

SORPTION OF VOCs AND PAHs ONTO RECYCLED TIRE CRUMB RUBBER

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ABSTRACT

Sorption of Volatile Organic Compounds (VOCs) (ethylbenzene, toluene and xylene) and Poly Aromatic Hydrocarbons (PAHs) (acenaphthene, acenaphthylene and phenanthrene) by tire crumb rubber (TCR) and its main components were evaluated: carbon black (CB) and styrene-butadiene polymer (SBP). The initial concentrations of VOCs and PAHs in aqueous solutions ranged from 0.05 mg/L to 100.0 mg/L and 0.03 mg/L and 3.0 mg/L, respectively. The amounts of CB and SBP used in the sorption tests were determined considering their typical contents in tire crumb rubber (30% and 60% w/w, respectively). Freundlich's isotherms and Scatchard plot parameters suggested a two-step sorption process when TCR was used as the sorbent; whereas a single-step route was apparent when the sorption experiments were carried out with CB or SBP. Freundlich's 'n' parameters for toluene, xylene, acenaphthene and phenanthrene were estimated at 1.018, 0.90, 1.207 and 0.655, respectively using TCR. The maximum uptake capacities (K_f) calculated from Freundlich's equation for toluene, xylene, acenaphthene and phenanthrene were 0.239 mg/g, 0.723 mg/g, 3.32 mg/g and 54.6 mg/g, respectively, using TCR as the sorbent.

In a different set of experiments, the effect of TCR concentration in the sorption of VOCs such as ethylbenzene, toluene and xylene, and PAHs such as acenaphthene, acenaphthylene and phenanthrene was evaluated for single and multi-component experiments. The maximum uptake capacities (K_f) calculated from Freundlich's equation for ethylbenzene, toluene and xylene for single component experiments were 1.8, 0.17 and 1.9 mg/g, respectively, and the (K_f) for multi-component experiments were 0.67, 0.35 and 0.81 mg/g, respectively. The (K_f) for acenaphthene,

acenaphthylene and phenanthrene for single component experiments were 10.2, 5.02 and 46.9 mg/g, respectively, and the (K_f) for multi-component experiments were 6.23, 4.38 and 11.1 mg/g, respectively.

TCR also was used to remove gasoline components from aqueous solutions. The qualitative analysis showed that all components in the gasoline water samples of 30 mg/L were partially removed. The components with high molecular weight were almost completely removed using 5 g/L of TCR. A gas chromatographic analysis using Single Ion Monitoring (SIM) analysis allowed the quantification of the amount of toluene and o-xylene present in the gasoline water samples. The removal (after 6 hours of contact time) of total gasoline compounds was 96%, and the removal of toluene and o-xylene in the gasoline samples was 73% and 86%, respectively, using an initial concentration of 30 mg/L of gasoline and 5.0 g/L of TCR.

A modified gas chromatograph and a column packed with 25 g of TCR (mesh 14-20) were used to remove toluene in gas phase. The toluene was injected using a constant syringe pump at rates between 0 and 30 μ L/h. Sorption isotherms were constructed by changing the system pressure between 0 and 50 psi. The 'n' value and the uptake capacity (K_f) calculated from Freundlich's equation were 1.19 and 0.54 mg/g, respectively. The uptake capacity for the removal of toluene in gas phase was higher than in the aqueous phase.

A modification of TCR using microorganisms was studied. *Pseudomonas sp.* was isolated and immobilized onto TCR to improve its removal capacity against phenanthrene. After 7 days, the modified TCR (1.0 g/L) adsorbed and degraded 92% of phenanthrene. The removal was due to the TCR sorption (90%) and microorganism biodegradation (10%).

The sorption capacity and its low cost compared with commercially available sorbents make TCR a promising sorbent for VOCs, PAHs and gasoline components in aqueous and gas phases.

RESUMEN

La ab/adsorción de compuestos orgánicos volátiles (VOCs) (etilbenceno, tolueno y xileno) e hidrocarburos poli aromáticos (PAHs) (acenapteno, acenaptileno and fenantreno) por partículas de goma de neumáticos (TCR) y sus principales componentes fueron evaluadas: negro de carbón (CB) y polímero de estireno-butadieno (SBP). Las concentraciones iniciales de VOCs y PAHs en soluciones acuosas estuvieron en el rango de 0.05 mg/L a 100.0 mg/L y 0.03 mg/L a 3.0 mg/L, respectivamente. Las cantidades de CB y SBP usadas en las pruebas de ab/adsorción fueron determinadas considerando su contenido típico en las partículas de goma de neumáticos (30% y 60% w/w respectivamente). Las isothermas de Freundlich y los parámetros de las gráficas de Scatchard sugieren un proceso de ab/adsorción de dos pasos cuando TCR fue usado como ab/adsorbente, mientras que una ruta de un solo paso fue aparente cuando los experimentos de ab/adsorción fueron llevados a cabo con CB y SBP. Los parámetros 'n' de Freundlich para tolueno, xileno, acenapteno y fenantreno fueron estimados de 1.018, 0.90, 1.207 and 0.655 respectivamente, usando TCR. Las máximas capacidades de carga (K_f) calculadas de la ecuación de Freundlich para tolueno, xileno, acenapteno y fenantreno fueron 0.239mg/g, 0.723mg/g, 3.32 mg/g y 54.6 mg/g respectivamente, usando TCR como ab/adsorbente.

En un grupo de experimentos diferente, el efecto de la concentración de TCR en la absorción de VOCs tales como etilbenceneo, tolueno y xileno, y PAHs tales como acenapteno, acenaptileno and fenantreno, fue evaluada para experimentos de un solo componente y muti-componentes. Las máximas capacidades de carga (K_f) calculadas de la ecuación de Freundlich

para etilbenceno, tolueno y xileno para experimentos de un solo componente fueron 1.8, 0.17 y 1.9 mg/g, respectivamente, mientras que los K_f para experimentos de multi-componente fueron 0.67, 0.35 and 0.81 mg/g, respectivamente. Los K_f para acenapteno, acenaptileno y fenantreno para experimentos de un solo componente fueron 10.2, 5.02 and 46.9 mg/g, respectivamente. Los K_f para los experimentos de multi-componente fueron 6.23, 4.38 and 11.1 mg/g, respectivamente.

TCR además fue usado para remover los componentes de gasolina de soluciones acuosas. El análisis cualitativo mostró que todos los componentes en las muestras acuosas de gasolina de 30 mg/L fueron parcialmente removidos. Los componentes con alto peso molecular fueron completamente removidos usando 5 g/L de TCR. Un análisis de cromatografía usando monitoreo de un solo ion (SIM) permitió la cuantificación de la cantidad de tolueno y o-xileno presentes en las muestras acuosas de gasolina. La remoción (después de 6 horas de tiempo de contacto) de todos los compuestos de la gasolina fue 96%, y la remoción de tolueno y o-xileno en las muestras de gasolina fueron 73% y 86%, respectivamente, usando una concentración inicial de 30 mg/L de gasolina y 5 g/L de TCR.

Un cromatógrafo de gas modificado y una columna empacada con 25g de TCR (mesh 14-20) fueron usados para remover tolueno en fase gaseosa. El tolueno fue inyectado usando una bomba de jeringuilla constante a una proporción entre 0 y 30 μ L/h. Isotermas de ab/adsorción fueron construidas cambiando la presión del sistema entre 0 y 50 psi. El valor 'n' y la capacidad de carga (K_f) calculadas fueron de 1.19 y 0.54 mg/g, respectivamente. La capacidad de carga para tolueno en fase gaseosa fue más grande que en fase acuosa.

Una modificación de TCR usando microorganismos fue estudiada. *Pseudmona sp.* fue aislada e inmovilizada sobre TCR para mejorar su capacidad de remoción contra fenantreno. Después de 7 días, el TCR modificado (1.0 g/L) ab/adsorbió y degradó 92% de fenantreno. La remoción fue debida a la ab/adsorción de TCR (90) y a la biodegradación de los microorganismos (10%).

La capacidad de ab/adsorción y su bajo costo, comparado con ab/adsorbentes disponibles comercialmente, hacen del TCR un ab/adsorbente prometedor para VOCs, PAHs y componentes de la gasolina en fase gaseosa y acuosa.

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1 INTRODUCTION

Protecting water bodies (surface, aquifers and coastal) from organic and inorganic contamination is essential for health and safety. The principal organic contaminant groups are Volatile Organic Compounds (VOCs), Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs). Heavy Metals (HMs) are considered by EPA as the principal inorganic contaminant group (Amari, Themelis et al. 1999). Pollution in many cases involves more than one group of contaminants and requires a simple and cost effective broad-spectrum sorbent material.

The US-Environmental Protection Agency (EPA) is in charge of identifying and regulating the permissible levels of pollutants agents in air, water and soil. Despite the existent environmental protection policies, pollution events are still frequent not only in Puerto Rico but also in the rest of the world (EPA 2005).

1.1 Statement of the Problem

Protecting water bodies (surface, aquifers and coastal) from contamination is essential for our health and safety. In Puerto Rico, heavy metal pollution (mainly Pb, Cu, Zn and Cd) has been reported in effluents from municipal wastewater, electroplating, metal finishing and printed circuit board manufacturing plants. Contamination by hazardous organic compounds such as hexane and toluene has also been reported in some laundries and gas stations (EPA 2007).

The contamination of two lagoons with halogenated solvents in Guayama by a fiber manufacturer was detected in 1982 (EPA 2005). In Barceloneta, Upjohn Manufacturing Co.

(a pharmaceutical company) contaminated 2-acre soil with carbon tetrachloride in 1982. In this later case, a leak from an underground storage tank was the problem. In 1982, contamination by volatile organic compounds (VOCs) in a municipal landfill in Barceloneta was also reported (EPA 2005). Since 2002, the Puerto Rico Aqueduct and Sewer Authority (PRASA) have detected tetrachloroethene (PCE) and trichloroethene (TCE) in public supply wells within the Cabo Rojo urban areas. In October 2010, EPA included these findings in the National Priorities List (NPL) (EPA 2010).

1.2 Water pollution by Organic Contaminants

1.2.1 Volatile Organic Compounds (VOCs)

Ethylbenzene, toluene and xylene (ETX) are a mixture of aromatic compounds usually contained in oil. This is the reason why these compounds are always involved in oil pollution problems such as the oil spill in the Gulf of Mexico in April 2010 (figure 1.1). ETX compounds are used in the elaboration of plastics, rubber, and resins and as solvents in the pigment, printing and dry cleaning industries.



Figure 1.1 Images from the Gulf of Mexico Pollution by oil. 2010.

Some physical properties of ETX compounds are summarized in table 1.1. The high vapor pressure values exhibited by these compounds suggest their high volatility. Furthermore, their low density when compared to water explains their trend to be solubilised (Oxford-University 2006; Oxford-University 2006).

TABLE 1.1 Physical properties of VOCs

	Boiling point (°C)	Vapor pressure (mm Hg at 20° C)	Density (g cm ⁻³)	Solubility (mg/L)
Ethylbenzene (a)	136	10	0.867	152
Toluene (b)	110.6	22	0.865	515
Xylene (c)	137	5.1	0.87	200

* Structures are show below

The chemical structures of ETX shown in figure 1.2 are typical of non-polar compounds, where the particular arrangement of the lateral chains explains the differences in the corresponding boiling points. ETX structures consist of an aliphatic (methyl and ethyl groups) and an aromatic (benzene ring) component.

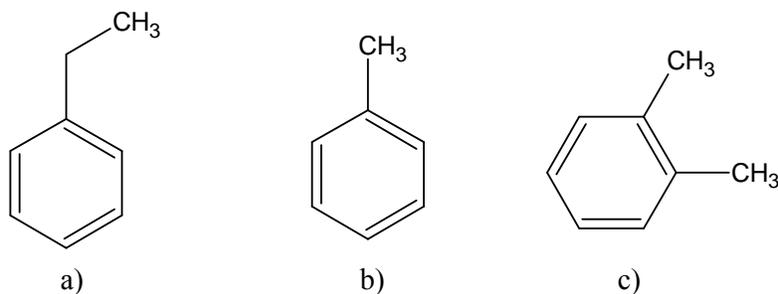


Figure 1.2 Chemical structures of ethylbenzene (a), toluene (b) and xylene (c) used in this research.

The US EPA established maximum contaminant levels (MCL) in drinking water for ethylbenzene, toluene and xylene of 0.7, 1.0 and 10 mg/L, respectively (EPA 2006).

Exposure to ETX solvents can cause disturbances in the central nervous system and damage to kidney and liver. The relationship between long time exposure to benzene and cancer has been well documented (Wilbur and Bosch 2004).

Several approaches to remove ETX compounds from water have been reported in the technical literature. Granular activated charcoal (GAC) is the most common adsorbent. Other approaches consider zeolites and surfactant-modified zeolites (Ranck, Bowman et al. 2005), however the prohibitive sorbent fabrication costs limits their applicability. Evidently, the ideal sorbent should exhibit removal capacities comparable to commercial sorbents under cost-effective conditions. For the sorption of organic compounds, a polymeric matrix with non polar components (like rubber) is required.

1.2.2 Polyaromatic Hydrocarbons (PAHs)

PAHs are fused rings (figure 1.3) with low solubility and high boiling points (table 1.2). PAHs can be classified according to their source: biogenic, petrogenic and pyrogenic. Biogenic PAHs are formed from natural biological processes; petrogenic PAHs are derived from petroleum and usually enter the aquatic environment dissolved in water, air or a co solvent such as crude oil; and pyrogenic PAHs are formed as a result of incomplete combustion of fuels and enter the environment sorbed to particulate matters. These recalcitrant compounds can be carcinogenic and constitute risk for human health (NIOSH 1994; Reyes, Rosario et al. 2000).

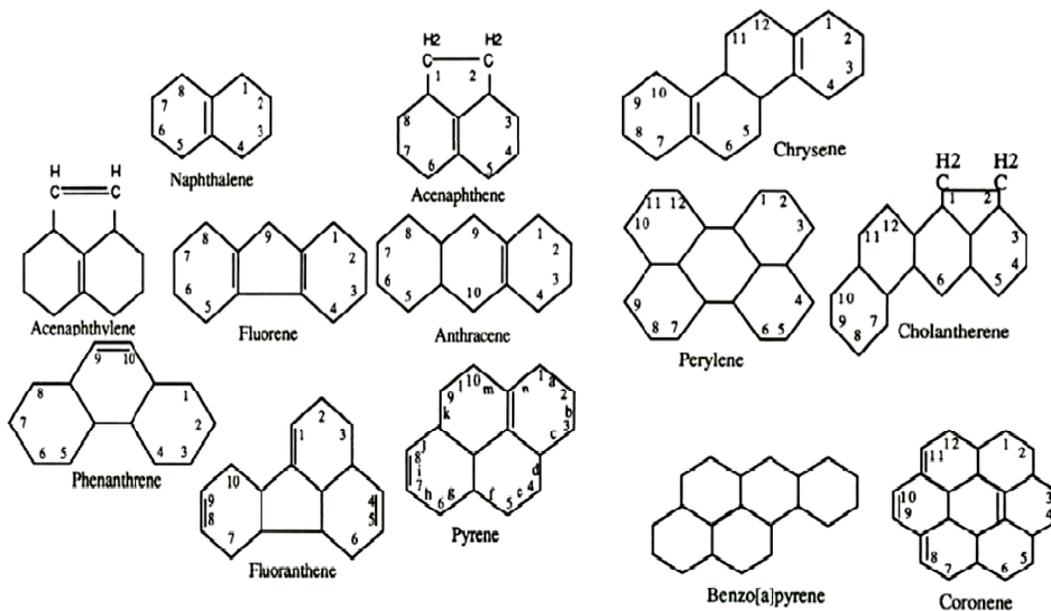


Figure 1.3 Chemical structures of some PAHs

	Solubility (mg/L)	Boiling point (° C)	Vapor pressure (mm Hg at 20° C)	Benzene rings (total)
Acenaphthylene	2.6	270	10 ⁻³ – 10 ⁻⁴	2
Acenaphthene	3.8	277	-	2
Phenanthrene	1.002	339	6.8 x 10 ⁻⁴	3
Fluorene	1.685	295	-	2 (3)
Anthracene	0.0446	340	2.4 x 10 ⁻⁴	3
Pyrene	0.132	404	6.9 x 10 ⁻⁷	4
Benzo[a]anthracene	0.011	-	1.1 x 10 ⁻⁷	4

TABLE 1.2 Physical properties of PAHs

Generally speaking, two major sources of PAHs have been identified in drinking water: 1) contamination of raw water supplies from natural and anthropogenic sources, and 2) leachate from coal tar and asphalt linings in water storage tanks and distribution lines. Likewise, the release of fossil fuels and derivatives into inland water bodies is responsible for the significant presence of PAHs in aquatic environments (Khodadoust, Li et al. 2005). It has been confirmed that PAHs can enter water directly from the air with dust and precipitation, or on particles washed from the soil by runoff (Khodadoust, Li et al. 2005). PAHs dissolved in water can be "taken up" by plants and are released into soil and water when the plants either die or decompose. PAHs can also be mobilized into the aquatic environment through discharges from industrial and domestic sewage effluents, leaks of PAHs-containing materials (e.g. oils), runoff from paved roads, parking lots, and the ground of wood preservation plants, among other sources. PAH concentrations have been increasing over the past 30-35 years in many urban and suburban lakes across the United States (Mahler, Van Metre et al. 2005).

In the Caribbean, water and sediment of two marinas (Crown Bay Marina and Independent Boatyard) in St. Thomas reported elevated concentrations of PAHs in water and sediment. The highest concentrations of PAHs in water were found at the fuel dock of Crown Bay Marina (1.1235 mg/L) (EPA 1997). Flushing patterns indicated, however, that petroleum from the fuel dock could have migrated through the water column and deposited in sediments at the ship dock (which had a PAH concentration of 1.1029 mg/g in sediments) and the sampling station located in the low flushing area of the marina (which had a concentration of 0.0821 mg/g in sediments). At the Crown Bay Marina, in addition to vessel and fuel dock operations, another likely source of pollution was spills from oil tanks located across the road and entering the marina through a storm drain and road run-off (EPA 1997).

Typically, concentrations of 2-6 ng/L of individual PAHs were also found in rainwater throughout the Great Lakes and Chesapeake Bay regions (EPA 1997). PAHs are also ubiquitous contaminants in urban environments. Although numerous sources of PAHs to urban runoff have been identified, their relative importance remains uncertain. It has been shown that parking lot sealcoat may dominate loading of PAHs to urban water bodies in the United States. Particles in runoff from parking lots with coal-tar emulsion sealcoat had mean PAHs concentrations of 3500 mg/kg, 65 times higher than the mean concentration from unsealed asphalt and cement lots. Diagnostic ratios of individual PAHs were similar for particles from coal-tar emulsion sealed lots and suspended sediment from urban streams, indicating the same origin (Mahler, Van Metre et al. 2005).

R. Lohmann et al. (Lohmann, Macfarlane et al. 2005) studied the sorption of PAHs compounds by the sediments in Boston and New York harbors. They found that the solid-water distribution ratios (K_d values) of "native" PAHs in those sediments exceeded the corresponding $f_{(oc)}K_{oc}$ products by 1-2 orders of magnitude. The same work suggested that black carbon measured about 0.6% in the Boston harbor sediment and about 0.3% in the New York harbor sediment, and that it was responsible for the additional sorption of native PAHs by the harbor sediments.

