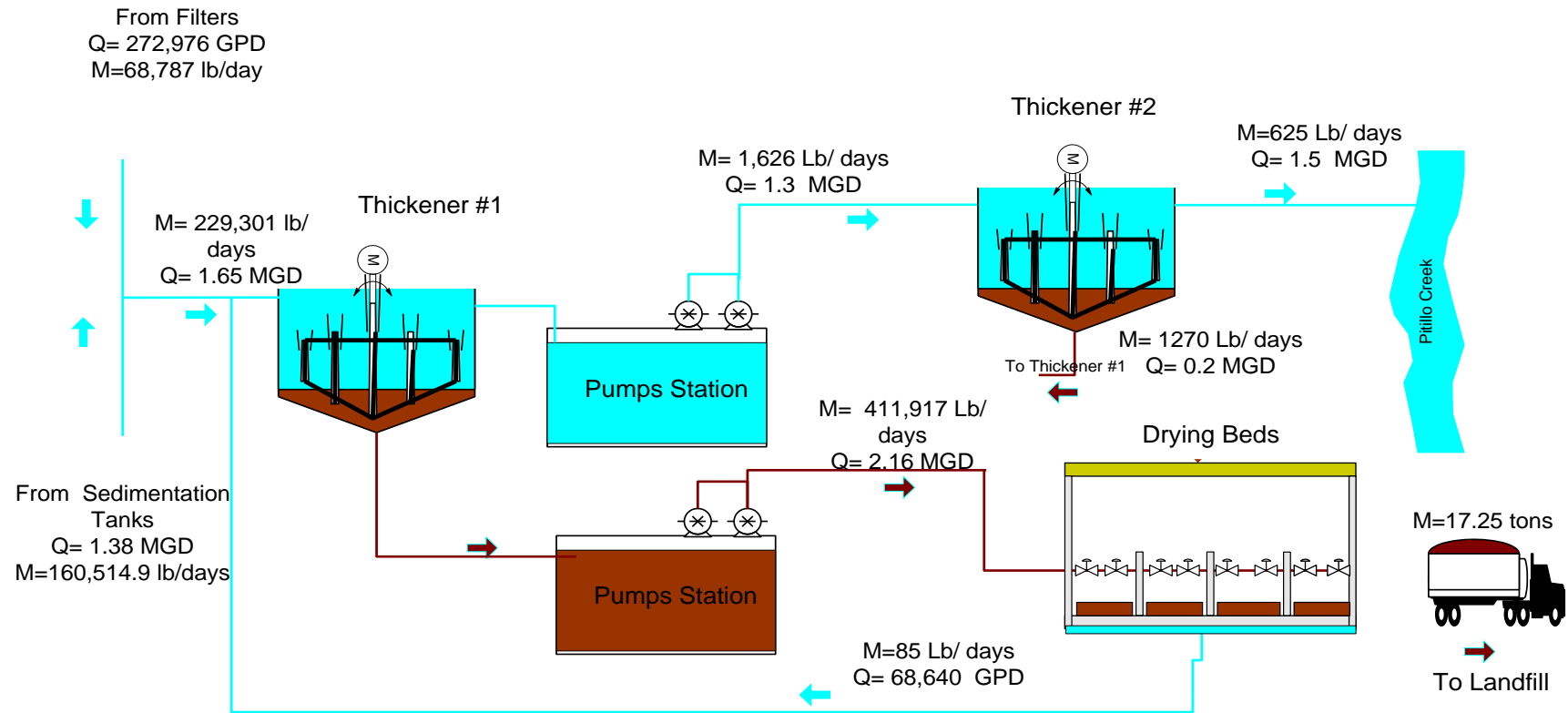


Figure A.5 Mass Balance for existing sludge system

APPENDIX B. EXISTING HEAVY METALS CONCENTRATION

Existing average concentrations and regulated parameters

Heavy Metals	Existing Average Concentrations (µg/L)	Regulated Concentrations (µg/L)	New Regulated Concentrations (µg/L)
Copper (Cu)	155.27	10	8
Lead (Pb)	21.53	2.6	1.8
Zinc (Zn)	108.52	50	50
	New Average Concentrations Until June 2008 (µg/L)	Regulated Concentrations (µg/L)	New Regulated Concentrations (µg/L)
Copper (Cu)	114	10	8
Lead (Pb)	14.6	2.6	1.8
Zinc (Zn)	74.5	50	50

APPENDIX C. NPDES PERMIT

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION II

AUTHORIZATION TO DISCHARGE UNDER THE NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM

PERMIT NUMBER
PR0023990

In compliance with the provisions of the Clean Water Act, as amended, 33 U.S.C. §1251 et. seq. (the "Act"),

Puerto Rico Aqueduct and Sewer Authority
P.O. Box 7066
Barrio Obrero Station
San Juan, Puerto Rico 00916

hereinafter referred to as "the Permittee" is authorized to discharge from a facility located at

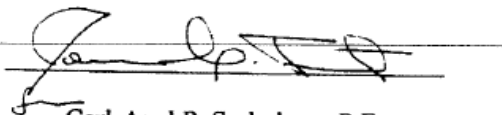
Miradero Filter Plant
Mayaguez, Puerto Rico

to receiving waters named **Pitillos Creek** in accordance with effluent limitations, monitoring requirements and other conditions set forth in Parts I and II hereof. All references to Title 40 of the Code of Federal Regulations are to regulations that are in effect on the effective date of this permit, including all amendments thereto published in the Federal Register. Unless otherwise specified herein, all terms are defined as provided in the applicable regulations under Title 40 of the Code of Federal Regulations.