Diesel emissions are known to include particulates containing PAHs that could also be washed out by rain to pollute surface water or percolate to groundwater streams, which in turn can contaminate the soil. In Puerto Rico, diesel trucks emissions represent a significant source of air pollution. Thousands of trucks travel the highways every day generating a visible cloud of smoke. A toxic evaluation of organic extracts from airborne particulate matter in Puerto Rico has been reported (Reyes, Rosario et al. 2000). It was found that

extracts from the Guaynabo industrialized site with high concentration of PAHs were more cytotoxic than the extracts from Fajardo coastal reference site with low PAHs concentration. In addition, the nonpolar extracts of the samples exerted the greatest cytotoxicity (Reyes, Rosario et al. 2000). Evidently, the PAH-related pollution problem cannot be ruled out in Puerto Rico, and the consideration of simple and effective alternatives for the removal of these compounds is needed.

PAHs and VOCs are not the only components present in contaminated places, and in many cases pollution involves more than a group of contaminants. Military activities have produced contamination of water and soil with explosives such as trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX); organic compounds such as tetrachloroethylene (PCE), trichloroethylene (TCE), and PAHs; and heavy metals such as arsenic, cadmium, chromium and lead.

Common military activities such as firing practices, ammunition storage and disposal, use of degreasers (PCE and TCE), fuels (PAHs) and metal ware can cause contamination of water and soil. The Lake City Army Ammunition Plant located in Jackson County Missouri (ATSDR 2001) has reported several surface and groundwater sites contaminated with arsenic, cadmium, chromium, lead, TCE, dichloroethane, toluene and RDX. Soils were also contaminated with RDX, TCE, 1,1,2 trichloroethane, PAHs (benzo-a-anthracene, benzo-a-pyrene and benzo-b-fluoranthene), arsenic and lead. Mather Air Force Base located in Mather, Sacramento County, California also reported (ATSDR 2001) groundwater contamination with PCE, TCE, carbon tetrachloride, benzene and 1,2 dichloroethane; surface water contamination with PAHs, polychlorinated biphenyls, arsenic, lead and manganese; and soil contamination with PAHs, arsenic, cadmium and lead. The Naval Air Warfare

Center located in Warminster Township, Pennsylvania has reported (ATSDR 2002) groundwater, surface water and soil contamination with PCE, TCE, PAH (benzo-a-pyrene, benzo-a-anthracene, benzo-b-fluoranthene), and arsenic, chromium, cadmium and lead among others. The Whiting Field Naval Air Station, Milton, Santa Rosa, Florida has reported (ATSDR 2000) contamination (site 7) of groundwater with organic compounds such as TCE (1400 ppb), benzene (14,000 ppb), toluene (47,000 ppb), ethylbenzene (2,400 ppb), xylene (12,000 ppb) among others and heavy metals such as arsenic, cadmium, chromium, and lead. The Fairchild Air Force Base located in Spokane Washington (ATSDR 1997) and the March Air Force Base located in California (ATSDR 2001) have also reported groundwater contamination with TCE.

1.2.3 Gasoline

Gasoline is a complex mixture of organic volatile and semi volatile compounds (ATSDR 1990). The typical composition of gasoline hydrocarbons (% volume) is as follows: 4-8% alkanes; 2-5% alkenes; 25-40% isoalkanes; 3-7% cycloalkanes; 1-4% cycloalkenes; and 20-50% total aromatics (0.5-2.5% benzene). Gasoline is not soluble in water and its density is 0.7 – 0.8 g/cm³. Some aromatic compounds are benzene, toluene, xylenes, ethylbenzene, C₃-benzene, C₄-benzenes (IARC 1998).

Leaking storage tanks are the main problem of contamination with gasoline and gas additives. A major hazard associated with automotive gasoline is benzene, which was used in the past as a solvent in inks, rubber, lacquers, and paint removers. Today, it is used mainly in closed processes to synthesize organic chemicals. Gasoline is a risk to human health because it is classified in the group 2b by the International Agency for Research on Cancer (IARC). Group 2b contains agents or mixtures of agents for which there is limited evidence of

carcinogenicity in humans and less than sufficient evidence of carcinogenicity in experimental animals (IARC 1998).

Spilling of gasoline is the principal source of contamination with VOCs. Some examples of areas contaminated with VOCs in Puerto Rico as reported by On-site Environmental, Inc are the following: (On-site environmental 2009)

- US Naval Station Roosevelt Road Ceiba, P.R. -Bioremediation of 2,060 cubic yards of soil contaminated with gasoline from underground storage tanks.
- Puerto Rico Ports Authority, Aguadilla, PR. - Bioremediation of approximately 5,000 cubic yards of soil contaminated with aviation gas at former U.S. Air Force Ramsey Base.
- Cooperativa Camioneros Transporte de Carga, Maunabo, P.R. - In-Situ Bioremediation of 700 cubic yards of soil contaminated with diesel fuel at truck accident site, Maunabo, P.R.
- Avis Rental Car System, Carolina, PR. - Closure of Underground Storage Tanks (8) and Bioremediation of approximately 4,000 cubic yards of hydrocarbon affected soil at Luis Muñoz Marín International Airport.
- Municipality of Dorado - Site assessment for hydrocarbon affected soils at “Taller de Obras Públicas” in the Municipality of Dorado, Dorado, PR

1.3 Tires and Crumb Rubber Composition

About 4 million tires are discarded annually in Puerto Rico, of which approximately 800,000 tires are reused each year, and the remainder is land filled, stockpiled or illegally dumped (see figure 1.3). Land filling is a poor management option for scrap tires (Velasquez 2001). Whole tires take up large amounts of valuable space in a landfill and come up to

surface shortly. New environmental regulations eliminate land filling as a disposal method, greatly increasing the environmental recycle of scrap tires. Under this premise, the search of different alternatives to expand the re-use possibilities for scrap tires is justified.



<http://www.apwa.net/publications/reporter/reporteronline/index.asp>

Figure 1.4 Waste tires contamination.

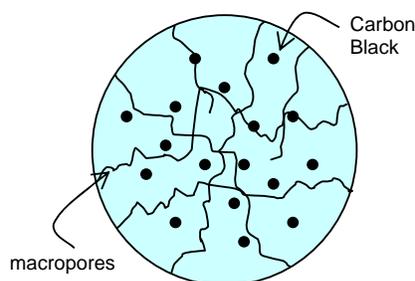
In order to prevent waste rubber and particular discarded automobile tires from damaging the environment, it is highly desirable to recycle this material. Recycling of waste materials is an important goal for all industries and especially for the rubber industry. In 2005, approximately 259 million tires were fabricated in the US. Although markets for scrap tires consume around 80% of them, the remaining 20% is still stockpiled or land filled (Association 2006; RMA 2006; EPA 2007) and it has been estimated that the amount of discarded tires reaches 10 billion every year worldwide (ISRI. Institute of Scrap Recycling Industries 2007). Only a small portion of the waste tires are recycled, and a very small portion is de-vulcanized by tedious processes. The asphalt highway construction business holds the greatest potential for the demand of scrap and used tires in the form of ground rubber (Shulman 2000).

Tire crumb rubber is composed of a complex mixture of elastomers like polyisoprene, polybutadiene and styrene-butadiene. Figure 1.4a shows a schematic representation of this material. Crumb rubber also consists of curatives (sulphur and peroxide), cure system-activators (stearic acid), fillers and reinforcing agents (carbon black, fibers, etc.), process oils, plasticizers and additives (antioxidants, antiozonents). The most commonly used rubber matrix is the co-polymer styrene-butadiene (SBR) or a blend of natural rubber and SBR. From a rubber-composition point of view, the major components of tires are rubber vulcanized with sulphur (1.1%), stearic acid (1.2%), ZnO (1.9%), extender oil (1.9%) and carbon black (31.0%) (Amari, Themelis et al. 1999). Carbon black is used to strengthen the rubber and improve its abrasion resistance. This component should exhibit adsorbing characteristics similar to activated charcoal, a well-known agent used to remove organic and inorganic compounds from aqueous and gaseous effluents. This fact that makes the removal of target species through sorption/adsorption mechanisms viable (Carratala-Abril, Lillo-Rodenas et al. 2009; Yu, Peldszus et al. 2009). Therefore, carbon black present in waste tires would promote the removal of target species through sorption/adsorption mechanisms (Knocke and Hemphill 1981; Arocha, Jackman et al. 1997; Zarraa 1998; Al-Asheh and Banat 2000). Stearic acid could also behave as an ionic exchanger. Moreover, non-polar organic pollutants are expected to interact with the rubber matrix via Van der Waals interactions (Stom and Morgan 1996).

Crumb rubber is the result of shredding tires, separating metals and fibers, and pulverizing the clean rubber into different sizes. It can be reutilized to manufacture new products or used as an aggregate in other products. New technologies allow scrap tires be reduced to various sizes and consistencies depending upon the targeted end use market.

Lehmann et al. 1998 and Murillo et al. 2005 (Lehman, Rostam-Abadi et al. 1998; Murillo, Navarro et al. 2005) proposed the production of activated coal from waste tire crumb rubber to be used in the treatment of polluted gas effluents. The main drawback for the project was the high costs involved with the carbonization process, which requires a thermal treatment of rubber under atmosphere-controlled conditions.

a)



b)

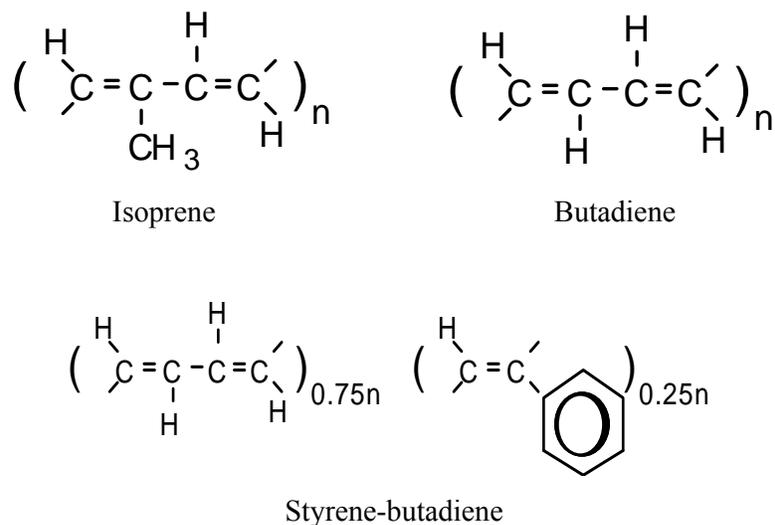


Figure 1.5 a) Schematic representation of crumb rubber. b) Chemical structures of some polymer components of crumb rubber.

Non-polar organic compounds are expected to interact with the non-polar matrix of the rubber and other constituents such as carbon black (figure 1.5) (present as a disperse phase that acts as reinforcement in tires) mostly by Van der Waals interactions (Unnikrishnan, Thomas et al. 1996). The kinetics of the sorption process will depend on the access of sorbate species to the sorption sites, the number of sorption sites and the nature of the sorption interactions. An important factor related to the sorption process is the fact that crumb rubber is vulcanized and therefore its molecular structure contains a large number of cross-links. The amount of solvent that will diffuse into the crumb rubber depends on the number of cross-links and the compatibility of the solvent and rubber at a molecular level (Arocha, Jackman et al. 1997).

Thousands of abandoned scrap tires are found in streams, rivers and roadsides throughout Puerto Rico and other countries. The mismanagement of millions of scrap tires every year represents a significant waste of resources. One example is the case of the 8,000 tons of chopped-up tires in the barge docked in Guayama since July 23rd, 2002, a problem without a definitive solution, at least in the short term (EPA 2005).

The remediation option detailed in this research is based on the presence of components in crumb rubber such as carbon black, zinc oxide, and sulfur, which are embedded in an elastomeric matrix with potential capability to sorb hazardous species from aqueous solutions. This fact has been verified by several investigators (Guanasekara, Donovan et al. 2000; Alamo-Nole 2006; Nieto-Zambrano 2006; Sánchez-Rivera 2007). The sorbent material was pre cleaned, downsized to different particle sizes and kindly provided by Rubber Recycling and Manufacturing Corporation (REMA), a Puerto Rican company that produces crumb rubber at different particle sizes from scrap tires.

On this basis, the present research deals with the systematic investigation of the practical applicability for this “waste material” to remove different VOCs and PAH’s such as ethylbenzene, toluene, xylene, phenanthrene, acenaphthene, and acenaphthylene. The conditions leading to maximization of the uptake capacity and sorption rate for these hydrocarbons were investigated.

1.4 Sorption theory

Sorption is a term that covers adsorption and absorption processes in a solid matrix. When the analyte is concentrated at the surface of a phase, the process is called adsorption. In absorption, the compound interpenetrates a phase to form a “solution” (Stom and Morgan 1996).

Physical and chemical phenomena can be involved in adsorption processes. In *chemisorption*, sorbed species are chemically bonded to specific active surface sites. In turn, *physisorption* involves weak interaction forces, like Van der Waals forces, and it is not site specific (Stom and Morgan 1996).

For organic compounds like ethylbenzene, toluene and xylene, physical sorption is more probable than chemical (Stom and Morgan 1996).

1.4.1 Sorption Isotherms

Plotting of amount of solute adsorbed per unit of adsorbent vs. the equilibrium concentration remaining in the solution is named sorption isotherm. The shape of isotherms gives qualitative information related to the adsorption process (Faust and Aly 1987). There are some models that explain the experimental trends. The Langmuir model assumes that the

adsorbent has definite sites, which can only fix one molecule (monolayer). In this case, gas is adsorbed in a solid phase and the temperature and pressure play a significant role increasing or decreasing the concentration at equilibrium. For a solid-liquid adsorption:

$$q_e = \frac{Q^o b C_e}{1 + b C_e} \quad \mathbf{1.1}$$

where:

C_e : Concentration of adsorbate at equilibrium

q_e : Concentration of adsorbate in the sorbent

b : Langmuir constant representing the affinity between the adsorbate and the sorbent

Q^o : Langmuir constant representing the concentration of adsorbate in the sorbent considering a complete coverage of available sites

The next equations transform the data in a linear relation that can be plotted to get sorption parameters.

$$\frac{C_l}{C_s} = \frac{1}{Q^o b} + \frac{C_l}{Q^o} \quad \mathbf{1.2,}$$

$$\frac{1}{C_s} = \frac{1}{Q^o} + \frac{1}{b Q^o C_l} \quad \mathbf{1.3}$$

or

$$C_s = Q^o - \frac{C_s}{b C_l} \quad \mathbf{1.4}$$

where:

C_s : Equilibrium concentration of adsorbate in the sorbent

C_l : Equilibrium concentration of adsorbate in solution (terminal concentration)

When the surface is heterogeneous and the distribution of sites and energies are exponentials, the Freundlich model represents better the adsorption behaviour (Slejko 1985; Faust and Aly 1987). Therefore:

$$C_s = K_f C_l^{1/n} \quad \mathbf{1.5}$$

and

$$\ln C_s = \ln K_f + \frac{1}{n} \ln C_l \quad \mathbf{1.6}$$

where:

K_f : Freundlich constant representing the relative indicator of adsorption capacity

$1/n$: Freundlich constant representing sorption behaviour (linearity factor)

Linear model only considers solid-liquid partitioning and is described by equation 1.7 (Faust and Aly 1987):

$$C_s = K_p C_l \quad \mathbf{1.7}$$

where:

K_p : Linear constant or partition coefficient

The Scatchard relationship (Eq. 2) is derived from Langmuir's equation. It provides qualitative information about the types of binding sites involved in a sorption process. The interactions between the adsorbate and the sorbent can be evaluated from the shape of the corresponding Scatchard plot; e.g. a single interaction would be suggested by a linear trend

with one slope, whereas multiple slopes imply a multi-interactions (Ayar, Gürsal et al. 2008).

$$\frac{q}{C} = q_m K_b - q K_b \quad \mathbf{1.8}$$

where:

q_m : number of binding sites in the sorbent

K_b : association (affinity) constant.

The linearity of the isotherms can be evaluated using the factor P (Eq. 3) or the probability that the experimental results fit the model. Low P values will indicate best fitting (Ayar, Gürsal et al. 2008).

$$P = \left(\frac{100}{N} \right) \sum_{i=1}^{i=N} \left[\frac{|q_{i(\text{exp})} - q_{i(\text{pred})}|}{q_{i(\text{exp})}} \right] \quad \mathbf{1.9}$$

where:

P: probability of the model

$q_{i(\text{exp})}$: experimental value, $q_{i(\text{pred})}$ representing the value calculated from the model.

N: number of replicates.

2 RELATED WORKS

Knocke and Hemphill (1981) (Knocke and Hemphill 1981) evaluated the sorption behaviour of waste tire rubber for inorganic Hg from aqueous solution. In these experiments, rubber particles were obtained by shredding the vulcanized tire rubber and separating it by size using the standard sieve procedure. The batch sorption studies evaluated the effect of particle size, crumb rubber concentration and Hg concentration on the removal efficiency and

uptake capacity. The results showed that pH was the most important factor, with an optimum range between 5.5 and 6.0. It was suggested that the diffusion of Hg through pores in the rubber sorbent was the rate-limiting step regarding final uptake.

Rowley et al. (1984) proposed a tentative mechanism of adsorption for Cd (II), Hg (II) and Pb (II) onto shredded rubber. Rubber particles were treated with liquid nitrogen and crushed to obtain sizes between 2.4 and 3.3 mm in diameter which were then packed in columns. The suggested mechanism was dependent on the type of metal ion; Hg and Cd uptake took place with a simultaneous release of Zn, probably from ZnO, suggesting an ion exchange mechanism. On the other hand, Pb adsorption did not involve any Zn displacement. They exhibited the best uptake capacity at low pH values which is not in agreement with other authors (Knocke and Hemphill 1981; Zarraa 1998; Gunasekara, Donovan et al. 2000).

Zarraa (1998) worked in the sorption equilibrium of single-component (Cu, Cd and Zn) and multi-component (Cu-Cd, Cu-Zn and Cu-Cd-Zn) metal ions onto scrap rubber. Rubber particles with a diameter of 605 μm were contacted with aqueous solutions at pH between 5.1 and 5.6. The order of preference of scrap rubber for metal ions in single component was $\text{Cd} > \text{Cu} > \text{Zn}$. This order appears to be related to the electronegativity of the ions (Zarraa 1998).

Gunasekara et al. (2000) have shown that ground discarded tires can remove inorganic Hg ions from aqueous solutions. Two types of ground tire rubber were used; a mixture of natural and synthetic rubbers and a completely natural rubber were used in the form of black powder. The sorption of Hg was slower in comparison to organic compounds such as naphthalene, and its sorption affinity was found to be concentration dependent. The results showed that for 1 g of rubber powder in 100 mL of Hg (II) solution, there was a complete

sorption for all Hg concentrations below 4 µg/mL. The kinetic data for the sorption behaviour for Hg was considered insufficient to determine if the rubber particles had reached saturation after three days of contact time. Although the effect of ions speciation on the “binding” of Hg to rubber powder was studied, the authors stated the need for a more detailed evaluation of the process rate and a better explanation of the involved sorption mechanisms in the system (Guanasekara, Donovan et al. 2000).

Sameer and Fawzi (2000) studied the adsorption of copper ions on to tire rubber. Non-activated, chemically activated, physically activated and carbonized rubber was used. Uptake capacity varied between 6.54 and 8.93 mg/g of rubber. Once more, the adsorption process was found to be dependent on initial pH. The high copper uptake values at pH 5 were attributed to the change in the charge on the carbon black surface (Sameer and Fawzi 2000).

Calisir et al. (2009) in a batch sorption system also found that the copper sorption onto tire crumb rubber was pH dependent. The highest uptake was found at pH 6. The sorption of copper was accompanied with the release of zinc that could suggest an ion exchange mechanism (Calisir, Roman et al. 2009).

Kim et al. (1997) conducted batch sorption test for m-xylene, ethylbenzene, toluene, trichloroethylene, 1,1,1-trichloroethane, chloroform and methylene chloride using ground tire granules from Tire Technology, Inc. with a surface area ranging between 0.16 and 0.56 m²/g. The corresponding partition coefficients decreased from 977 L/kg for m-xylene down to 13 L/kg for methylene chloride. Although different experimental conditions were tested, e.g. ionic strength, pH, ground tire particle size and temperature, no significant effect on the sorption behaviour was observed. It was suggested that the organic compounds were sorbed primarily by polymeric components and partially by carbon black (Kim, Park et al. 1997).

Quantification at low pH values and concentration of inorganic produced significant analytical errors because direct injection in a gas chromatography (GC) was used. Solid phase microextraction (SPME) in the headspace was used in the present project as an alternative to overcome the described analytical drawback.

Kershaw et al. (1997) used scrap tire rubber, granulate rubber WRF series provided by Baker Rubber, Inc. with a particle size of 425 μm to remove toluene and xylene from ground water. The mass of benzene and xylene sorbed per gram of ground rubber (mg/g) were 7.13 and 19.87, respectively (Kershaw, Crouthamel Kulik et al. 1997). The use of volumetric flasks to prepare the solvent standards could produce lost of analytes due to their high volatility. Also, low pH values were not evaluated, however a release of zinc was observed (Rowley, Husband et al. 1984) which may have a possible effects in the sorption.

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 $\mu\text{g/L}$ (Guanasekara, Donovan et al. 2000). 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 the difficulty of recovery.

Alamo et al. (2007) reported that crumb rubber removed efficiently ethylbenzene, toluene and xylene in single-component systems. Using 30 mg/L as the initial concentration for each compound, crumb rubber removed 99, 95 and 77% of xylene, ethylbenzene and toluene respectively. The sorption capacity of crumb rubber was xylene > ethylbenzene > toluene (Alamo-Nole, Roman et al. 2007).

Other related efforts to remove PAHs species can be summarized as follows. Mastral et al., discussed the equilibrium between PAHs and granular carbonaceous materials in adsorption systems based on carbon beds for air pollution control. The adsorption of the most volatile PAHs (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene) was measured for initial concentrations ranging from 0.020 mg/L to 25 mg/L at 150 °C. Experimental results showed that their adsorption capacity was strongly dependent on the initial concentration of PAHs (Mastral, García et al. 2003).

Regarding the sorption behavior of PAHs contained in soils or water bodies, L. Zhu has investigated the sorption of PAHs in soil-water systems containing surfactants to understand the fate of contaminants in natural systems and the feasibility of using surfactants for remediation of contaminated soils (Zhu, Chen et al. 2004). Batch studies were conducted on the sorption of three PAHs (naphthalene, acenaphthene, and phenanthrene) from water in four different soils with and without a non-ionic surfactant (Triton X-100). The ratio of apparent PAH sorption coefficients (K_d^*) when surfactant was added, to the intrinsic coefficients (K_d) in absence of surfactant, varied from greater to less than 1, depending on the system. For phenanthrene on high- f_{oc} (f_{oc} = fraction organic carbon) soils at low to moderate Triton X-100 initial concentration, the ratio K_d^*/K_d was below one, which suggested the enhancement of the PAH mobility, and hence the corresponding efficiency (Zhu, Chen et al. 2004).

A series of organobentonites synthesized by exchanging organic cation such as dodecyltri-methylammonium (DTMA) and benzyldimethyltetradecylammonium (BDTDA) on bentonite were also evaluated as sorbents for PAHs dissolved in water (Chen and Zhu 2001). The interlayer spacing and organic carbon contents of organobentonites, removal rate

and sorption capacities for organobentonites to treat targeted PAHs were correlated to the length of alkyl chains and the amounts of cation surfactant exchanged on the bentonite. PAHs sorption were characterized by linear isotherms, indicating solute partition between water and the organic phase composed of the large alkyl functional groups of quaternary ammonium cations. PAHs distribution coefficients (K_d) between organobentonites and water were proportional to the organic carbon contents of organobentonites; however, the partition coefficients (K_{oc}) were nearly constants in the system of organobentonite-water. The high K_{oc} values make organobentonites a potential material for remediation of polluted soil and groundwater bodies (Wiles, Huebner et al. 2005).

Oren and Chetetz studied the sorption and desorption behaviors of phenanthrene and naphthalene with whole sediment, humic acid (HA) and humin samples from downstream and upstream sites along the Kishon River, Israel. Results from the ^{13}C nuclear magnetic resonance analyses and the corresponding sorption coefficients suggest that sorption occurs in both aromatic and aliphatic moieties of the sedimentary organic matter and those rigid paraffinic domains probably contribute to the sorption non-linearity. On the basis of the measured affinity values, the sorbents were ranked as: humin > HA > whole sediment (Oren and Chetetz 2005).

From the above considerations and based on the well-established ionic exchange and sorption behavior of PAHs in presence of activated clays, silica-based sands and granular activated coals, the use of crumb rubber containing similar active ionic exchange and sorption sites (provided by ZnO and carbon black raw constituents) can be considered as a very promising alternative to remove VOCs and PAHs compounds from aqueous solutions.

2.1 Scope and objectives

The present work is focused on the systematic evaluation of tire crumb rubber (TCR) as a suitable material to remove Volatile Organic Compounds (VOCs) and Polycyclic Aromatic Hydrocarbons (PAHs) from aqueous and gaseous effluents through a low-cost and easy-to-scale technology based on the sorption properties of this waste material.

The general and specific objectives of this investigation were the following:

- Sorption study of VOCs on to tire crumb rubber (TCR), carbon black (CB) and styrene butadiene polymer (SBP).
 - Analyze isotherms generated for VOCs.
 - Analyze Scatchard plots generated for VOCs.
 - Analyze Freundlich parameters generated for VOCs.
 - Analyze the effect of tire crumb rubber concentration in the sorption process.
- Sorption study of gasoline, and toluene and xylene in gasoline onto tire crumb rubber.
- Sorption study of PAHs on to TCR, CB and SBP.
 - Analyze isotherms generated for PAHs.
 - Analyze Scatchard plots generated for PAHs.
 - Analyze Freundlich parameters generated for PAHs.
 - Analyze the effect of tire crumb rubber concentration in the sorption process.
- Sorption study of toluene on to TCR in gaseous phase.
 - Analyze isotherms generated.
 - Analyze Scatchard plots generated.
 - Analyze Freundlich parameters generated.

- Sorption study of phenanthrene using TCR modified with immobilized microorganism.
 - Isolation and immobilization of microorganism onto TCR.
 - Analyze the removal and biodegradation of the TCR modified.

3 EXPERIMENTAL SECTION

In our work, solutions of VOCs and PAHs were contacted with TCR, CB and SBP at pH 6.0. The effect of changing the concentration of TCR in single component and multi-component systems with VOCs and PAHs were studied. The sorption behaviours of TCR, CB and SBP were investigated by analyzing the fitting of our results to Linear, Freundlich and Langmuir adsorption models. The removal of toluene in gas phase was also evaluated using TCR. A modified TCR with immobilized microorganisms was prepared and evaluated for the removal and biodegradation of phenanthrene as a model PAH.

3.1 Reagents and Materials

A. Reagents

- Ethylbenzene Certified Fisher. CAS # 100-41-4 (>99%).
- Toluene ACS. Fisher. CAS# 108-88-3 (>99%).
- O-Xylene Certified Fisher. CAS # 95-47-6O5078-1 (>99%).
- Acenaphthene. Sigma Aldrich CAS #208-96-8 (>99%)
- Acenaphthylene. Sigma Aldrich CAS# 83-32-9 (99%)
- Phenanthrene. Sigma Aldrich CAS# 85-01-8. (98%)
- Carbon Black amorphous N330. Sid Richardson Carbon Company (CAS 1333-86-4). density 1.7 – 1.9 g/cm³.
- Poly(styrene-co-butadiene), $[\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)]_x(\text{CH}_2\text{CH}=\text{CHCH}_2)_y$ Sigma Aldrich (CAS 9003-55-8). It was trimmed to the same size as crumb rubber.
- Nitric acid (HNO₃) (trace metal. ACS Certified, Fisher, CAS # A509-212, 70%) was used to acidify to 1.5 pH.

- NaOH Lab grade. Fisher CAS # 1310-73-2 (95-100%) was used to acidify to 9.0 pH.
- Deionized water was used to prepare all samples and wash materials.
- Helium High Purity gas was used as mobile phase in the GC-MS.

All reagents were used as received.

B. Glassware

- Amber screw cap bottles with hole caps and septa 120 mL
- Teflon coated silicone septa 22 mm. Cat # 23245-U.
- Micropipettes: 10 and 100 μ L.
- Beakers: 50, 100 and 600 mL.
- Volumetric flask: 5 and 10 mL.

C. Solid Phase Microextraction set up

- Solid Phase Micro Extraction fiber holder. Supelco Cat. # 57330-U
- SPME fiber assembly 100 μ m polydimethylsiloxane (PDMS) Coating. Supelco Cat. # 57300-U.
- Ice blue septa 17 mm Restek Cat. # 22396
- Magnetic stirring bar. Fisher Cat # 14-512-146-2.

The experimental set-up is shown in the Figure 3.1.

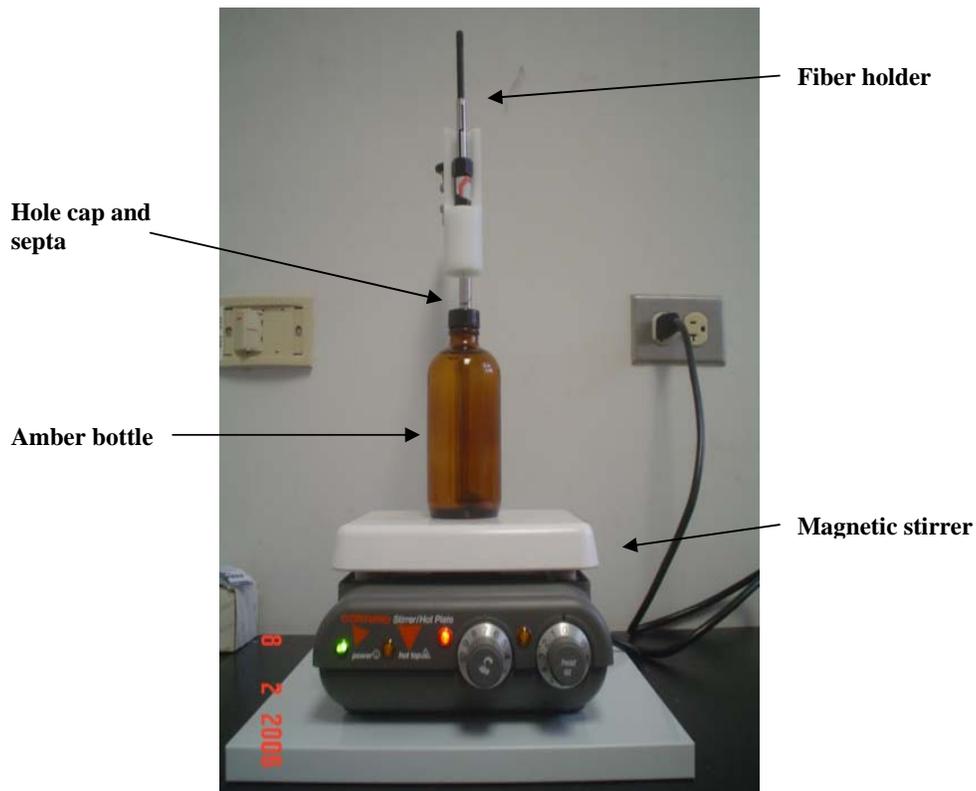


Figure 3.1 Solid Phase Microextraction system.

D. Miscellaneous equipment

- Oakton pH meter 510.
- Analytical balance. Adventurer Ohaus. (Max cap. 210g; readability 0.0001).
- Magnetic stirrer (60 – 1100 rpm; 25 – 550° C)
- Digital flow check-HR meter. NIST traceable. Alltech

E. Instrumentation

- Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) from LEEMAN INC.
- Bioreactors. Biostat A plus from Sartorius.

- Trace Gas Chromatograph coupled to a Mass Spectrometer detector from Finnigan – GCQ Plus (Polaris), Figure 3.2, equipped with electron impact ionization with 70 eV, split/splitless injector and controlled with Xcalibur software.
 - * Column: Crossbond 5% diphenyl – 95% dimethyl polysiloxane. 30 meter, 0.25 mm ID, 0.25 μ m df. Restek Cat.# 12623. Serial # 187526. Max. Programmable temp 350° C, minimal bleed at 330° C.



Figure 3.2 Gas Chromatography with Mass Spectrometry Detector.
Finnigan – GCQ Plus (Polaris).

3.2 The Sorbent: Waste tires crumb rubber

Tire crumb rubber (TCR) was provided by REMA Corporation, a tire rubber recycling company located in Caguas, Puerto Rico. The TCR (mesh 14 -20), Figure 3.3, was washed with deionized water for 24 hours and dried at room temperature.



Figure 3.3 Tire crumb rubber mesh 14-20.

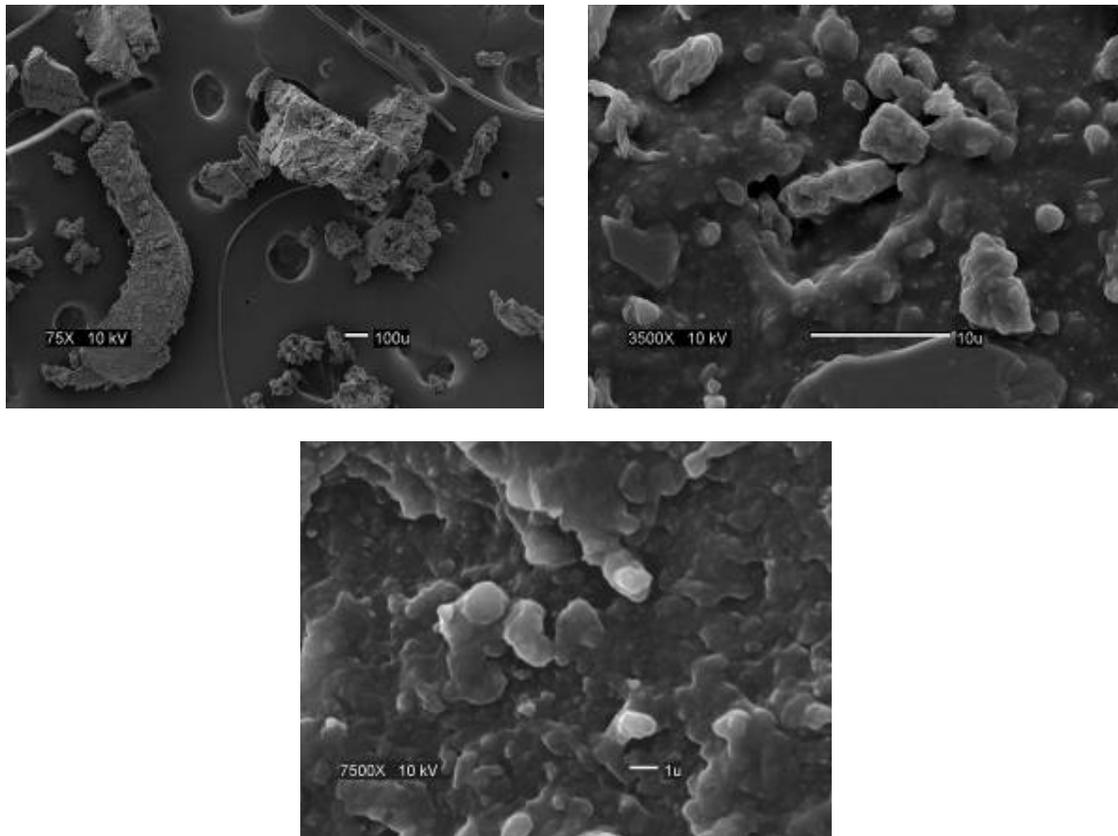


Figure 3.4 SEM pictures of tire crumb rubber.

Scanning Electron Microscopy (SEM) studies (figure 3.4) showed that TCR has an irregular surface. TCR mesh 14-20 has different sizes between 1.5 to 4.0 mm. The average size is 2.45 ± 0.09 mm of diameter and the superficial area was roughly estimated at $18.86 \pm$

0.05 mm². The average weight was 1.82 ± 0.07 mg and the specific surface area was 10.36 mm²/mg or 0.1036 m²/g. In cleaning treatment procedures this size is very useful because TCR can be recovered easily and these particles can be used in packed column for continuous water treatment operations.

3.3 Instrumental techniques

3.3.1 Solid Phase Microextraction

Solid Phase Microextraction (SPME) is a solvent-free technique that uses a small fused silica fiber coated with a polymeric phase. Absorption or adsorption processes can be present in the extraction of analytes from the matrix. This technique extracts and concentrates the analytes allowing direct introduction into the desorption unit of the analytical instrument for qualitative or quantitative analysis (Pawlisyn, 1999).

The headspace mode is a very useful procedure for analysis of volatile compounds. Headspace is defined as the gaseous portion inside the closed vessel containing the solutions to be analyzed. Stirring or sonication is used to reduce diffusional transport of analytes. This mode allows using this technique in solutions with strong pH values without damage to the fiber. Exposition time of the fiber to the sample is very important because the analytes in the headspace are first removed. For this reason, short exposition time of fiber is recommended when using high concentrations of volatile compounds (Pawlisyn, 1999).

High vapor pressure of volatile compounds gives short equilibrium time in the headspace. Temperature directly affects the vapor pressure and the equilibrium. Small

changes in the temperature can produce large changes in the headspace concentration (Pawlisyn, 1999).

On the basis of the rule of “like dissolves like”, the polydimethylsiloxane (non polar liquid phase) coating is used to extract non polar analytes. This coating can resist high temperatures and gives a wide linear range (Pawlisyn, 1999 and Woolley and Mindrup, 1996).

SPME is very useful for environmental analysis and it is generally combined with other techniques such as HPLC, GC-MS and Raman spectroscopy (Wittkamp and Tilotta, 1995) to detect organic compounds like pesticides, pharmaceuticals, methyl tert-butyl ether (MTBE) (Richardson, 2001 and Koester et al., 2003), among others.