This permit shall become effective on **December 1, 2009**, which is the effective date of the permit (EDP).

This permit and the authorization to discharge shall expire on **November 30, 2014**.

Signed this 25th day of September 2009.



Carl-Axel P. Soderberg, P.E.
Director
Caribbean Environmental
Protection Division

A. EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

1. Required Effluent Limitations

During the period beginning on the effective date and lasting until the expiration date of this permit, discharges from outfall 001* shall be limited and monitored by the permittee as specified below:

- a. Permittee shall achieve water quality requirements as determined by the Commonwealth of Puerto Rico. See EQB Intent to Issue a Water Quality Certificate requirements.
- b. See Table A-I.

The location of outfall 001 is as follows:

Latitude: 18 °13' 44.8 " N

Longitude: 67° 08' 23.4 " W

2. Environmental Quality Board Certification Requirements

As required by the Puerto Rico Environmental Quality Board (EQB) Final Water Quality Certification of **September 23, 2009**, for the purpose of assuring compliance with EQB's water quality standards and other appropriate requirements of Commonwealth law as provided by Section 401(d) of the Act, the permittee shall comply with the following effluent limitations and other limitations:

See pages 4 through 12.

TABLE A-1

EFFLUENT LIMITATIONS AND
MONITORING REQUIREMENTSPage 4 of 27
Permit No. PR0023990

During the period beginning on the EDP and lasting through the expiration date of the permit, the permittee is authorized to discharge from outfall serial number 001 (filters and settling tanks washwater). Such discharge shall be limited and monitored by the permittee as specified below:

Receiving Water Classification: SD

<u>Effluent Characteristics</u>	<u>Gross Discharge Limitations</u>		<u>Monitoring Requirements</u>	
	Monthly Avg.	Daily Max	Measurements Frequency	Sample Type
✓ 2,4,6-Trichlorophenol (µg/L) ^{2,3}		---	φ	Grab
✓ 2,4-Dichlorophenol (µg/L) _{2,3}		---	φ	Grab
✓ 2,4-Dimethylphenol (µg/L) ^{2,3}		---	φ	Grab
✓ 2,4-Dinitrophenol (µg/L) _{2,3}		---	φ	Grab
✓ 2-Chlorophenol (µg/L) ^{2,3}		---	φ	Grab
✓ 2-Methyl-4,6- Dinitrophenol (µg/L) ^{2,3}		---	φ	Grab
✓ BOD ₅ (mg/L) ^{1,2,3}		5.0	Monthly	Grab
✓ Color (Pt-Co Units) ^{2,3}		15	Monthly	Grab
✓ Copper (Cu) (µg/L) ^{2,3}		9	Monthly	Grab
✓ Dissolved Oxygen (mg/L) ^{1,2,3}	Shall contain not less than 5.0 mg/L.	Daily	Grab	
<u>Effluent Characteristics</u>	<u>Gross Discharge Limitations</u>		<u>Monitoring Requirements</u>	

	Monthly Average	Daily Maximum	Measurements Frequency	Sample Type
✓ Fecal Coliforms (colonies/100 mL) ^{1,2,3}	The coliforms geometric mean of a series of representative samples (at least five samples), of the waters taken sequentially shall not exceed 200 colonies/100 mL. Not more than 20% of the samples shall exceed 400 colonies/100 mL.		Annually	Grab
✓ Flow m ³ /day (MGD) ^{3,4}		5,458.58(1.442)	Continuous Recording or Estimated	
✓ Lead (Pb) (µg/l) ^{2,3}		2.9	Monthly	Grab
✓ Pentachlorophenol (µg/L) ^{2,3}		---	φ	Grab
✓ pH (SU) ^{2,3}	Shall always lie between 6.0 – 9.0.		Daily	Grab
✓ Residual Chlorine (mg/l) γ ^{2,3}		0.50	Daily	Grab
Solids and Other Matters ^{2,3}	The waters of Puerto Rico shall not contain floating debris, scum or other floating materials attributable to discharge in amounts sufficient to be unsightly or deleterious to the existing or designed uses of the water body.		---	---
Suspended, Colloidal or Settleable Solids (mL/L) ^{1,2,3}	Solids from wastewaters source shall not cause deposition in, or be deleterious to the existing or designated uses of the waters.		Daily	Grab
Taste and Odor-producing Substances ^{2,3}	Shall not be present in amounts that will render any undesirable taste and/or to edible aquatic life.		---	---

<u>Effluent Characteristics</u>	<u>Gross Discharge Limitations</u>		<u>Monitoring Requirements</u>	
	Monthly Average	Daily Maximum	Measurements Frequency	Sample Type
✓ Temperature °F (°C) ^{2,3}	Except for natural causes no heat may be added to the waters of Puerto Rico, which would cause the temperature of any site to exceed 90 °F (32.2°C).		Daily	Grab
✓ Total Ammonia (NH ₃) (mg/l) ^{2,3}		1.000	Monthly	Grab
✓ Total Dissolved Solids (mg/L) ^{2,3}		500	Quarterly	Grab
✓ Total Phosphorus (P) (mg/L) ^{2,3}		1.00	Monthly	Grab
Turbidity (NTU) ^{2,3}		50	Monthly	Grab
✓ Zinc (Zn) (µg/L) ^{2,3}		111.38	Quarterly	Grab
Special Conditions	See attached sheet, which contains special conditions that constitute part of this certification.		---	---

To comply with the monitoring requirements specified above, samples shall be taken at the outfall of discharge serial number 001.

All flow measurements shall achieve accuracy within the range of plus or minus 10%.

γ See Special Conditions 6 and 7.

β See Special Condition 10.

φ The permittee shall implement a monthly monitoring program using the analytical method approved by EPA with the lowest possible detection level, in accordance with Section 6.2.3 of the PRWQSR, as amended, for one (1) year period, after which they will be conducted annually. The monitoring program shall commence not later than thirty (30) days after the EQB's written approval of the Quality Assurance Project Plan (QAPP). The QAPP must be submitted for evaluation and approval of EQB not later than thirty (30) days after the EDP. The results of the monitoring program shall be submitted to EQB and EPA-Region II no later than sixty (60) days of completion of the one year monitoring program. Based on the evaluation of the results obtained, EQB will

2. The discharge 001 will consist of washwaters coming from the filters and settling tanks treated in the Sludge Treatment System constructed for these purposes.
3. Within thirty (30) days after the Effective Date of the NPDES Permit (EDP), the permittee shall submit to the EQB for its evaluation and approval, the engineering report, plans and specifications of the constructed Sludge Treatment System.⁴
4. Prior to the construction of any additional treatment system, or the modification of the existing one, the permittee shall obtain the approval from EQB of the engineering report, plans and specifications.⁴
5. The permittee shall install, maintain and operate all water pollution control equipment in such manner as to be in compliance with the applicable Rules and Regulations.³
6. No toxic substances shall be discharged, in toxic concentrations, other than those allowed as specified in the NPDES permit. Those toxic substances included in the permit application, but not regulated by the NPDES permit, shall not exceed the concentrations specified in the applicable regulatory limitations.^{2,3}
7. The waters of Puerto Rico shall not contain any substance attributable to discharge 001, at such concentration which, either alone or as result of synergistic effects with other substances, is toxic or produces undesirable physiological responses in human, fish or other fauna or flora.²
8. The discharge 001 shall not cause the presence of oil sheen in the receiving water body.²
9. All sample collection, preservation, and analysis shall be carried out in accordance with the Code of Federal Regulation (CFR) Number 40, Part 136. All chemical analyses shall be certified by a licensed chemist authorized to practice the profession in Puerto Rico. All bacteriological tests shall be certified by a licensed microbiologist or medical technician authorized to practice the profession in Puerto Rico.^{1,3}
10. Within thirty (30) days after the EDP, the permittee shall submit to EQB a method to measure or estimate flow at discharge 001. If a flow measuring device is installed; it shall be periodically calibrated and properly maintained. Calibration and maintenance records must be kept in compliance with the applicable Rules and Regulations.³
11. If a flow measuring device is installed, the sampling point for discharge 001 shall be located immediately after it.^{3,4}
12. The sampling point for discharge 001 shall be labeled with a 18 in. X 12 in.

(minimum dimensions) sign that reads as follows: ⁴

“Punto de Muestreo para la Descarga 001”

13. All water or wastewater treatment facilities, whether publicly or privately owned, must be operated by a person licensed by the Potable Water and Wastewater Treatment Plants Operators Examining Board of the Commonwealth of Puerto Rico.^{3,4}
14. The permittee shall conduct quarterly acute toxicity tests, for a period of one (1) year, of its wastewater discharge through outfall serial number 001 in accordance with the following:
 - a. The toxicity tests shall be conducted in accordance with the EPA publication, EPA-821-R-02-012 Methods for *Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms* (Fifth Edition), October 2002, or the most recent edition of this publication, if such edition is available.
 - b. The tests shall provide a measure of the acute toxicity as determined by the wastewater concentration, which cause 50 percent mortality of the organisms over a 48 hour period. Test results shall be expressed in terms of *Lethal Concentration* (LC) and reported as 48 hour LC50.
 - c. The test species should be the *Fathead Minnow* (*Pimephales promelas*) and *Cladocera* (*Daphnia magna*). The tests should be static renewal type..
 - d. A procedure report shall be submitted to both agencies, EQB and EPA, ninety (90) days after the effective date of the NPDES permit (EDP). The following information shall be included in the procedure report:
 1. An identification of the organizations responsible for conducting the test and the species to be tested.
 2. A detailed description of the methodology to be utilized in the conduct of the tests, including equipment, sample collection, dilution water and source of test organisms.
 3. A schematic diagram which depicts the effluent sampling location. The diagram shall indicate the location of effluent sampling in relation to wastewaters treatment facility and discharge monitoring point.
 - e. The tests shall be conducted quarterly for a period of one (1) year and shall commence not later than one hundred eighty (180) days after EDP. The results shall be submitted to EPA Region II and EQB within sixty (60) days of

completion of each test. Based on a review of the test results, EPA or the EQB may require additional toxicity tests, including chronic toxicity analyses. In addition to submitting the procedures report and test results to the addresses listed in Part I.B. of this permit, results shall be submitted to:

MUNICIPAL WATER PROGRAM BRANCH
CARIBBEAN ENVIRONMENTAL PROTECTION AGENCY
U.S. ENVIRONMENTAL PROTECTION AGENCY, REGION II
1492 PONCE DE LEON AVE. SUITE 417
CENTRO EUROPA BUILDING
SAN JUAN, PUERTO RICO 00907

f. Reopener Clause for Toxicity Testing Requirements

Based on a review of the test results, the Regional Administrator of EPA or the EQB can require additional toxicity tests, including chronic tests and toxicity/treatability studies, and may impose toxicity limitations. This permit may be reopened by EPA to include such requirements as enforceable permit conditions.