3.3.2 Preparation of Standard Solutions

Volatile Organic Compounds (VOCs) Standards

Stock solutions of 1000 mg/L of ethylbenzene, toluene and xylene in acetonitrile were prepared. Standards were prepared in 120 mL amber bottles leaving a 10 mL of headspace. Two sets of standards were prepared to cover all sorption experiments (120 to 10 mg/L and 10 to 0.01 mg/L of adsorbates). Each bottle had a magnetic stirrer and was capped with septa and sealed with paraffin. Bottles were placed in magnetic stirrer and sampled in triplicates after 20 minutes using head space SPME. The SPME fiber was introduced into the headspace of the 120 mL amber bottles and equilibrated for 10 seconds for ethylbenzene, toluene and xylene followed by injection into the GC-MS.

Polyaromatic Hydrocarbons (PAHs) Standards

Stock solutions of 100 mg/L of acenaphthene, acenaphthylene and phenanthrene in acetonitrile were prepared in 120 mL amber bottles leaving a 10 mL of headspace. Standards for acenaphthene and acenaphthylene ranged from 3.0 to 0.01 mg/L. Standards for phenanthrene ranged from 1.0 to 0.01 mg/L. Each bottle had a magnetic stirrer and was capped with septa and sealed with paraffin. Bottles were placed in magnetic stirrer and sampled in triplicates after 20 minutes using SPME. The SPME fiber was introduced into the headspace of the 120 mL amber bottles and equilibrated for 5 minutes followed by injection into the GC-MS.

3.3.3 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The technique of Gas Chromatography coupled to a mass spectrometry (GC-MS) allows the identification and quantification of analytes in complex samples. The GC-MS has been used in environmental analysis, criminal forensics, food, beverage, and perfume analysis. The compounds are separated in a capillary column and they are analyzed based on the ions formed and detected in the mass spectrometer.

A precise determination of the GC-MS parameters is critical to achieve good peak shape and resolution. Table 3.1 summarizes the optimum measurement conditions for VOCs standards and samples and Table 3.2 summarizes the parameters for PAHs standard and samples. The injector and detector were used at high temperatures to avoid condensation of the sample solution.

TABLE 3.1 Parameters used in the quantification of ethylbenzene, toluene and xylene in aqueous samples by SPME and GC-MS.

Mass Spectrometry	
Ion source temperature: 200	Transfer line temperature: 275
Total Ion Current: 70 eV.	Microscans: 3
Gas Chromatography	
Equilibration time: 0.5 min	Oven max temperature: 350° C
Initial temperature: 45° C	Initial time: 0.5 min
Rate 1: 30° C/min	Final temperature: 120° C
Final time: 2 min	
Total gas flow: 50 mL/min	
Injector temperature: 200° C	Injector mode: splitless

TABLE 3.2 Parameters used in the quantification of acenaphthene, acenaphthylene and phenanthrene in aqueous samples by SPME and SIM-GC-MS.

Mass Spectrometry	
Ion source temperature: 200	Transfer line temperature: 275
Single Ion Monitoring (SIM)	Microscans: 3
Acenaphthene : 154	
Acenaphthylene: 152	
Phenanthrene: 178	
Gas Chromatography	
Equilibration time: 0.5 min	Oven max temperature: 350° C
Initial temperature: 130° C	Initial time: 0.5 min
Rate 1: 15° C/min	Final temperature: 180° C
Final time: 2 min	
Total gas flow: 50 mL/min	
Injector temperature: 250° C	Injector mode: splitless

3.4 Sorption experiments

3.4.1 VOCs sorption experiments

Sorption experiments using tire crumb rubber, carbon black and styrene-butadiene polymer

Ethylbenzene, toluene and xylene are non-polar compounds with low solubility in water (see table 1.1). Low concentrations in the ppb – ppm range of these compounds should assure complete solubility in aqueous phase. The initial concentrations of toluene and xylene ranged from 0.05 to 120 mg/L, while the concentration of TCR was 5 g/L. The concentration of CB and SBP were 1.5 and 3.0 g/L, respectively; these values represent their typical contents in tire crumb rubber (30% and 60% w/w, respectively).

Amber bottles of 120 mL of capacity were used and filled with 110 mL of deionized water samples at pH 6.0. All solutions were prepared directly in the bottles to avoid any loss of analyte. The water samples at room temperature were mechanically stirred (600 rpm) and samples were withdrawn at specific intervals using headspace SPME. The fiber stayed in the injector until 30 seconds before the end of the run for cleaning and conditioning purposes.

Quality controls (QC) samples of 50, 30 and 10 mg/L for each solvent were run in all experiments and the results were accepted if the error was below 20%. If the error of QC samples was outside the accepted range a new calibration curve was prepared.

Effect of tire crumb rubber concentration in single-component and multi-component sorption experiments

To assess the effect of the TCR concentration in single-component system, 30 mg/L aqueous solutions of ethylbenzene, toluene and xylene were contacted with TCR mesh 14-20 in the 0.1g/L - 10 g/L range at pH 6.0. The results for single-component system were taken from Alamo experiments (Alamo-Nole 2006).

In multi-component sorption tests, an aqueous solution containing a total concentration of ETX species of 30 mg/L (10 mg/L of ethylbenzene, 10 mg/L of toluene and 10 mg/L of xylene) was contacted with TCR in the 0.1g/L - 10 g/L range at pH 6.0.

Quality controls (QC) samples of 30 mg/L solvent mixture were run and the results were accepted if the error was below 20%. If the error of QC samples was outside the accepted range a new calibration curve was conducted.

3.4.2 PAHs sorption experiments

Sorption experiments using tire crumb rubber, carbon black and styrene-butadiene polymer

Low concentrations of PAHs below solubility in water were used to assure complete solubility in aqueous phase. The initial concentrations of acenaphthene and phenanthrene ranged from 0.01 to 3.0 mg/L and 0.01 to 1.0 mg/L, respectively and the concentration of TCR was kept constant at 5 g/L. The concentrations of CB and SBP were 1.5 and 3.0 g/L,

respectively; these values represent their typical contents in tire crumb rubber (30% and 60% w/w, respectively).

Amber bottles of 120 mL of capacity were used and filled with 110 mL of deionized water samples at pH 6.0. All solutions were prepared directly in the bottles to avoid any loss of analyte. The water samples were mechanically stirred and samples were withdrawn at specific intervals using headspace SPME. The fiber stayed in the injector for 4 minutes for cleaning and conditioning purposes.

Quality controls (QC) samples of 0.1 and 1.0 mg/L for each solvent were run in all experiments and the results were accepted if the error was below 20%. If the error of QC samples was outside the accepted range, a new calibration curve was prepared.

Effect of tire crumb rubber concentration in single-component and multi-component sorption experiments

To evaluate the effect of TCR concentration in single component system, 0.9 mg/L aqueous solutions of acenaphthene and acenaphthylene and 0.5 mg/L of phenanthrene were contacted with varying quantities of crumb rubber mesh 14-20 in the range of 0.1g/L - 10 g/L at pH 6.0.

In multi-component sorption tests, an aqueous solution containing a total concentration of PAHs species of 1.0 mg/L (0.33 mg/L of acenaphthene, 0.33 mg/L of acenaphthylene and 0.33 mg/L of phenanthrene) was contacted with TCR at the same concentrations as previous experiments.

Quality controls (QC) samples of 0.5 mg/L solvent mixture were run and the results were accepted if the error was below 20%. If the error of QC samples was outside the accepted range, a new calibration curve was conducted.

3.5 Sorption of gasoline components onto tire crumb rubber in water samples

To evaluate the sorption capacity of TCR for complex mixtures as gasoline, stock solutions of 10,000 mg/L of gasoline, toluene and xylene were prepared in acetonitrile. Aqueous standards were prepared in 120 mL amber bottles leaving 10 mL of headspace. The concentration of the gasoline aqueous standards ranged between 1 and 40 mg/L. The concentration of toluene and xylene standards ranged between 0.10 and 5 mg/L of each component. Each bottle was capped with septa and sealed with paraffin. Bottles were placed in magnetic stirrer and sampled in triplicate after 20 minutes using the headspace SPME technique. The fiber was exposed to the headspace for 60 seconds followed by injection into the GC-MS system. All analyses were run in triplicate. Quality controls (QC) samples were prepared at mid concentrations of calibration standard of gasoline (20 mg/L) and used to evaluate both the integrity of the SPME fiber and the calibration status. The Q-test was used to evaluate outlier values.

Gasoline water samples of 40, 30, 20, 15, 10 and 5 mg/L were prepared in 120 mL amber bottles leaving a 10 mL headspace and contacted with 5 g/L of TCR. The bottles (triplicate) were capped with septa and sealed with paraffin. Bottles were placed in magnetic stirrer and sampled in triplicate after 6 hours of contact using the SPME technique. The fiber was exposed to the headspace for 60 seconds followed by injection into the GC-MS system.

The removal of total components in gasoline water samples was evaluated using the total ion chromatogram (TIC) mode and the area obtained from the sum of all integrated peaks was considered. TIC mode monitors all ions formed during electron ionization. This mode allows the identification and evaluation of the removal of all components present in gasoline. Single ion monitoring (SIM) mode was used to quantify toluene and xylene standards and gasoline samples. SIM mode allows monitoring specified ions formed during the ionization step, which facilitates the elimination of peaks that interfere with the quantification of the analytes with improved sensitivity. The ions monitored for toluene were 65 m/z, 91 m/z and 92 m/z and for xylene were 72 m/z, 91 m/z and 106 m/z.

The removal of gasoline and its components by TCR was compared to the removal by TCR principal components like carbon black (CB) and styrene butadiene polymer (SBP). The concentrations of CB and SBP were calculated considering the actual tire composition (30% of CB and 60% of SBP). Gasoline aqueous solutions (30 mg/L) were contacted with 1.5 g/L of CB and 3.0 g/L of SBP. The removal of gasoline aqueous solutions was evaluated using TIC mode. In contrast, the removal of toluene and xylene in the gasoline water solutions was evaluated using SIM mode.

3.6 Toluene sorption experiments in gas phase

3.6.1 Instrument configuration

A Gas chromatography Hewlett Packard 5890 series II was modified to conduct the experiments. Air was used as the mobile phase. The inlet pressure (60 psi) was regulated by

an external manometer. The flow and pressure were regulated using a control valve situated at the exit of the column setup. The internal pressure was monitored using the sensor of the GC system. Toluene was injected using a constant syringe pump (30 $\mu\text{L/h}$) that was connected to the inlet port (A). An aluminium column 14.1 cm (5 $\frac{1}{2}$ ") long, 3.3 cm (1 $\frac{1}{4}$ ") in diameter and a volume of 60.8 ± 0.1 mL was connected to the inlet and sampling ports using copper lines. The inlet and sampling ports temperatures were set to 250° C and 180° C respectively. The pressure of the system was monitored using the GC system display and it was changed to elaborate the isotherm. A diagram and a picture of the modified GC instrument are presented in the figures 3.5 and 3.6.

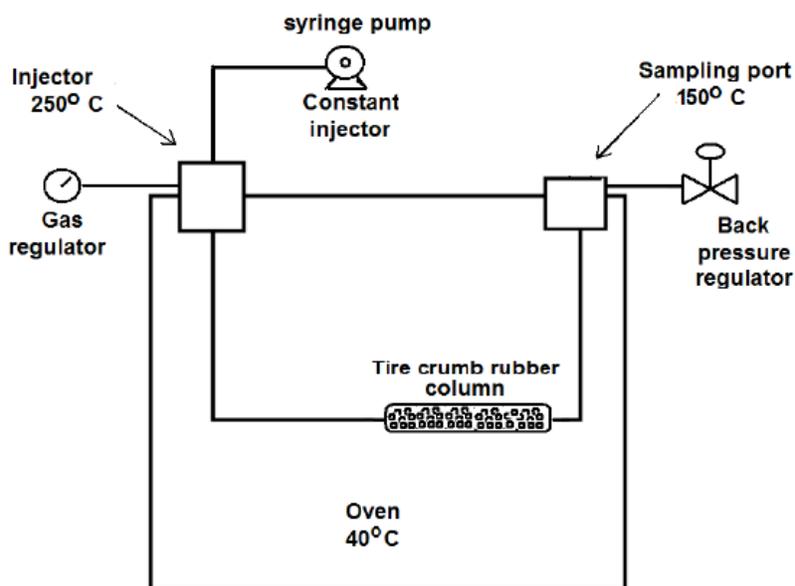


Figure 3.5 System configuration.

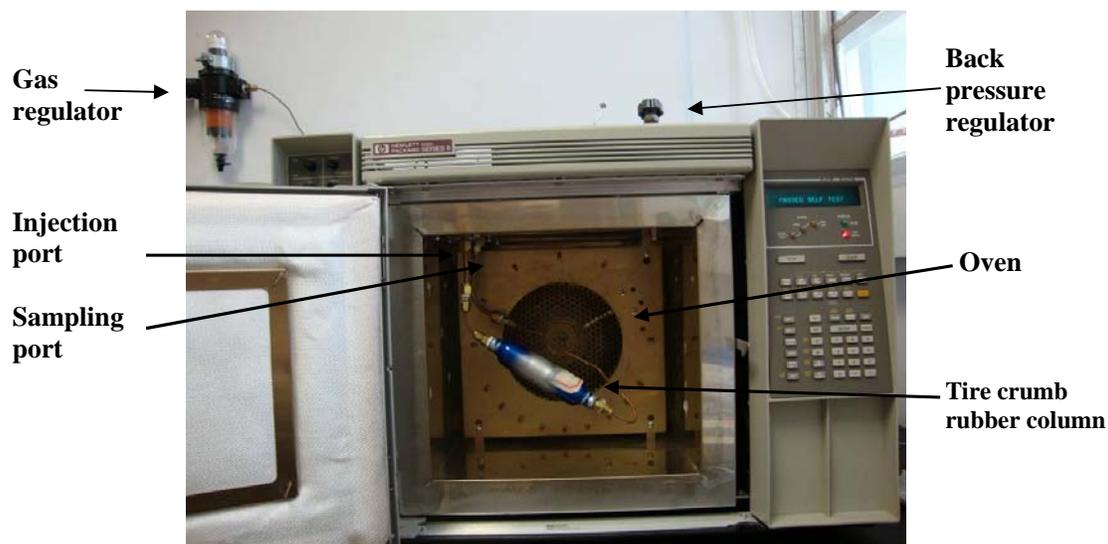


Figure 3.6 Modified GC HP 5890 System.

3.6.2 Sorption of toluene in gas phase

Calibration curves were elaborated changing the injection rate of toluene between 0 and 30 $\mu\text{L}/\text{h}$ at each flow and pressure value and used to prepare the isotherms. Toluene samples were collected at the sampling port using a gas tight syringe. The toluene samples (0.1 mL) were analyzed by direct injection in a GC-MS.

Approximately 25 g of TCR was packed in the column. The column was closed, installed and heated in the GC system for 2 hours using the work parameters to eliminate dirt and gases adsorbed. Toluene was injected at a rate of 30 $\mu\text{L}/\text{h}$ and 0.1 mL air samples were taken at specific times using a gas-tight syringe. The isotherm was elaborated changing the system pressure between 0 and 50 psi and the flow was measure at the end of the instrument using a digital flow meter.

3.7 Phenanthrene sorption experiments with modified tire crumb rubber

To improve the sorption capacity of TCR, microorganism were isolated and immobilized onto the TCR. The sorption capacity of the modified TCR to remove phenanthrene was evaluated using a batch bioreactor.

3.7.1 Isolation of penanthrene-degrading microorganism

For the microorganism isolation a minimum media (MM) was prepared using (L^{-1}) $NaNO_3$ 2.0g, $NaCl$ 0.8 g, KCl 0.8 g, $CaCl_2 \cdot 2H_2O$ 0.1 g, KH_2PO_4 2.0 g, $Na_2HPO_4 \cdot 2H_2O$ 2.0, $MgSO_4$ 0.2 g and $FeSO_4 \cdot 7H_2O$ 0.001 g. It also contained 2 mL of trace elements (L^{-1}): $FeCl_3 \cdot 6H_2O$ 0.08 g, $ZnSO_4 \cdot 7H_2O$ 0.75 g, $CoCl_2 \cdot 6H_2O$ 0.08 g, $CuSO_4 \cdot 5H_2O$ 0.075 g, $MnSO_4 \cdot H_2O$ 0.75, H_3BO_3 0.15 g and $Na_2MoO_4 \cdot 2H_2O$ 0.05 g. The pH was adjusted to 6.8. The solid minimum medium (SMM) was prepared by adding 2 g of agar to 100 mL of MM. Solid Lurea Broth (LB) plates (10 g $NaCl$, 10 g peptone, 5 g yeast extract and 15 g agar L^{-1}) were used to cultivate the isolated microorganism.

Five milliliters of water samples from contaminated bioreactors containing phenanthrene were incubated with 250 mL of MM containing 1 mg/L of phenanthrene with shaking at 150 rpm at 30° C. After 6 days 5 mL aliquot was transferred to 250 mL of fresh MM containing the same concentration of phenanthrene and it was incubated under the same conditions for 5 days. A 100 μL aliquot of medium was sprayed on SMM plates containing 1 mg/L of phenanthrene. The plates were incubated at 30° C for 3 days. The colonies were isolated and incubated in LB medium for identification and for degradation essays. Figure 3.7 shows the colonies of the microorganism in LB solid media.

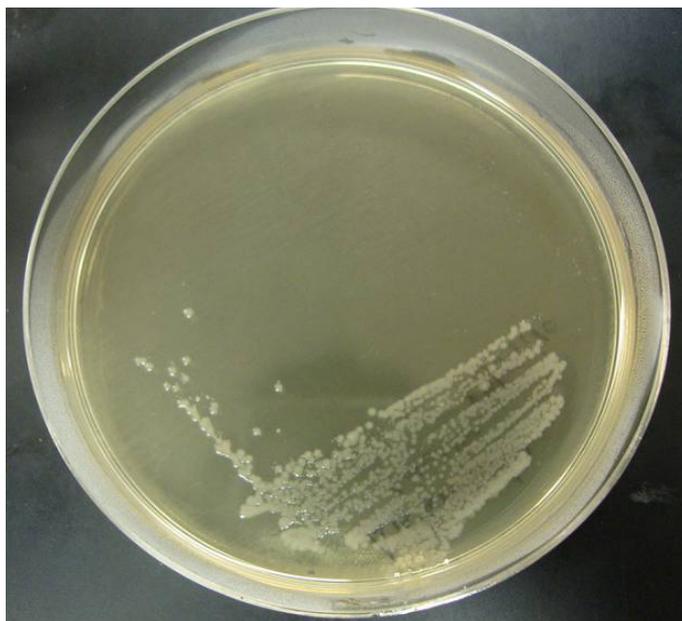


Figure 3.7 Microorganism isolated in LB solid medium.

Figure 3.8 show a view of the microorganism in a microscopy at 100 X. The figure shows the microorganism after Gram staining. The microorganism is a gram (-) bacteria. The biochemical assays applied to the bacteria (table 0.1 in appendix B) confirm that the microorganism is a *Pseudomona sp.*



Figure 3.8 Microorganism isolated. Optical microscopy at 100 X

3.7.2 Sorption and Biodegradation of phenanthrene using modified crumb rubber

Phenanthrene biotransformation was evaluated using 250 mL of MM with 1.0 mg/L of phenanthrene and inoculated with the microorganism isolated. The flasks were incubated at 30° C and 150 rpm. After 8, 24 and 48 hours the process was stopped and the solution was evaluated for biodegradation products using SPME technique. The PDMS fiber was introduced into the headspace for analytes sorption. A 100 µm Polydimethylsiloxane (PDMS) fiber, a 65 µm Carbowax-divinylbenzene fiber, a 85 µm Polyacrylate fiber and a 65 µm Polydimethylsiloxane-divinylbenzene fiber were evaluated at 1, 5, 10 and 20 minutes of fiber exposure into the headspace. The PDMS fiber gave the best results by expressing the higher quantity of peaks when analyzed in the GC-MS.