The solid wastes (sludge, screenings and grit) generated due to the sludge treatment systems operation shall be:

- a. Disposed in compliance with the applicable requirements established in the 40 CFR Part 257. A semiannual report shall be submitted to EQB and EPA notifying the method or methods used to dispose the solid waste generated in the facility. Also, copy of the approval or permit applicable to the disposal method used shall be submitted, if any.
- b. Transported adequately in such way that access is not gained to any body of water or soil. In the event of a spill of solid waste on land or into a body of water, the permittee shall notify the Point Sources Permits Division of EQB's Water Quality Area in the following manners:
 1. By telephone communication within a term no longer than twenty-four (24) hour after the spill (787-767-8073).
 2. By letter, within a term no longer than five (5) days after the spill.

These notifications shall include the following information:

- a. Spill material.
- b. Spill volume.

- c. Measures taken to prevent the spill material to gain access to any body of water.

This special condition does not relieve the permittee from its responsibility to obtain the corresponding permits from the EQB's Solid Wastes Program and other state and federal agencies, if any.⁵

16. A log book must be kept for the material removed from the sludge treatment system detailing the following items:
 - a. Material removed, date and source of it.
 - b. Approximate volume and weight.
 - c. Method by which it is removed and transported.
 - d. Final disposal and location.
 - e. Person that performs the service.

A copy of the Non-Hazardous Solid Waste Collection and Transportation Services Permit issued by the authorized official from EQB must be attached to the log book..³

17. If septic tanks are used to discharge the sanitary wastewater coming from the facility, the permittee must request and obtain from the EQB the corresponding permits for the operation of the septic tanks according to the Underground Injection Control Regulation and the Regulation for the Certification of Plans and Documents under Consideration of the Environmental Quality Board.⁴
18. The permittee shall comply with all the applicable provisions established in the amendment of the Puerto Rico Water Quality Standards Regulation immediately upon the date of effectiveness of such amendment, unless the permittee requests and obtains a Compliance Plan in accordance with the applicable Rules and Regulations.

1, 2, 3, 4 and 5 see next page

1. According to Article 1, Puerto Rico Water Quality Standards Regulation, as amended.
2. According to Article 3, Puerto Rico Water Quality Standards Regulation, as amended.
3. According to Article 6, Puerto Rico Water Quality Standards Regulation, as amended.
4. According to the Environmental Public Policy Act of September 22, 2004, Act No. 416, as amended.

5. According to the Section 405 (d) (4) of Federal Clean Water Act, as amended (33 U.S.C. 466 et. seq.).

PART II

A. DEFINITIONS

1. "Average monthly discharge limitation" means the highest allowable average of "daily discharges" over a calendar month, calculated as the sum of all daily discharges measured during a calendar month divided by the number of daily discharges measured during that month.
2. "Average weekly discharge limitations" means the highest allowable average of "daily discharges" over a calendar week, calculated as the sum of all daily discharges measured during a calendar week divided by the number of daily discharges measured during that week.
3. "Bypass" means the intentional diversion of wastes from any portion of a treatment facility.
4. "Composite" means a combination of individual (or continuously taken) samples of at least 100 milliliters, collected at periodic intervals over the entire discharge day. The method used must be "time composite" which collects a fixed volume at equal intervals. Samples may be collected manually or automatically. For a continuous discharge, a minimum of 24 individual samples shall be collected and combined to constitute a 24-hour composite sample. For intermittent discharges of less than four (4) hours duration, samples shall be taken at a minimum of 15 minute intervals. For intermittent discharges of more than four (4) hours duration, samples shall be taken at a minimum of 30 minute intervals.
5. "Daily discharge" means the discharge of a pollutant measured during a calendar day or any 24-hour period that reasonably represents the calendar day for purposes of sampling. For pollutants with limitations expressed in units of mass, the "daily discharge" is calculated as the total mass of the pollutant discharge over the day. For pollutants with limitations expressed in other units of measurement, the "daily discharge" is calculated as the average measurement of pollutant over the day. For purposes of sampling, "daily" means an operating day or 24-hour period.
6. "Director" means the "Regional Administrator" or the "State Director", as the context requires, or an authorized representative. Until the State has an approved State program authorized by EPA under 40 C.F.R. Part 123, "Director" means the Regional Administrator. When there is an approved State program, "Director" normally means the State Director. Even in such circumstances, EPA may retain authority to take certain action (see, for example, 40 C.F.R. 123.1(d), 45 Federal Register 14178, April 1, 1983, on the retention of jurisdiction over permits EPA issued before program approval). If any

condition of this permit requires the reporting of information or other actions to both the Regional Administrator and the State Director, regardless of who has permit-issuing authority, the terms "Regional Administrator" and "State Director" will be used in place of "Director".

7. "Discharge Monitoring Report" or "DMR" means the EPA uniform national form, including any subsequent additions, revisions, or modifications, for the reporting of self-monitoring results by permittees.
8. "Grab" means an individual sample collected in less than 15 minutes.
9. "Gross" means the weight or the concentration contained in the discharge. (Unless a limitation is specified as a net limitation, the limitation contained in this permit is a gross limitation).
10. "Maximum daily discharge limitation" means the highest allowable "daily discharge".
11. "Monthly" means one day each month (the same day each month) and a normal operating day (e.g., the 2nd Tuesday of each month).
12. "Net" means the amount of a pollutant contained in the discharge measured in appropriate units as specified herein, less the amount of a pollutant contained in the surface water body intake source, measured in the same units, over the same period of time, provided:
 - a. The intake water source must be drawn for the same body of water into which the discharge is made; and
 - b. In cases where the surface water body intake source is pretreated for the removal of pollutants, the intake level of a pollutant to be used in calculating the net is that level contained after the pretreatment steps.
13. "Regional Administrator" means the Regional Administrator of Region II of EPA or the authorized representative of the Regional Administrator.
14. "Severe property damage" means that substantial physical damage to the treatment facilities which would cause them to become inoperable or substantial and permanent loss of natural resources which can reasonably be expected to occur in the absence of a bypass. Severe property damage does not mean economic loss caused by delays in production.