The immobilization of the microorganism was carried out using phosphate buffer at a pH of 7.0. TCR (4.0 g) was contacted with 5% glutaraldehyde solution in phosphate buffer. After 24 hours the solution was decanted and the TCR was washed two times with 100 mL of phosphate buffer (TCR was placed in contact with the phosphate buffer for 20 minutes to allow the glutaraldehyde to leave the matrix). The activated TCR was placed in contact with a microorganism solution that had absorption of 0.300 measured at 540 nm using a spectrophotometer. After 24 hours the modified TCR was washed two times with 100 mL of phosphate buffer.

The removal and biodegradation of phenanthrene using the modified TCR was evaluated using a 5 liters Sartorius bioreactor with air agitation. Figure 3.9 show the bioreactor used in the experiments. Three liters of MM were sterilized and added to the sterile bioreactor. A 3 mL aliquot of 1,000 mg/L solution of phenanthrene was added to give a final

concentration of 1.0 mg/L. The solution was agitated and mixed using an air flow of 300 mL/minute. The pH and temperature were set at 7.0 and 30° C, respectively. A solution of 1.0 mg/L of phenanthrene was used as a blank to evaluate the volatilization of phenanthrene during 5 days. An experiment using only TCR was also evaluated separately to determine the removal of phenanthrene by TCR alone. 2.0 g of TCR and 2.0 g of TCR modified with the microorganism were used in the experiments. A 30 mL sample was taken at specific times to evaluate the removal and the biodegradation. Samples were quantified using the SPME technique and SIM-GC-MS monitoring the fragment 178 m/z.



Figure 3.9 Sartorius Bioreactor.

To evaluate the use of the microorganism in seawater environments, their capacity to survive in salt water environment was also evaluated. Salt water medium (SWM) was prepared using (L^{-1}) 24.5 g NaCl; 0.03 g H_3BO_3 ; 1.54 g $CaCl_2 \cdot 2H_2O$; 4.09 g Na_2SO_4 ; 0.1 g

KBr; 0.003 g NaF; 0.2 g NaHCO₃; 0.7 g KCl; 0.017 g SrCl₂·6H₂O; 11.1 g MgCl₂·6H₂O(Xue-Qin, Jie-Ping et al. 2010). Four solutions containing MM, 50% SWM diluted in distilled water, 50% SWM diluted in distilled water plus micronutrients and 50% SWM diluted in MM were contaminated with phenanthrene, inoculated with the microorganism, incubated at 30° C and shaken at 150 rpm. The results shown in Appendix C confirm that the isolated *Pseudoma* sp can survive in salt water environments.

3.7.3 Characterization of fluorescent compound

The solution of the bioreactors was passed through a 0.2 µm filter and analyzed in a Shimadzu RF-5301 spectrofluorometer. The samples were also analyzed in High Performance Liquid Chromatographer with Fluorescence Detector (HPLC-FLD) and the most intensive peak was isolated using 407 nm excitation and 455 nm emission wavelengths. The results are shown in Appendix D.

4 RESULTS AND DISCUSSION

4.1 VOCs sorption experiments

Toluene and xylene in aqueous solutions (10 mg/L) were totally removed within 30 minutes of contact time when using TCR as sorbent at pH 6.0 and room temperature. The highest removal achieved for toluene and xylene using 5 g/L of TCR were 76.1% and 82%, respectively (table 4.1). However above 90% of xylene and 68% of toluene were removed when using 10 g/L of TCR. The results are in agreement with previous studies (Kim, Park et al. 1997; Guanasekara, Donovan et al. 2000).

The highest removal for toluene and xylene using 1.5 g/L of CB were 72% and 91%, respectively (table 4.1). The removal was highest at low concentrations of analytes. The achieved removals for toluene and xylene using 3.0 g/L of SBP were 58% and 83.1% respectively, and were almost constant at different concentrations of analytes. The removal of xylene was higher than toluene for all three sorbents. The quantity of CB (30%) and SBP (60%) used in the experiments represent the real concentration of these components in a tire (TCR). The other 10% correspond to other components like zinc oxide, fiber, oils, steel and other additives.

TABLE 4.1 Removal (%) of toluene and xylene using 5.0 g/L TCR, 1.5 g/L CB and 3.0 g/L

SBP

Init. Conc.	Toluene			Xylene		
	TCR	CB	SBP	TCR	CB	SBP
120	-	-	-	62 ± 3	-	--
100	67.9 ± 0.4	15.9 ± 0.5	41.7 ± 0.8	64 ± 1	32 ± 1	-
80	72.0 ± 0.8	18.0 ± 0.8	43.2 ± 0.7	70.9 ± 0.3	35 ± 1	72 ± 1
60	72 ± 1	21 ± 1	49 ± 1	76.5 ± 0.3	43 ± 2	73 ± 1
50	67.3 ± 0.9	21.8 ± 0.7	50 ± 2	81.0 ± 0.2	-	-
40	69.4 ± 0.9	21 ± 1	54 ± 1	80.7 ± 0.4	46 ± 2	73 ± 1
30	67.9 ± 0.1	23.1 ± 0.6	50 ± 2	78.6 ± 0.3	45 ± 2	72.8 ± 0.2
25	66.4 ± 0.7	-	-	75 ± 2	-	73.1 ± 0.5
20	69.7 ± 0.9	24 ± 1	52.2 ± 0.4	76 ± 1	42 ± 1	71.5 ± 0.8
10	76.1 ± 0.1	30.1 ± 0.9	48.1 ± 0.9	76.5 ± 0.3	43.7 ± 0.2	73.5 ± 0.5
5.0	76 ± 2	-	44.1 ± 0.6	80.9 ± 0.3	42 ± 2	78 ± 1
1.0	65.2 ± 0.9	45 ± 1	47.9 ± 0.6	83 ± 2	88 ± 2	78 ± 2
0.5	65 ± 1	72 ± 2	58 ± 2	81.1 ± 0.3	88.3 ± 0.4	83.2 ± 0.4
0.1	64.3 ± 0.6	-	-	82 ± 2	89 ± 3	73.3 ± 0.3
0.05	69 ± 2	-	-	81 ± 1	91 ± 2	-

- data not available

4.1.1 Isotherms for toluene and xylene experiments

TCR sorbent

The isotherms were plotted using the final concentrations obtained at equilibrium when the sorbent was saturated and no removal was observed. Each initial concentration represents a point in the isotherm plot. The figures 4.1 and 4.2 show the isotherms for toluene and xylene using 5 g/L of TCR. According to the corresponding isotherms, at least two kinds of interactions may have taken place between each adsorbate and TCR; i.e. each type of interaction could be due to two different sorption mechanisms in TCR. The profile suggested a sorption process where the sorbent is saturated in time, i.e. the first adsorbate molecules are

quickly adsorbed onto available sorption sites of the sorbent surface (exposed CB particles and SBP surface). The sorption rate would become slow as the sorption sites are occupied until adsorbate molecules finally cover available adsorption sites.

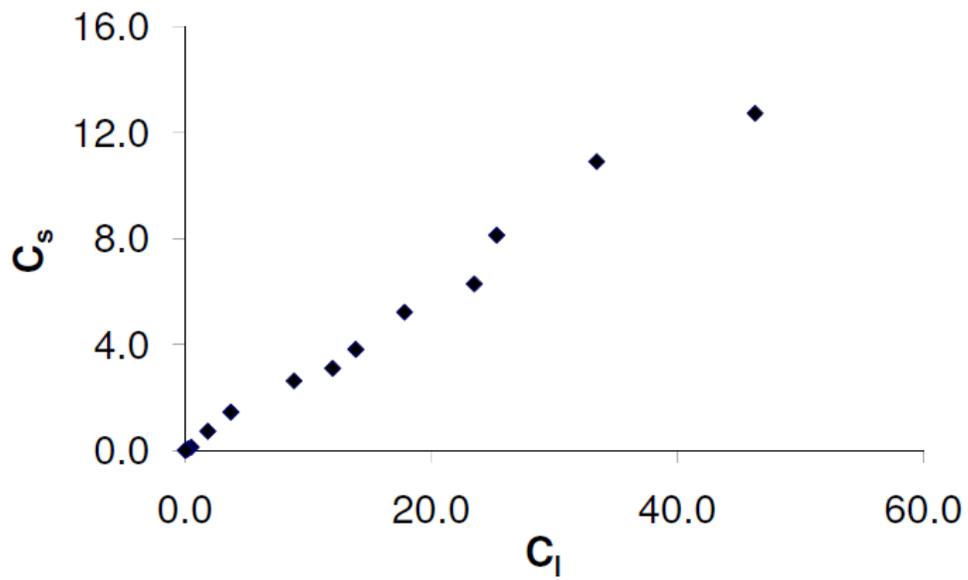


Figure 4.1 Isotherm for toluene sorption by TCR.

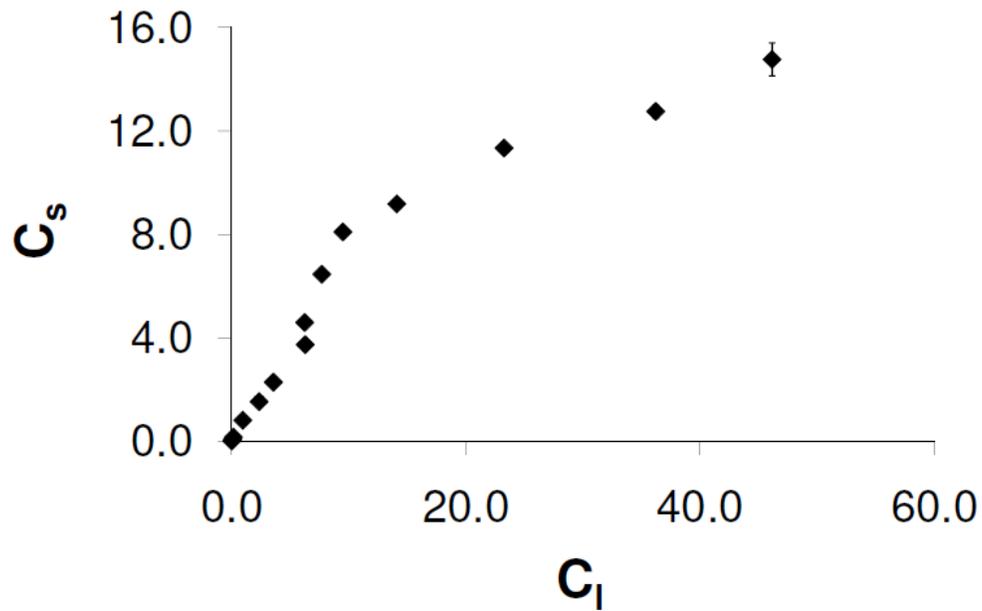


Figure 4.2 Isotherm for xylene sorption by TCR.

CB sorbent

The sorption of toluene and xylene by CB shows a non-linear pattern (figures 4.3 and 4.4) that is typical for adsorption processes onto amorphous and carbonaceous sorbents (Carratala-Abril, Lillo-Rodenas et al. 2009; Lai, Quio Chu et al. 2009). The sorption process onto CB corresponds to an adsorption mechanism where the adsorbent is located on the sorbent surface.

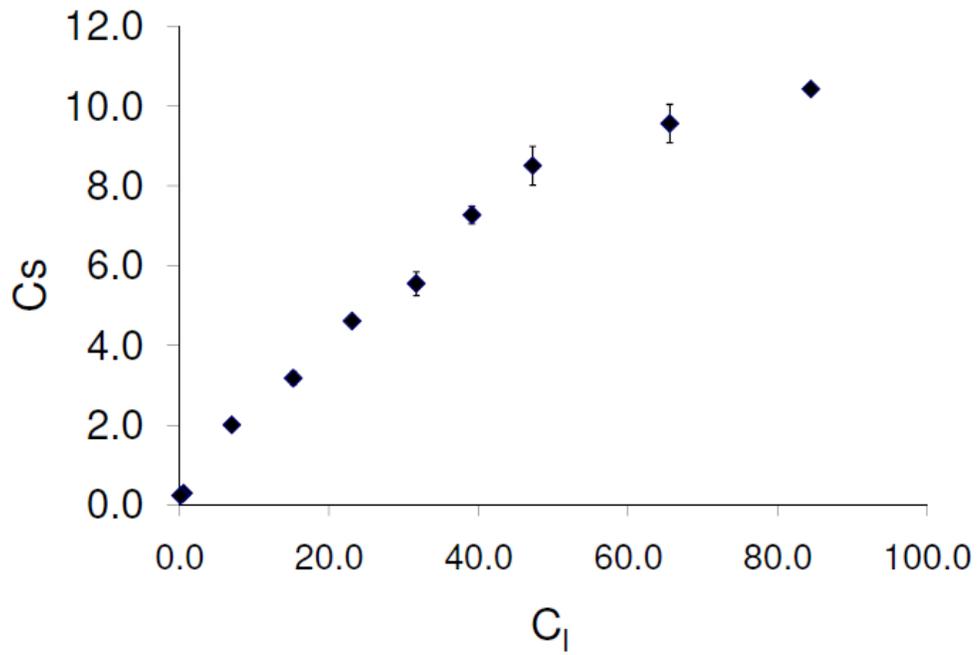


Figure 4.3 Isotherm for toluene sorption by CB.

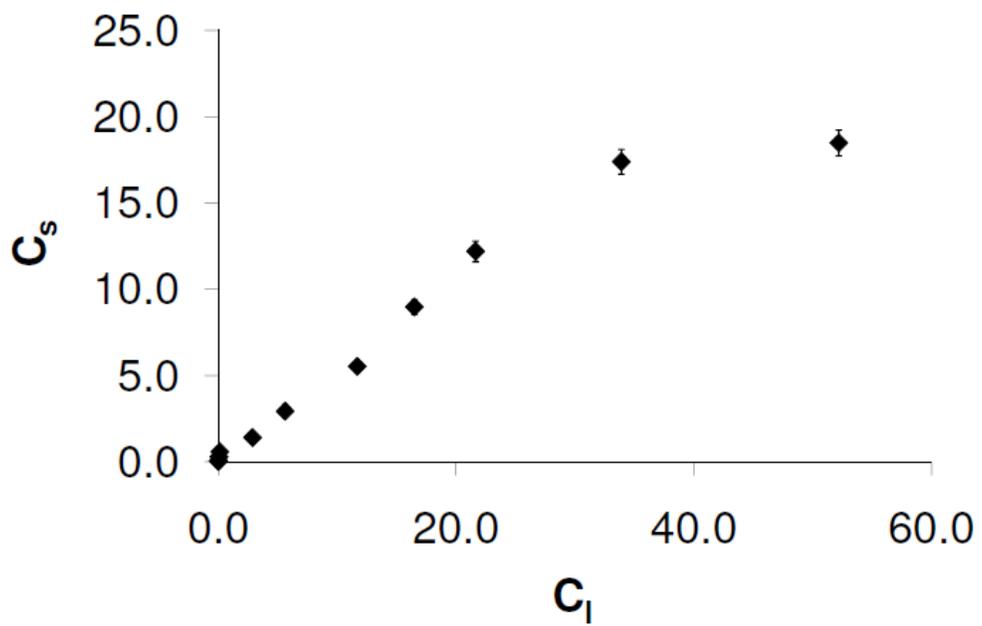


Figure 4.4 Isotherm for xylene sorption by CB.

SBP sorbent

On the other hand, the sorption behavior of SBP at 3.0 g/L, (figures 4.5 and 4.6) followed a linear relationship that can be attributed to an absorption mechanism rather than an adsorption-based one. Hence, the sorption behavior depends on the partition coefficient and not on the surface characteristic of the sorbent. If we consider TCR as a composite sorbent, the observed sorption capability can be understood as the result of a combined effect of adsorption by CB dispersoids and absorption by the SBP matrix.

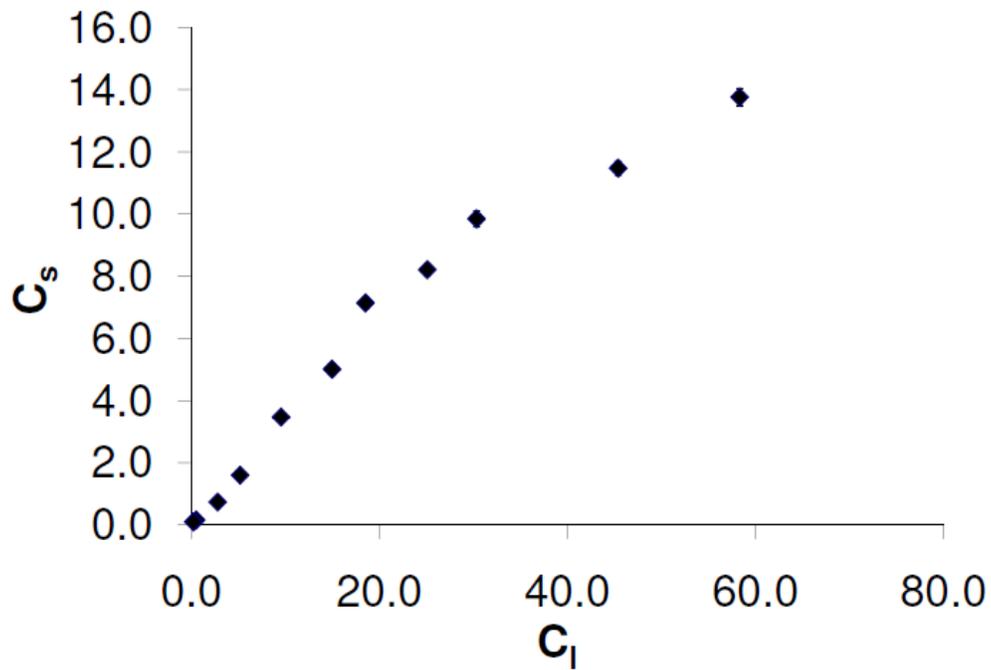


Figure 4.5 Isotherm for toluene sorption by SBP.