15. "State Director" means the chief administrative officer of the State water pollution control agency, or the authorized representative of the State Director.
16. "Toxic pollutant" means any of the pollutants listed in 40 CFR 401.15 (45 C.F.R. 44503, July 30, 1979) and any modification to that list in accordance with Section 307 (a)(1) of the Clean Water Act.
17. "Upset" means an exceptional incident in which there is unintentional and temporary noncompliance with technology-based permit effluent limitations because of factors beyond the reasonable control of the permittee. An upset does not include noncompliance to the extent caused by operational error, improperly designed treatment facilities, inadequate treatment facilities, lack of preventive maintenance, or careless or improper operation.
18. "Weekly" means every seventh day (the same day of each week) and a normal operating day.

3. MONITORING AND REPORTING REQUIREMENTS

1. Monitoring and Records. See Section C.10.
2. Discharge Monitoring Reports.
 - a. See Section C.12.d.
 - b. Monitoring results shall be obtained and recorded monthly on Discharge Monitoring Report Form (EPA-No. 3320-1). The monthly Discharge Monitoring Report Form shall be postmarked no later than the 28th day of the month following the completed reporting period. Signed copies of these, and all other reports required herein, shall be submitted to the Chief of the Compliance Assistance and Program Support Branch and State Director at the following addresses:

U.S. Environmental Protection Agency
Region II
290 Broadway, 21st Floor
New York, New York 10007-1866
ATTN: Chief, Compliance Assistance and
Program Support Branch

Environmental Quality Board of Puerto Rico
P.O. Box 11488
San Juan, Puerto Rico 00910
ATTN: Water Quality Bureau

3. Quality Assurance Practices. The permittee is required to show the validity of all data by requiring its laboratory to adhere to the following minimum quality assurance practices:

- a. Duplicate¹ and spiked² samples must be run for each constituent analyzed for permit compliance on 5% of the samples, or at least on one sample per month, whichever is greater. If the analysis frequency is less than one sample per month, duplicate and spiked samples must be run for each analysis.
- b. For spiked samples, a known amount of each constituent is to be added to the discharge sample. The amount of constituent added should be approximately the same amount present in the unspiked sample, or must be approximately that stated as maximum or average in the discharge permit.
- c. The data obtained in a. shall be summarized in an annual report submitted at the end of the fourth quarter of reporting in terms of precision, percent recovery, and the numbers of duplicate and spiked samples run.
- d. Precision for each parameter shall be calculated by the formula, standard deviation $s = (3d^2/2k)^{1/2}$, where d is the difference between duplicate results, and k is the number of duplicate pairs used in the calculation.
- e. Percent recovery for each parameter shall be calculated by the formula $R = 100(F - I)/A$, where F is the analytical result of the spiked sample, I is the result before spiking of the sample, and A is the amount of constituent added to the sample.
- f. The percent recovery, R, for each parameter in e. above shall be summarized yearly in terms of mean percent recovery and standard deviation from the mean. The formula, $s = ((X - x)^2 / (n - 1))^{1/2}$, where s is the standard deviation around the mean X, x is an individual recovery value, and n is the number of data points, shall be applied.
- g. The permittee and/or the permittee's contract laboratory is required to annually analyze an external quality control reference sample for each pollutant. These are available through an approved performance test provider at <http://www.a2la.org/dirsearchnew/nelacptproviders.cfm>

¹ Duplicate samples are not required for the following parameters: Color, Temperature, and Turbidity.

² Spiked samples are not required for the following parameters listed in Table 1 of 40 C.F.R. 136: Acidity, Alkalinity, Bacteriological, Benzidine, Chlorine, Color, Dissolved Oxygen, Hardness, pH, Oil and Grease, Radiological, Residues, Temperature, Turbidity. Procedures for spiking samples and spiked sample requirements for parameters not listed on the above-referenced table are available through EPA's Regional Quality Assurance Coordinator.

- h. The permittee and/or his contract laboratory is required to maintain records of the specific analytical methods used, including options employed, if any, within a particular method, and of reagent standardization and equipment calibration operations.
- i. If a contract laboratory is utilized, the permittee shall submit the name and address of the laboratory and the parameters analyzed at the time it submits its discharge monitoring reports (see Section 2.b. above). Any change in the contract laboratory being used or the parameters analyzed shall be reported prior to or together with the monitoring report covering the period during which the change was made.

C. GENERAL CONDITIONS

1. Duty to Comply

The permittee must comply with all conditions of this permit. Any permit noncompliance constitutes a violation of the Clean Water Act and is grounds for enforcement action; for permit termination, revocation and re-issuance, or modification; or for denial of a permit renewal application.