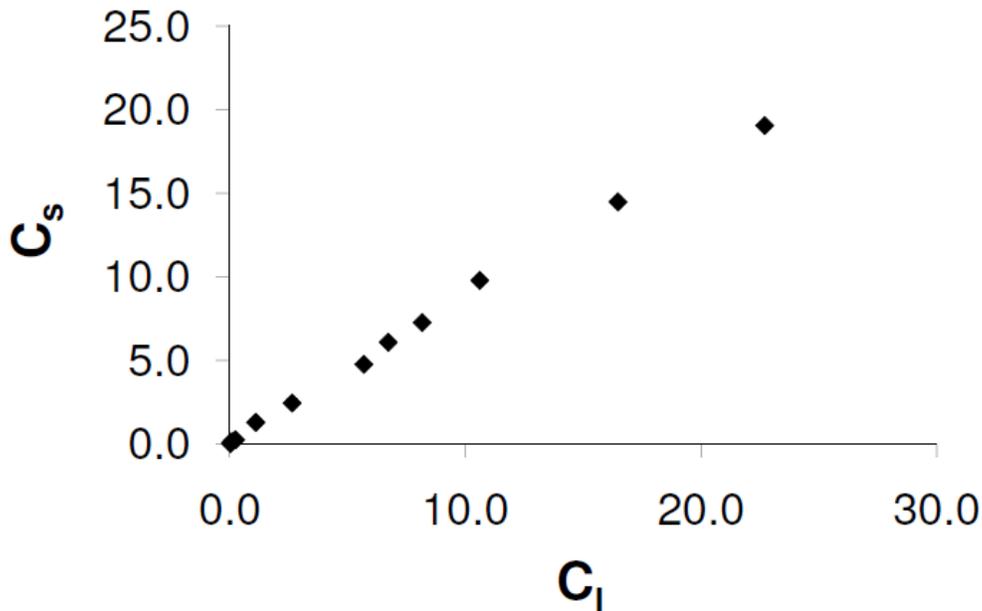


Figure 4.6 Isotherm for xylene sorption by SBP.

4.1.2 Langmuir isotherms for toluene and xylene experiments using TCR, CB and SBP

Langmuir is the simplest isotherm where it is assumed that the adsorption sites are occupied by the adsorbates from the solution forming a monolayer and that the energy of adsorption is equal at all surface sites (Stumm and Morgan 1996). Using the Langmuir equation, the data can be plotted providing a linear relation which gives some parameters that describe the sorption process. Figures 4.7 and 4.8 show the results adjusted to the Langmuir equation for toluene and xylene, respectively when using TCR.

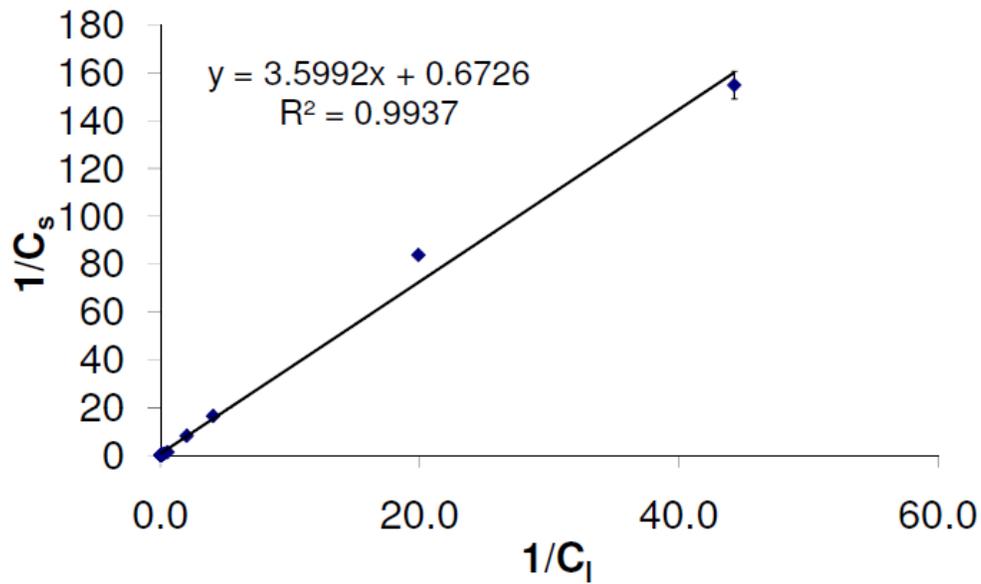


Figure 4.7 Langmuir isotherm for toluene sorption by TCR.

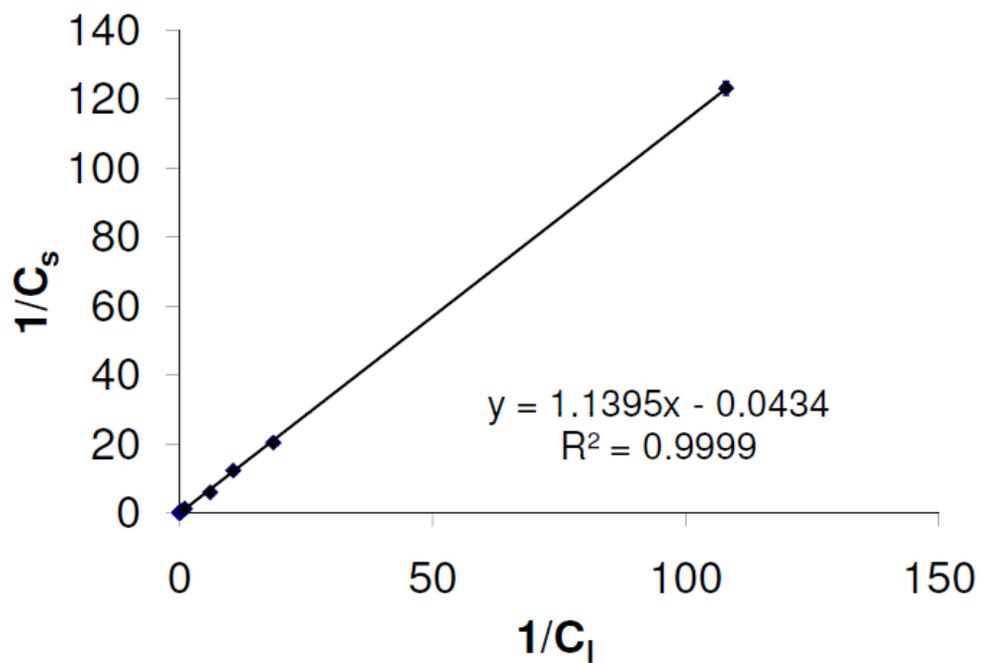


Figure 4.8 Langmuir isotherm for xylene sorption by TCR.

Figures 4.9 and 4.10 show the results adjusted to the Langmuir equation for toluene and xylene, respectively when using CB.

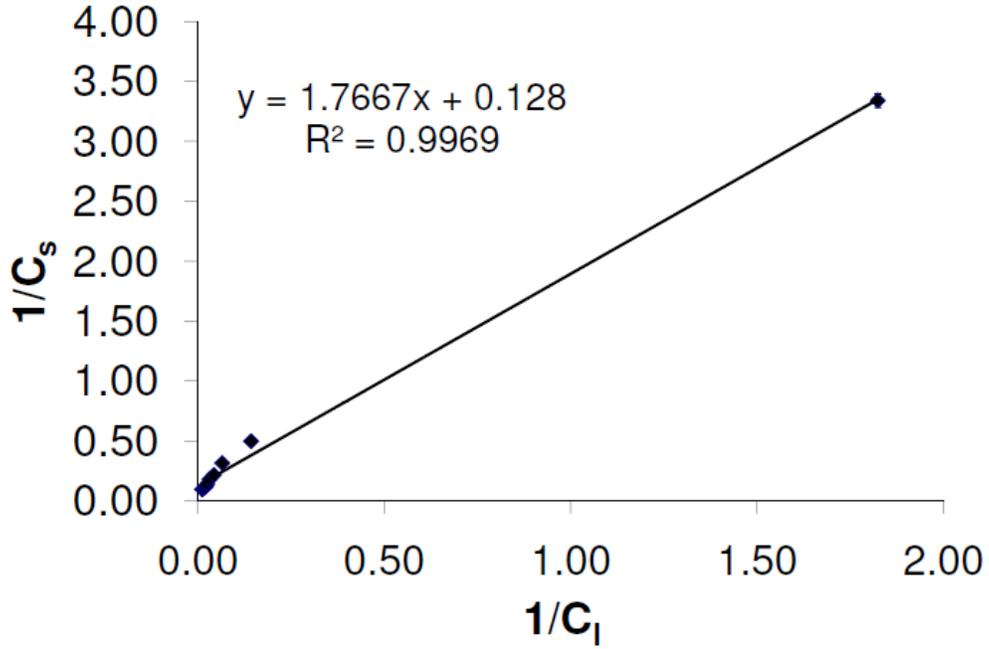


Figure 4.9 Langmuir isotherm for toluene sorption by CB.

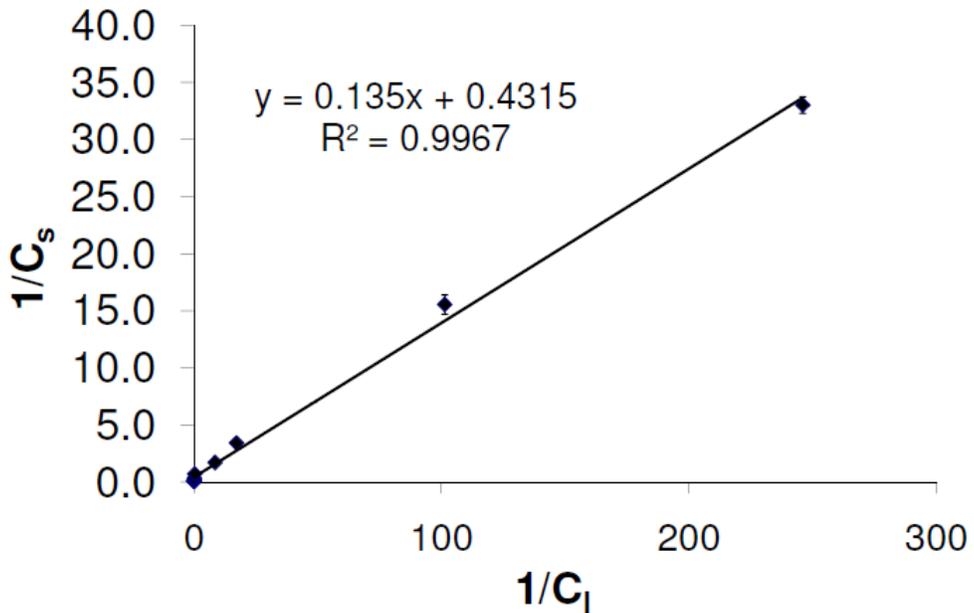


Figure 4.10 Langmuir isotherm for xylene sorption by CB.

Figures 4.11 and 4.12 show the results adjusted to the Langmuir equation for toluene and xylene, respectively when using SBP.

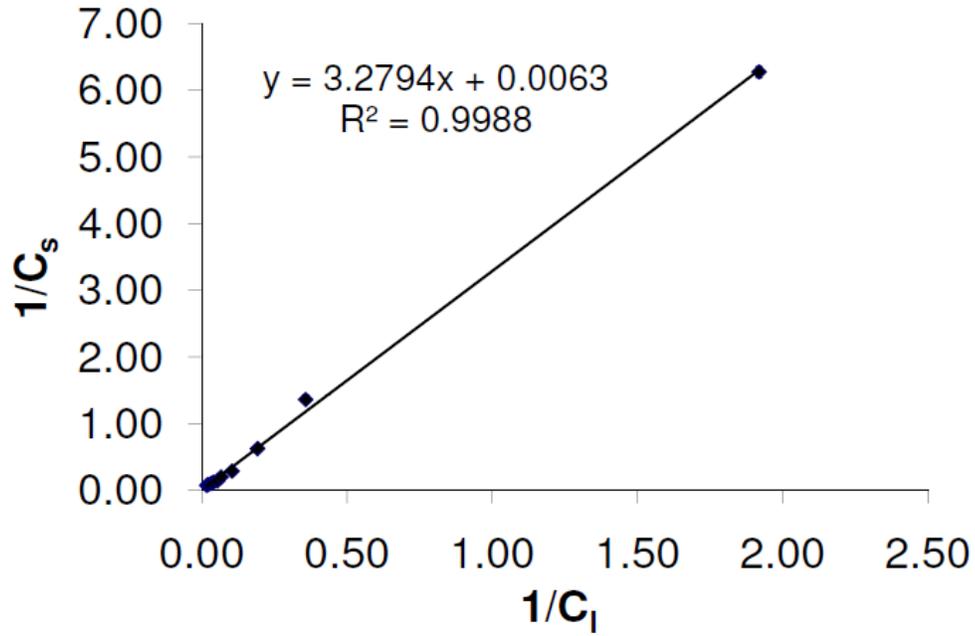


Figure 4.11 Langmuir isotherm for toluene sorption by SBP.

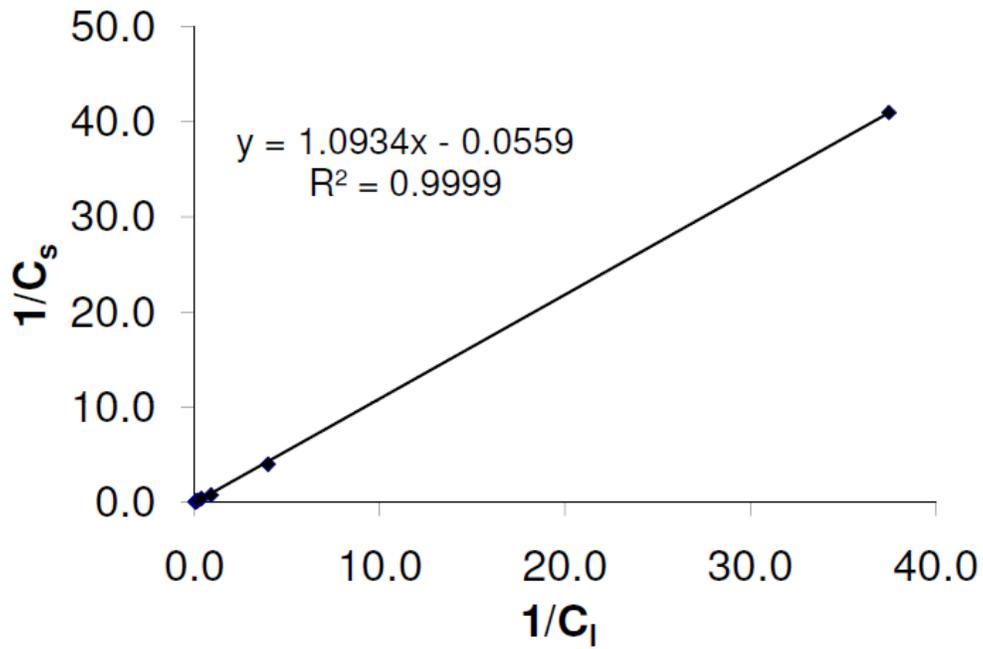


Figure 4.12 Langmuir isotherm for xylene sorption by SBP.

4.1.3 Freundlich isotherms for toluene and xylene experiments using TCR, CB and SBP

The Freundlich isotherm fits well for sorbents with heterogeneous solid surfaces. The equation uses a logarithmic relation to linearize the data and obtain parameters that describe the sorption process. Figures 4.13 and 4.14 show the results adjusted to the Freundlich equation for toluene and xylene, respectively when using TCR.

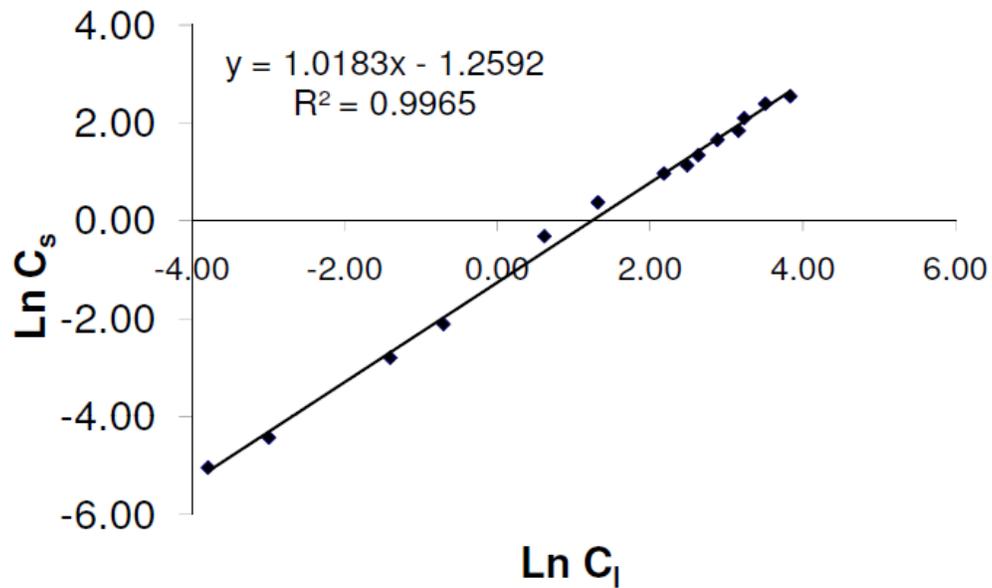


Figure 4.13 Freundlich isotherm for toluene sorption by TCR.

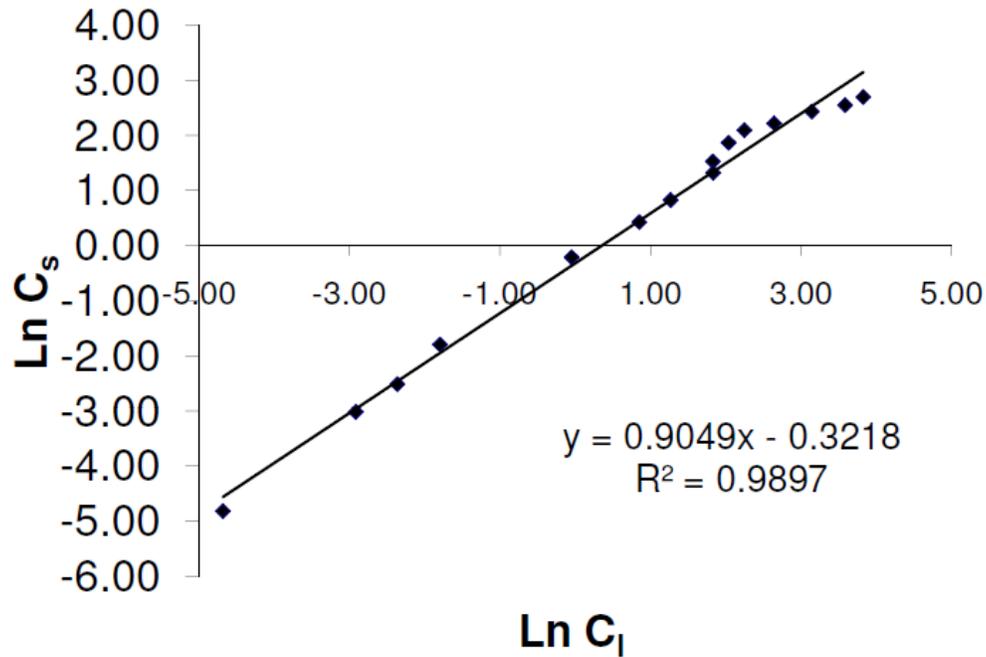


Figure 4.14 Freundlich isotherm for xylene sorption by TCR.

Figures 4.15 and 4.16 show the results adjusted to the Freundlich equation for toluene and xylene, respectively using TCR. The results were well fitted to the Freundlich relationship, which is common for carbonaceous sorbents (Lai, Quio Chu et al. 2009).