- a. The permittee shall comply with effluent standards or prohibitions established under Section 307(a) of the Clean Water Act for toxic pollutants and with standards for sewage sludge use or disposal established under section 405(d) of the CWA within the time provided in the regulations that establish these standards or prohibitions or standards for sewage sludge use or disposal, even if the permit has not yet been modified to incorporate the requirement.
- b. The Clean Water Act provides that any person who violates sections 301, 302, 306, 307, 308, 318, or 405 of the Act, or any permit condition or limitation implementing any such sections in a permit issued under section 402, or any requirement imposed in a pretreatment program approved under sections 402(a)(3) or 402(b)(8) of the Clean Water Act is subject to a civil penalty not to exceed \$25,000 per day for each violation. The Clean Water Act provides that any person who negligently violates sections 301, 302, 306, 307, 308, 318 or 405 of the Clean Water Act, or any condition or limitation implementing any of such sections in a permit issued under section 402 of the Act, or any requirement imposed in a pretreatment program approved under sections 402(a)(3) or 402(b)(8) of the Clean Water Act is subject to criminal penalties of \$2,500 to \$25,000 per day of violation, or imprisonment of not

more than 1 year, or both. In the case of a second or subsequent conviction for a negligent violation, a person shall be subject to criminal penalties of not more than \$50,000 per day of violation, or by imprisonment of not more than two years, or both. Any person who knowingly violates such sections, or such conditions or limitations is subject to criminal penalties of \$5,000 to \$50,000 per day of violation, or imprisonment for not more than three years, or both. In the case of a second or subsequent conviction for a knowing violation, a person shall be subject to criminal penalties of not more than \$100,000 per day of violation, or imprisonment of not more than six years, or both. Any person who knowingly violates sections 301, 302, 306, 307, 308, 318 or 405 of the Clean Water Act, or any permit condition or limitation implementing any of such sections in a permit issued under section 402 of the Act, and who knows at that time that he thereby places another person in imminent danger of death or serious bodily injury, shall, upon conviction, be subject to a fine of not more than \$250,000 or imprisonment of not more than fifteen years, or both. In the case of a second or subsequent conviction for a knowing endangerment violation, a person shall be subject to a fine of not more than \$500,000 or by imprisonment of not more than thirty years, or both. An organization as, defined in section 309(c)(3)(B)(iii) of the CWA, shall, upon conviction of violating the imminent danger provision, be subject to a fine of not more than \$1,000,000 and can be fined up to \$2,000,000 for second or subsequent convictions.

2. Any person may be assessed an administrative penalty by the Administrator for violating section 301, 302, 306, 307, 308, 318 or 405 of this Act, or any permit condition or limitation implementing any of such sections in a permit issued under section 402 of this Act. Administrative penalties for Class I violations are not to exceed \$11,000 per violation, with the maximum amount of any Class I penalty assessed not to exceed \$37,500. Penalties for Class II violations are not to exceed \$11,000 per day for each day during which the violation continues, with the maximum amount of any Class II penalty not to exceed \$157,500.

2. Duty to Reapply.

This permit and the authorization to discharge shall terminate on the expiration date indicated on the first page. In order to receive authorization to discharge after the expiration date of this permit, the permittee must apply for and obtain a new permit. If the permit issuing authority remains EPA, the permittee shall complete, sign, and submit an application to the Regional Administrator no later than 180 days before the expiration date.

Need to Halt or Reduce not a Defense.

It shall not be a defense for a permittee in an enforcement action that it would have been necessary to halt or reduce the permitted activity in order to maintain compliance with the conditions of this permit.

4. Duty to Mitigate.

The permittee shall take all reasonable steps to minimize or prevent any discharge or sludge use or disposal in violation of this permit which has a reasonable likelihood of adversely affecting human health or the environment.

5. Proper Operation and Maintenance.

The permittee shall at all times properly operate and maintain all facilities and systems for collection and treatment (and related appurtenances) which are installed or used by the permittee to achieve compliance with the conditions of this permit. Proper operation and maintenance also include adequate laboratory controls and appropriate quality assurance procedures. This provision requires the operation of back-up or auxiliary facilities or similar systems which are installed by a permittee only when the operation is necessary to achieve compliance with the conditions of the permit.

6. Permit Actions.

This permit may be modified, revoked and reissued, or terminated during its term for cause. The filing of a request by the permittee for a permit modification, revocation and reissuance, or termination, or a notification of planned changes or anticipated noncompliance, does not stay any permit condition.

7. Property Rights.

This permit does not convey any property rights of any sort, or any exclusive privilege.

8. Duty to Provide Information.

The permittee shall furnish to the Director within a reasonable time, any information which the Director may request to determine whether cause exists for modifying, revoking and reissuing, or terminating this permit, or to determine compliance with this permit. The permittee shall also furnish to the Director, upon request, copies of records required to be kept by this permit.

9. Inspection and Entry.

The permittee shall allow the Director, or an authorized representative (including an authorized contractor acting as a representative of the Administrator), upon presentation of credentials and other documents as may be required by law, to:

- a. Enter upon the permittee's premises where a regulated facility or activity is located or conducted, or where records must be kept under the conditions of this permit;
- b. Have access to and copy, at reasonable times, any records that must be kept under the conditions of this permit;
- c. Inspect at reasonable times any facilities, equipment (including monitoring and control equipment), practices, or operations regulated or required under this permit; and
- d. Sample or monitor at reasonable times, for the purposes of assuring permit compliance or as otherwise authorized by the Clean Water Act, any substances or parameters at any location.