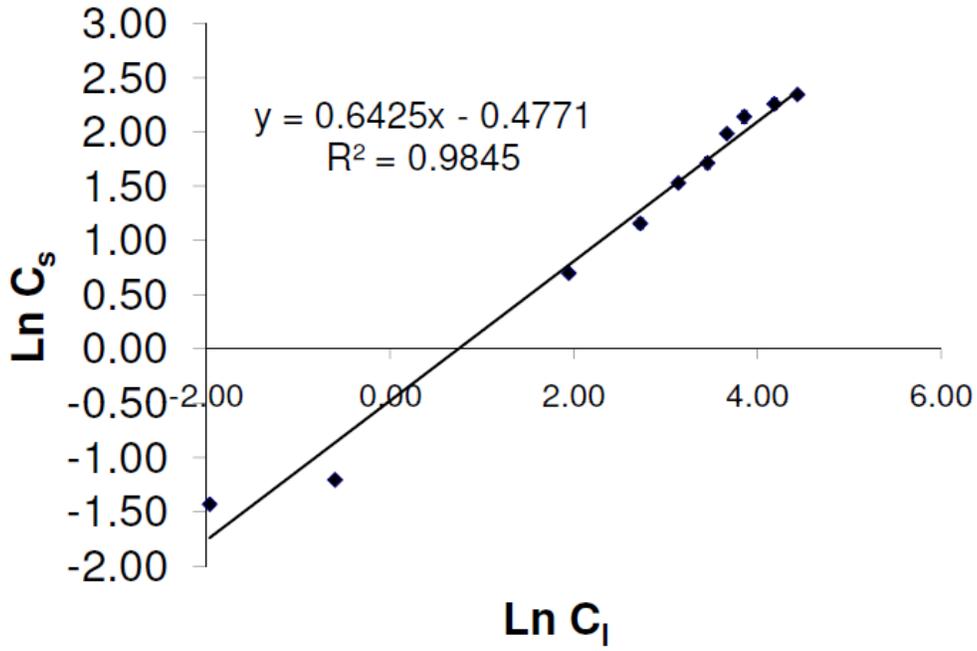


Figure 4.15 Freundlich isotherm for toluene sorption by CB.

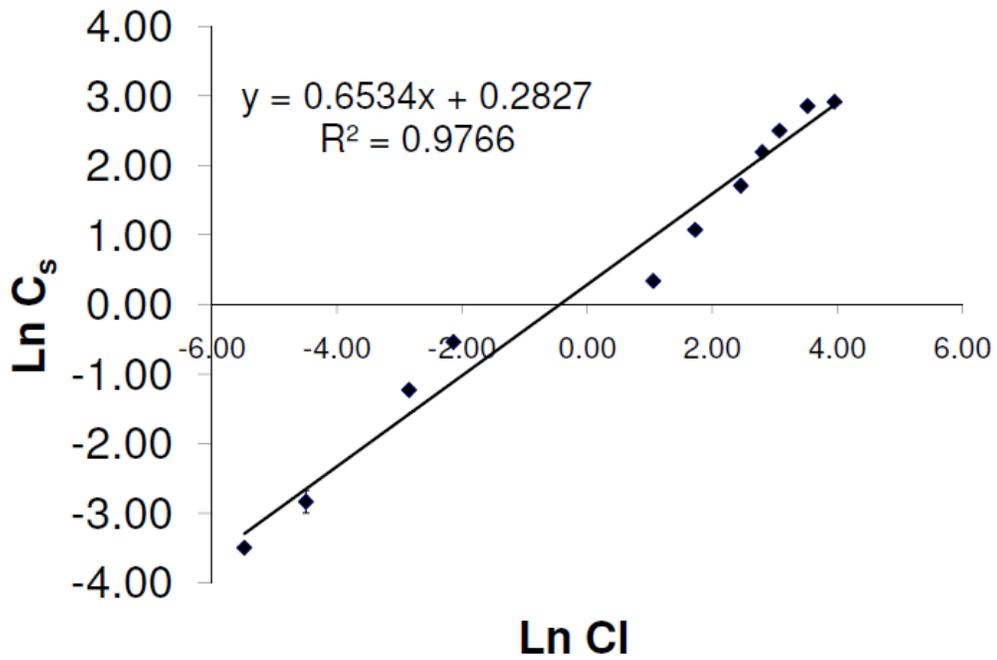


Figure 4.16 Freundlich isotherm for xylene sorption by CB.

Figures 4.17 and 4.18 show the results adjusted to the Freundlich equation for toluene and xylene, respectively when using SBP.

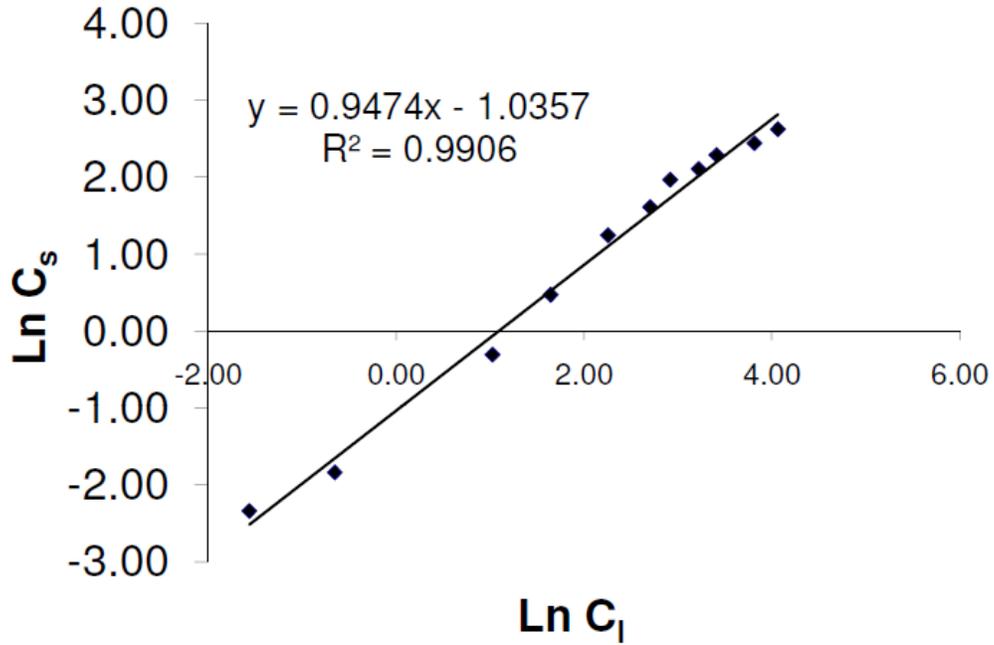


Figure 4.17 Freundlich isotherm for toluene sorption by SBP.

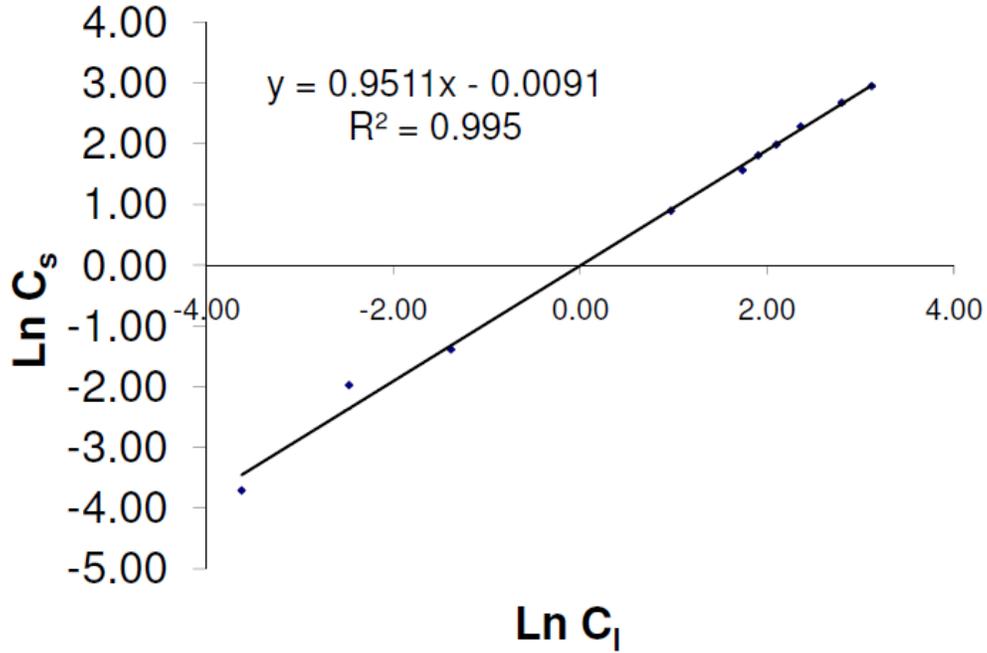


Figure 4.18 Freundlich isotherm for xylene sorption by SBP.

4.1.4 Scatchard plots for toluene and xylene experiments

TCR sorbent

Figures 4.19 and 4.20 show the results adjusted to the Scatchard equation for toluene and xylene, respectively when using TCR. The Scatchard plot for TCR can be used for a qualitative assessment of the sorption process. The Scatchard profiles clearly show negative and positive slopes, depending on the uptake capacity of TCR, which suggests a multi-interactions between the sorbent and the adsorbates due to the sorption capabilities of the main components in TCR (Harris 2003; Ayar, Gürsal et al. 2008).

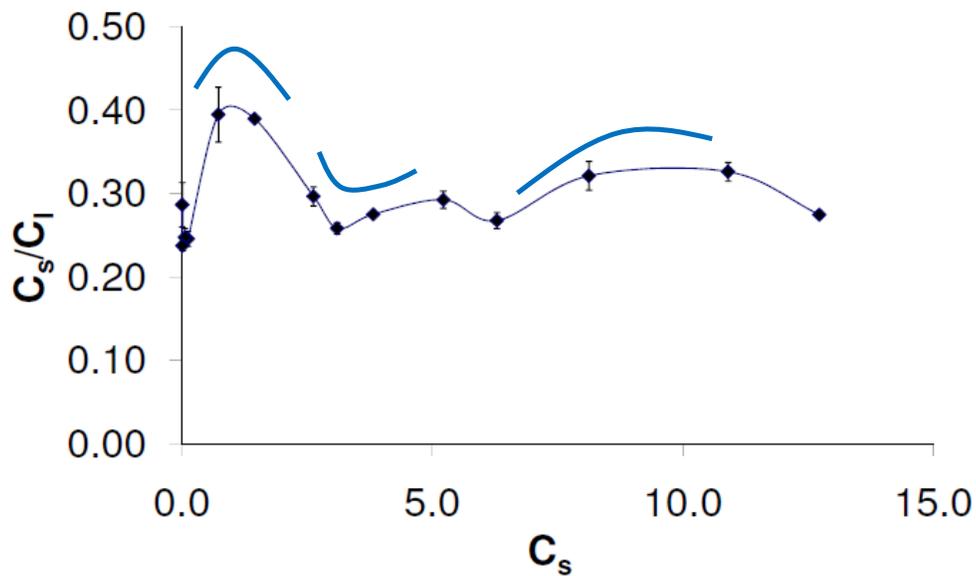


Figure 4.19 Scatchard plot for toluene sorption by TCR.

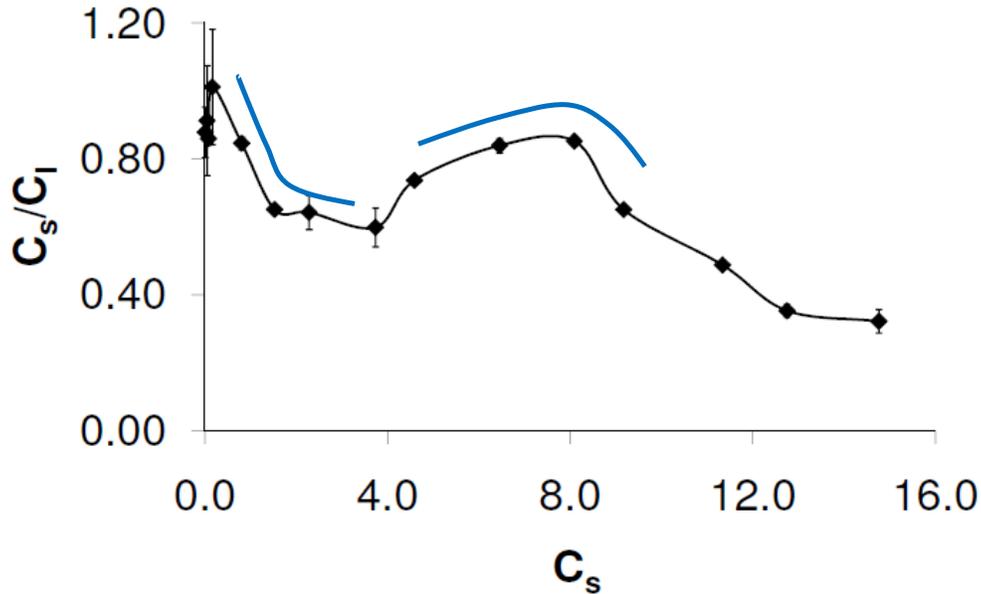


Figure 4.20 Scatchard plot for xylene sorption by TCR.

The curves formed between different slopes are also used for interpretation of the Scatchard plots. A convex curve formed between negative and positive slopes suggests a negative cooperativity among the different binding sites. A concave curve formed between positive and negative slopes suggests a positive cooperativity among the different binding sites (Ozturk, Artan et al. 2004; Gurten, Ucan et al. 2005). The Scatchard plots suggest different interactions (cooperativities) between VOCs and the components of the TCR: CB and SBP. The first molecules of the adsorbate should be adsorbed onto the TCR, principally on the surface of the CB (Figure 21b). The molecules that are absorbed in the polymeric matrix near to a CB particle could be adsorbed mainly on the surface of the CB, preventing the molecules going inside the polymeric matrix in a negative cooperativity (Figure 21c). When the surface of the CB (located on the surface of the TCR) is saturated, the molecules of the adsorbate could freely enter the polymeric matrix (Figure 21d). Also, some VOCs can be

adsorbed on the saturated CB (located on the surface) which can produce other molecules to be released rather quickly into the polymeric matrix in a positive cooperativity (Figure 21e). These interactions can occur near CB particles inside of the TCR, producing both negative and positive cooperativities. The Sactchard plots suggest that these interactions could occur during the sorption process, but no necessary in a particular order.

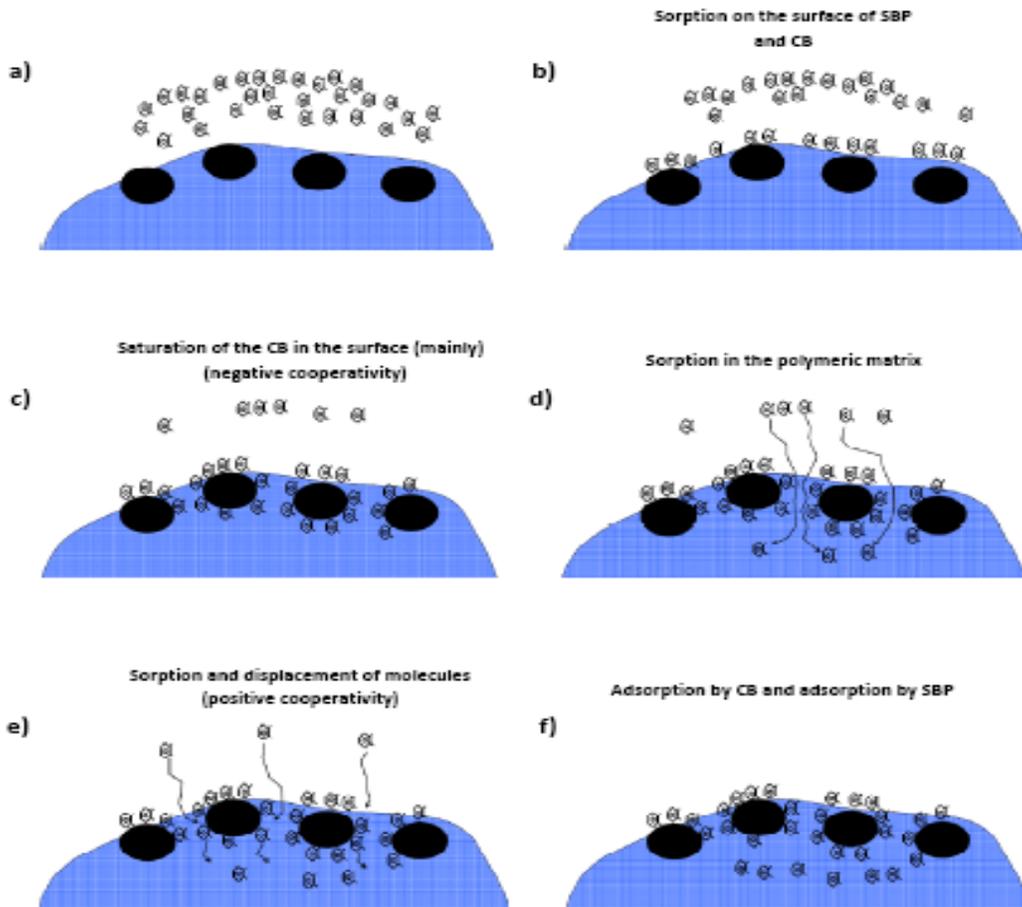


Figure 4.21 Cooperativities produced during the sorption process by TCR components

Accordingly, toluene and xylene should have been absorbed by the TCR by combining the adsorption and absorption by CB and SBP, respectively. The absorption

process by SBP is a physical process that follows the Nernst partition law or partition coefficient whereas adsorption onto the CB surface can be explained in terms of Van der Waals forces. The CB particles on the TCR surface should have adsorbed most of the adsorbates at early contact times, whereas SBP would be expected to absorb the remainder of the adsorbates through the incorporation of these molecules in the chains of the crumb rubber polymeric matrix at prolonged contact times (Alamo-Nole, Perales-Perez et al. 2010)

CB sorbent

Figures 4.22 and 4.23 show the results adjusted to the Scatchard equation for toluene and xylene, respectively when using CB. A linear Scatchard profile was obtained when CB was used as the adsorbent. The only negative slope would be evidence that the sorption process took place in a single-step (Harris 2003). Toluene and xylene are expected to be adsorbed on the CB surface through Van der Waals interactions including the London dipole-dipole interactions.