10. Monitoring and Records.

- a. Samples and measurements taken for the purpose of monitoring shall be representative of the monitored activity.
- b. Except for record of monitoring information required by this permit related to the permittee's sewage sludge use and disposal activities, which shall be retained for a period of at least five years (or longer as required by 40 CFR Part 503), the permittee shall retain records of all monitoring information, including all calibration and maintenance records and all original strip chart recordings for continuous monitoring instrumentation, copies of all reports required by this permit, and records of old data used to complete the application for this permit, for a period of at least 3 years from the date of the sample, measurement, report or application. This period may be extended by request of the Director at any time.
- c. Records of monitoring information shall include:
 - (1) The date, exact place, and time of sampling or measurement;
 - (2) The individual(s) who performed the sampling or measurements;
 - (3) The date(s) analyses were performed;
 - (4) The individual(s) who performed the analyses;

- (5) The analytical techniques or methods used; and
- (6) The results of such analyses.
- d. Monitoring results must be conducted according to test procedure approved under 40 C.F.R. Part 136 or, in the case of sludge use or disposal approved under 40 CFR Part 136 unless otherwise specified in 40 CFR Part 503, unless other test procedures have been specified in the permit.
- e. The Clean Water Act provides that any person who falsifies, tampers with, or knowingly renders inaccurate any monitoring device or method required to be maintained under this permit shall, upon conviction, be punished by a fine of not more than \$10,000, or by imprisonment for not more than 2 years, or by both. If a conviction of a person is for a violation committed after a first conviction of such person under this paragraph, punishment is a fine of not more than \$20,000 per day of violation, or by imprisonment of not more than four years, or both.

11. Signatory Requirements.

- a. All applications, reports, or information submitted to the Director shall be signed and certified.
- b. The Clean Water Act provides that any person who knowingly makes any false statement, representation, or certification in any record or other document submitted or required to be maintained under this permit, including monitoring reports or reports of compliance or noncompliance shall, upon conviction, be punished by a fine of not more than \$10,000, or by imprisonment for not more than 2 years, or by both.

12. Reporting Requirements.

- a. Planned changes. The permittee shall give notice to the Director as soon as possible of any planned physical alterations or additions to the permitted facility. Notice is required only when:
 - (1) The alteration or addition to a permitted facility may meet one of the criteria for determining whether a facility is a new source in §122.29(b); or
 - (2) The alteration or addition could significantly change the nature or increase the quantity of pollutants discharged. This notification applies to pollutants which are subject neither to effluent limitations in the permit, nor to notification requirements under §122.42(a)(1).

- (3) The alteration or addition results in a significant change in the permittee's sludge use or disposal practices, and such alteration, addition, or change may justify the application of permit conditions that are different from or absent in the existing permit, including notification of additional use or disposal sites not reported during the permit application process or not reported pursuant to an approved land application plan;
- b. Anticipated noncompliance. The permittee shall give advance notice to the Director of any planned changes in the permitted facility or activity which may result in noncompliance with permit requirements.
- c. Transfers. This permit is not transferable to any person except after notice to the Director. The Director may require modification or revocation and reissuance of the permit to change the name of the permittee and incorporate such other requirements as may be necessary under the Clean Water Act.
- d. Monitoring reports. Monitoring results shall be reported at the intervals specified elsewhere in this permit.
 - (1) Monitoring results must be reported on a Discharge Monitoring Report (DMR) or forms provided or specified by the Director for reporting results of monitoring of sludge use or disposal practices.
 - (2) If the permittee monitors any pollutant more frequently than required by the permit, using test procedures approved under 40 C.F.R. 136 or, in the case of sludge use or disposal, approved under 40 CFR Part 136 unless otherwise specified in 40 CFR Part 503, or as specified in the permit, the results of this monitoring shall be included in the calculation and reporting of the data submitted in the DMR or sludge reporting form specified by the Director.
 - (3) Calculations for all limitations which require averaging of measurements shall utilize an arithmetic mean unless otherwise specified by the Director in the permit.
- e. Compliance Schedules. Reports of compliance or noncompliance with, or any progress reports on, interim and final requirements contained in any compliance schedule of this permit shall be submitted no later than 14 days following each schedule date.
- f. Twenty-four hour reporting.

- (1) The permittee shall report any noncompliance which may endanger health or the environment. Any information shall be provided orally within twenty four hours from the time the permittee becomes aware of the circumstances. A written submission shall also be provided within five days of the time the permittee becomes aware of the circumstances. The written submission shall contain a description of the noncompliance and its cause; the period of noncompliance, including exact dates and times, and if the noncompliance has not been corrected, the anticipated time it is expected to continue; and steps taken or planned to reduce, eliminate, and prevent reoccurrence of the noncompliance.
 - (2) The following shall be included as information which must be reported within twenty four hours under this paragraph.
 - (a) Any unanticipated bypass (see 13 below) which exceeds any effluent limitation in the permit;
 - (b) Any upset (see 14 below) which exceeds any effluent limitation in the permit;
 - (c) The violation of a maximum daily discharge limitation for any of the pollutants listed by the Director in the permit to be reported within twenty four hours.
 - (3) The Director may waive the written report on a case-by-case basis for report under paragraph (12)(f)(ii) of this section if the oral report has been received within twenty four hours.
- g. Other noncompliance. The permittee shall report all instances of noncompliance not reported under paragraphs (12)(a), (d), (e), and (f) of this section, at the time monitoring reports are submitted. The reports shall contain the information listed in paragraph (12)(a) and (f) of this section.
- h. Other information. Where the permittee becomes aware that it failed to submit any relevant facts in a permit application, or submitted incorrect information in a permit application or in any report to the Regional Administrator and State Director, it shall promptly submit such facts or information to the Regional Administrator and State Director.

Bypassing

- a. Bypass not violating limitations. The permittee may allow any bypass to occur which does not cause effluent limitations to be violated, but only if it also is for essential

maintenance to assure efficient operation. These bypasses are not subject to the provisions of subsections b and c.

b. Notice.

- (1) Anticipated bypass. If the permittee knows in advance of the need for a bypass, it shall submit prior notice, if possible at least ten days before the date of the bypass.
- (2) Unanticipated bypass. The permittee shall submit notice of an unanticipated bypass as required in section 12 above.

c. Prohibition of bypass.

- (1) Bypass is prohibited, and the Director may take enforcement action against a permittee for bypass, unless:
 - (a) Bypass was unavoidable to prevent loss of life, personal injury, or severe property damage;
 - (b) There were no feasible alternatives to the bypass, such as the use of auxiliary treatment facilities, retention of untreated wastes, or maintenance during normal periods of equipment downtime. This condition is not satisfied if adequate back-up equipment should have been installed in the exercise of reasonable engineering judgment to prevent a bypass which occurred during normal periods of equipment downtime or maintenance; and
 - (c) The permittee submitted notices as required under subsection b.
- (2) The Director may approve an anticipated bypass, after considering its adverse effects, if the Director determines that it will meet the three conditions listed above in paragraph (13)(c)(1).

14. Upset.

- a. Effect of an upset. An upset constitutes an affirmative defense to an action brought for noncompliance with technology-based permit effluent limitations if the requirements of subsection b are met. No determination made during administrative review of claims that noncompliance was caused by upset, and before an action for noncompliance, is final administrative action subject to judicial review.

- b. Conditions necessary for a demonstration of upset. A permittee who wishes to establish the affirmative defense of upset shall demonstrate, through properly signed, contemporaneous operating logs, or other relevant evidence that:
 - (1) An upset occurred and that the permittee can identify the cause(s) of the upset;
 - (2) The permitted facility was at the time being properly operated; and
 - (3) The permittee submitted notice of the upset as required in subsection f of section 12 above; and
 - (4) The permittee complied with any remedial measures required under section 4 above (duty to mitigate).
- c. Burden of proof. In any enforcement proceeding the permittee seeking to establish the occurrence of an upset has the burden of proof.

15. Removed Substances.

Solids, sludge, filter backwash or other pollutants removed in the course of treatment or control of wastewater and/or the treatment of intake waters shall be disposed of in a manner such as to prevent any pollutant from such materials from entering navigable waters. The following data shall be reported together with the monitoring data required in Section B.2.:

- (a) The sources of the materials to be disposed of;
- (b) The approximate volumes and weights;
- (c) The method by which they were removed and transported; and
- (d) Their final disposal locations.

16. Oil and Hazardous Substance Liability.

The imposition of responsibilities upon, or the institution of any legal action against the permittee under Section 311 of the Act shall be in conformance with regulations promulgated pursuant to Section 311 to discharges from facilities with NPDES permits.

17. Reopener Clause for Toxic Effluent Limitations.

Notwithstanding any other condition of this permit, if any applicable toxic effluent standard or prohibition is promulgated under Section 301(b)(2)(C) and (D), 304(b)(2) and 307(a)(2) of the Clean Water Act and that effluent standard or limitation is more stringent than any effluent limitation in the permit or controls a pollutant not limited in the permit, this permit shall be promptly modified or revoked and reissued to conform to that effluent standard or prohibition.

18. State Laws.

Nothing in this permit shall be construed to preclude the institution of any legal action or relieve the permittee from any responsibilities, liabilities, or penalties established pursuant to any applicable State law or regulation under authority preserved by Section 510 of the Act. The issuance of this permit does not preempt any duty to obtain State or local assent required by law for the discharge.

19. Availability of Information.

- a. NPDES permits, effluent data, and information required by NPDES application forms provided by the Director under 40 C.F.R. 122.4 and 122.53 (including information submitted on the forms themselves and any attachments used to supply information required by the forms) shall be available for public inspection at the offices of the Regional Administrator and State Director.
- b. In addition to the information set forth in subsection a., any other information submitted to EPA in accordance with the conditions of this permit shall be made available to the public without further notice unless a claim of business confidentiality is asserted at the time of submission in accordance with the procedures in 40 C.F.R. Part 2 (Public Information).
- c. If a claim of confidentiality is made for information other than that enumerated in subsection a, that information shall be treated in accordance with the procedures in 40 C.F.R. Part 2. Only information determined to be confidential under those procedures shall not be made available by EPA for public inspection.

20. Severability.

The provisions of this permit are severable, and if any provision of this permit, or the application of any provision of this permit to any circumstance, is held invalid, the application of such provision to other circumstances, and the remainder of this permit, shall not be affected thereby.

C. EFFECTIVENESS OF PERMIT

1. This permit shall become effective in its entirety on the date indicated on the first page of this permit unless a petition has been filed with the Environmental Appeals Board to review any condition of the permit decision pursuant to the provisions of 40 CFR 124.19. All contested conditions and any uncontested condition(s) that are in severable from the contested conditions shall be stayed. All other conditions shall become effective thirty (30) days after the date of notification specified in 40 CFR Part 124.16(a)(2)(ii).
2. For purposes of judicial review under Section 509(b) of the Clean Water Act, final agency action on a permit does not occur unless and until a party has exhausted its administrative remedies under 40 CFR Part 124. Any party which neglects or fails to seek review under 40 CFR 124.19, thereby waives its opportunity to exhaust available agency administrative remedies.