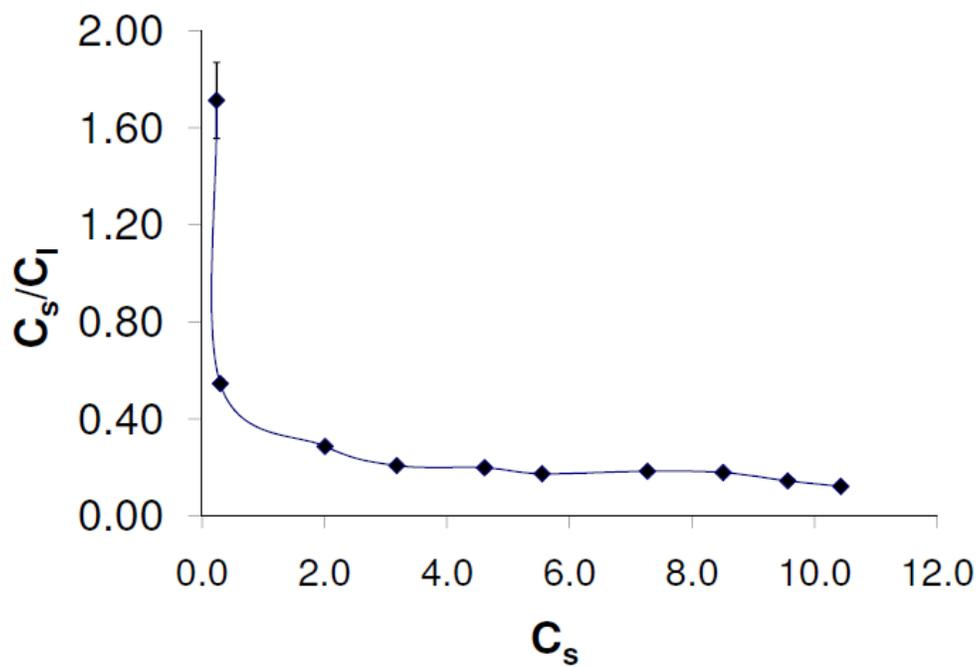


Figure 4.22 Scatchard plot for toluene sorption by CB.

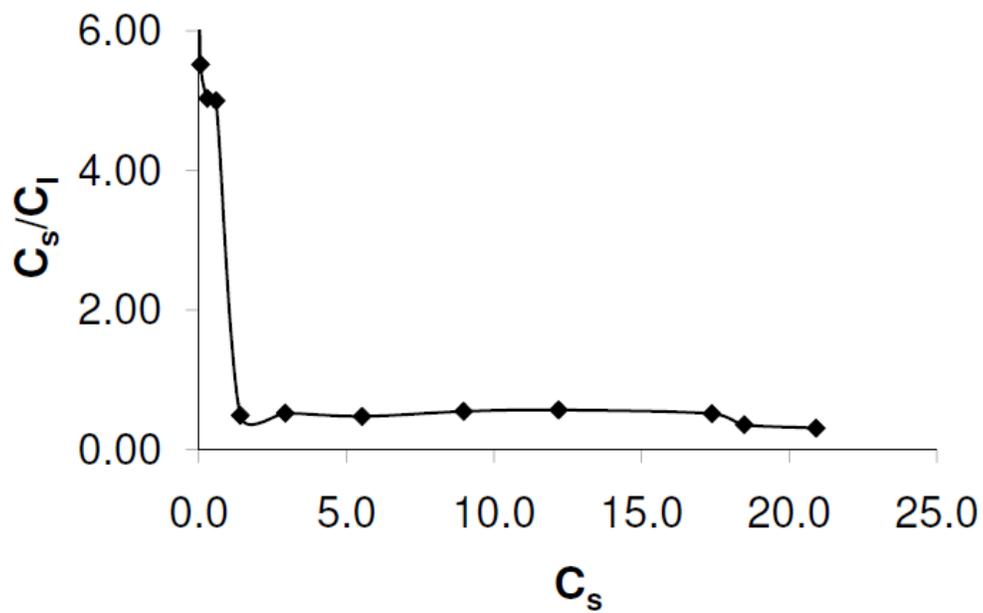


Figure 4.23 Scatchard plot for xylene sorption by CB.

SBP sorbent

Figures 4.24 and 4.25 show the results adjusted to the Scatchard equation for toluene and xylene, respectively using SBP. A linear Scatchard profile, exhibiting a negative slope was also observed for the absorption of toluene and xylene by CB (figures 4.22 and 4.23) and therefore, a one-step sorption process can also be suggested for the removal of these adsorbates by SBP in aqueous solutions.

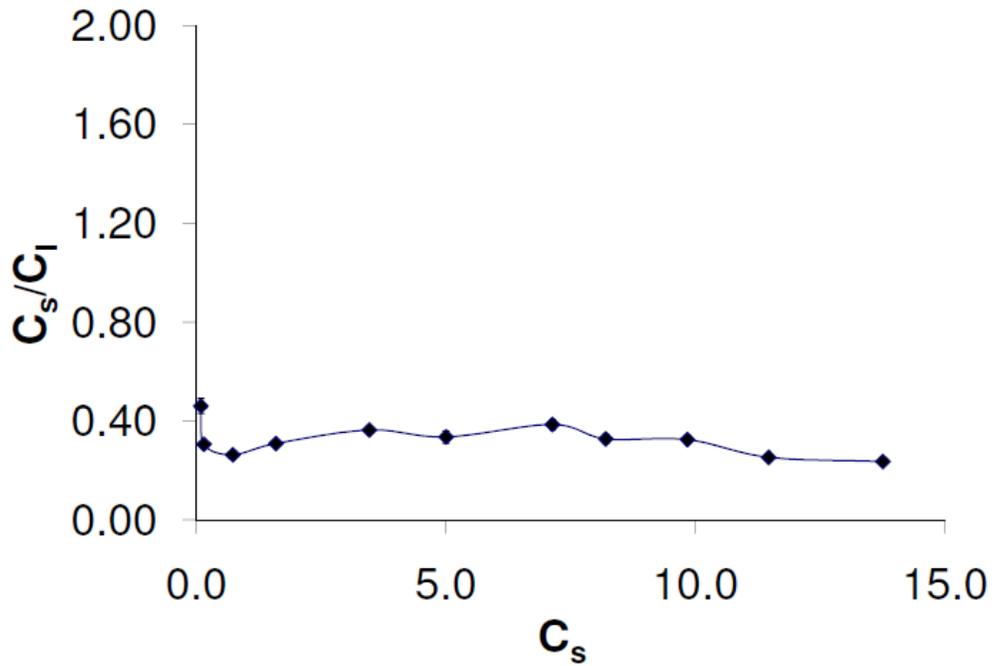


Figure 4.24 Scatchard plot for toluene sorption by SBP.

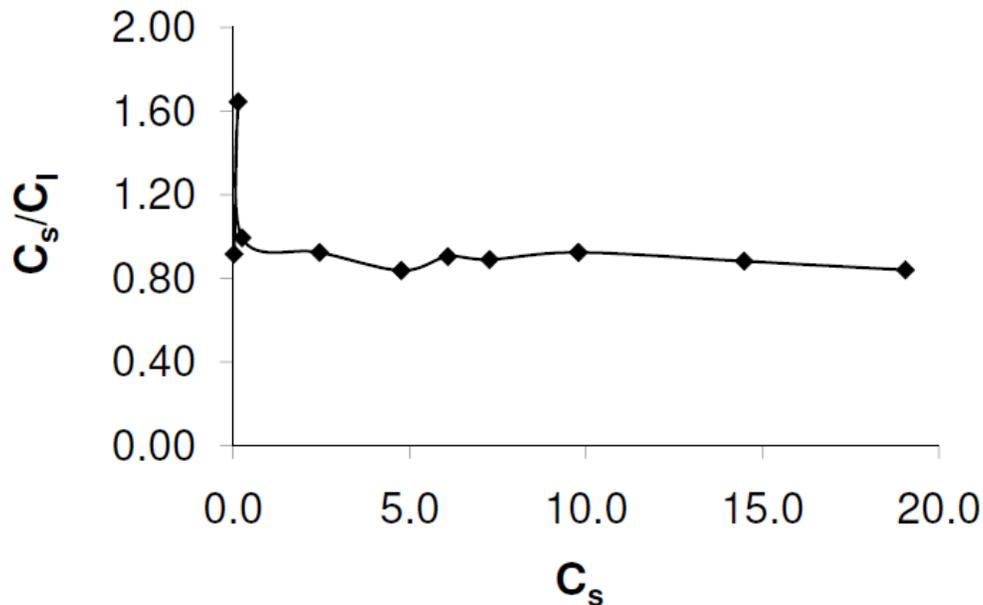


Figure 4.25 Scatchard plot for xylene sorption by SBP.

4.1.5 Isotherm parameters for toluene and xylene experiments using TCR, CB and SBP

Tables 4.2 and 4.3 show the Freundlich's parameters and the P values (probability of the model) for toluene and xylene sorption by TCR, CB and SBP. In all cases, the P values obtained for Freundlich isotherms were the lowest when compared to Langmuir and linear isotherms. The 'n' value in Freundlich's relationship is related to the sorption behavior, and a value close to one would indicate that the sorption process is independent of the adsorbate concentration; whereas a lower value would suggest the promotion of the adsorbate removal at high starting concentrations. In turn, K_f (mg adsorbate/g sorbent) is related to the loading factor of the sorbent, i.e. a large K_f represents a high uptake capacity.

TABLE 4.2 Isotherms parameters for the removal of toluene using TCR, CB and SBP

		Crumb Rubber	Carbon Black	Polymer
Linear	r^2	0.982 ± 0.004	0.94 ± 0.01	0.95 ± 0.01
	K	245 ± 4	128 ± 3	245 ± 5
	P	86 ± 34	51 ± 2	109 ± 10
Langmuir	r^2	0.992 ± 0.008	0.80 ± 0.04	0.967 ± 0.009
	B	0.0002 ± 0.00002	0.00060 ± 0.00009	0.00010 ± 0.00002
	X _m	$2 \pm 2 \times 10^3$	$2.8 \pm 0.2 \times 10^3$	$4.6 \pm 0.7 \times 10^3$
	P	255 ± 196	80 ± 8	77 ± 11
Freundlich	r^2	0.9955 ± 0.0005	0.984 ± 0.004	0.9903 ± 0.0006
	N	1.018 ± 0.003	0.642 ± 0.004	0.95 ± 0.01
	K _f (μg/g)	239 ± 4	621 ± 14	355 ± 3
	P	19 ± 1	6 ± 1	10.6 ± 0.5

m : slope
i : intercept
 r^2 : R square
n : Freundlich constant

K_f : Freundlich constant
b : Langmuir constant
X_m : Maximum amount adsorbed
P : Probability of the model

The ‘n’ values for the sorption of toluene and xylene when using TCR were 1.018 ± 0.003 and 0.90 ± 0.01 , respectively. The small differences in the ‘n’ values suggest similar sorption behaviour for these two adsorbates when contacted with TCR in aqueous solutions. On the other hand, the ‘n’ value for the sorption of toluene and xylene using CB were 0.642 ± 0.004 and 0.65 ± 0.01 respectively. These values are typical for carbonaceous sorbents (Lai, Quio Chu et al. 2009). In turn, the ‘n’ values for the sorption of toluene and xylene by SBP were close to unity (0.95 ± 0.01 and 0.951 ± 0.003 , respectively). These higher ‘n’ values suggest that the sorption process is independent of adsorbate concentration and only dependent on the partition coefficient.

TABLE 4.3 Isotherms parameters for the removal of xylene using TCR, CB and SBP

		Crumb Rubber	Carbon Black	Polymer
Linear	r^2	0.87 ± 0.03	0.91 ± 0.02	0.99 ± 0.01
	K	334 ± 24	334 ± 2	848 ± 4
	P	1634 ± 252	658 ± 61	73 ± 27
Langmuir	r^2	0.9996 ± 0.0003	0.95 ± 0.07	0.9999 ± 0.0001
	b	0.00006 ± 0.00008	0.002 ± 0.001	0.00005 ± 0.00003
	X_m	$4 \pm 3 \times 10^4$	$4 \pm 2 \times 10^3$	$2 \pm 1 \times 10^4$
	P	20 ± 7	161 ± 88	27 ± 14
Freundlich	r^2	0.989 ± 0.002	0.977 ± 0.003	0.9948 ± 0.0001
	n	0.90 ± 0.01	0.65 ± 0.01	0.951 ± 0.003
	K_f ($\mu\text{g/g}$)	723 ± 14	1327 ± 40	991 ± 2
	P	13 ± 1	34 ± 6	3.1 ± 0.6

m : slope
 i : intercept
 r^2 : R square
 n : Freundlich constant
 K_f : Freundlich constant
 b : Langmuir constant
 X_m : Maximum amount adsorbed
 P : Probability of the model

The K_f (uptake capacity) estimated results for toluene when using TCR, CB and SBP as sorbents were $239 \pm 4 \mu\text{g/g}$, $621 \pm 14 \mu\text{g/g}$ and $355 \pm 3 \mu\text{g/g}$ of sorbent, respectively. The corresponding uptake capacities for xylene were $723 \pm 14 \mu\text{g/g}$, $1,327 \pm 40 \mu\text{g/g}$ and $991 \pm 2 \mu\text{g/g}$. These uptake capacities for TCR are in agreement with previously reported values (Kim, Park et al. 1997; Guanasekara, Donovan et al. 2000). The uptake capacity for xylene was higher than toluene. Hydrophobic expulsion is a driving force of the adsorption process for such hydrophobic adsorbates as xylene and toluene. This force tends to reduce the contact of these adsorbates with water, thus the adsorbates are accumulated at the sorbent surface and become adsorbed (or absorbed) on organic sorbents such as TCR, CB and SBP (Stumm and

Morgan 1996). Xylene is the less soluble compound, thus it has the highest hydrophobicity and the highest uptake capacity.

The uptake capacity obtained for CB is significantly higher than that observed for TCR and SBP. This result was expected due to its similarities with activated charcoal. The larger uptake capacity of pure carbon black can also be explained in terms of the total accessibility of individual CB nanoparticles to the adsorbates solution; CB nanoparticles in the TCR are confined in the polymeric matrix and only a fraction of them would be accessible to the adsorbates. Organic molecules have the ability to migrate between polymeric chains in an absorption process (Iwai, Ishidao et al. 1991; Soney, Sabu et al. 1996; Ranimol, Kuruvilla et al. 2007), however the polymerization of the matrix during the vulcanization process could modify the sorption sites of the SBP.

4.1.6 Effect of TCR concentration for VOCs sorption experiments

4.1.6.1 Sorption of ethylbenzene, toluene and xylene in single-component experiments

The removal of ethylbenzene, toluene and xylene at pH 6.0 was a highly efficient and rapid process resulting in the sorption most of the pollutants (above 90%) during the first 30 minutes of contact time. Xylene was almost completely removed when 10 g/L of crumb rubber was used (which is the common adsorbent concentration). This high affinity of crumb rubber for xylene was followed by ethylbenzene and, lastly, toluene.

As shown in table 1.1, toluene has the highest solubility in water (515 mg/L), thus, the partition between the crumb rubber and water is expected to be significantly different from that observed for xylene and ethylbenzene with solubilities of 200 mg/L and 152 mg/L respectively. Xylene and ethylbenzene are more hydrophobic and as expected are more readily absorbed into the crumb rubber matrix (Alamo-Nole 2006).

Table 4.4 shows the terminal concentrations and percentage of removal for single-component sorption of ethylbenzene, toluene and xylene at pH 6.0. As stated before, xylene was removed almost completely when 10 g/L of crumb rubber was used in aqueous solutions. On the other hand, more than 40% of xylene and ethylbenzene were removed for 0.5 g/L of crumb rubber in aqueous solutions. The percent removal decreased to 17 and 18% for ethylbenzene and xylene respectively when using crumb rubber concentration as low as 0.1 g/L. This is 100 times less crumb rubber than at 10 g/L (Alamo-Nole 2006).

The chemical composition and structure of TCR is the key for its sorbent capability. Isoprene and butadiene are hydrocarbon chains present in TCR that can interact with the hydrophobic organic pollutants and non polar solvents. In turn, the presence of methyl groups in adjacent carbons in the ring structure of o-xylene can contribute to its increase sorption due to a strong chemical affinity with the hydrocarbon groups in the rubber matrix. This favorable chemical affinity between the methyl groups and the hydrocarbon groups in rubber can explain the very rapid and efficient removal of xylene by TCR. The second group in terms of affinity is the ethyl group, which is longer than the methyl group. This could be the reason why ethylbenzene, host of ethyl groups, is better removed by crumb rubber than toluene. The length of the ethyl group can be related to the comparatively higher adsorption of

ethylbenzene than toluene. Styrene is also a constituent of tire rubber and its aromatic ring will enable interaction with all three organic solvents under study (Alamo-Nole 2006).

TABLE 4.4 Final (terminal) concentrations and % of removal for single-component sorption of ethylbenzene, toluene and xylene at different concentrations of TCR (Alamo-Nole 2006).

Crumb Rubber conc.	Ethylbenzene		Toluene		Xylene	
	Final concentration (mg/L)	Removal (%)	Final concentration (mg/L)	Removal (%)	Final concentration (mg/L)	Removal (%)
10 g/L	1.4 ± 0.3	96	7.8 ± 0.6	75	ND	~ 100
5.0 g/L	4.0 ± 0.3	87	12.0 ± 0.9	61.2	2.8 ± 0.2	91
1.0 g/L	12.4 ± 0.4	59	20.2 ± 0.8	30.5	10.5 ± 0.4	66.0
0.5 g/L	16 ± 1	44	23.8 ± 0.8	17.2	18.7 ± 0.9	44.0
0.1 g/L	24.6 ± 0.3	17	27.2 ± 0.5	5.12	25.2 ± 0.9	18.3

ND: below the GC-MS quantification level.
Initial concentration of 30 mg/L

The participation of carbon black in the sorption process cannot be ruled out. Carbon black nanoparticles (10-50 nm in diameter used in most formulations of rubber tires) exhibit quite a large superficial area and have a well known adsorption capability, which are common properties of carbonaceous solids. Carbon black, a product of incomplete combustion of carbonaceous materials, exhibits little or negligible presence of macro, meso or micro pores when compared with GAC (Alamo-Nole 2006).

In a sorption process, linearization of results following adequate models describes the process involved. Freundlich parameters will be discussed because the experimental data fits this model very well (Table 4.5).

TABLE 4.5 Parameters of linear, Freundlich and Langmuir isotherm for single-component sorption of ethylbenzene, toluene and xylene at pH 6.0 (Alamo-Nole 2006).

ISOTHERMS								
	Linear		Freundlich			Langmuir		
	m	r ²	n	K _f (ug/g)	r ²	b	X _m	r ²
Ethylbenzene	1.9 x 10 ³	0.969	0.97	1.8 x 10 ³	0.970	4.9 x 10 ⁻²	4.4 x 10 ⁴	0.952
Toluene	0.6 x 10 ³	0.924	1.27	0.17 x 10 ³	0.992	1.4 x 10 ⁻²	1.0 x 10 ⁴	0.999
Xylene	2.0 x 10 ³	0.943	0.99	1.9 x 10 ³	0.978	4.4 x 10 ⁻²	4.5 x 10 ⁴	0.997

m : slope
i : intercept
r² : R square
n : Freundlich constant

K_f : Freundlich constant
b : Langmuir constant
X_m : Maximum amount adsorbed

Freundlich is the most commonly used isotherm when using solvents in aqueous solutions. The ‘n’ values for ethylbenzene, toluene and xylene were 0.97, 1.27 and 0.99 respectively. The ‘n’ values for ethylbenzene and xylene suggest that the removals are the same at different concentrations of these adsorbates. However, the removal of toluene increases with higher concentrations of the adsorbate. The ‘n’ value of ethylbenzene changed from 1.018 ± 0.003 (table 4.2) to 0.97 ± 0.02 and the ‘n’ value of xylene changed from 0.90 ± 0.01 (table 4.3) to 0.99 ± 0.04. These small changes suggest that there is no effect in the sorption pattern with the change of TCR. The uptake capacities for ethylbenzene, toluene and xylene were 1.8 x 10³, 0.17 x 10³ and 1.9 x 10³ respectively. The uptake capacity for toluene

increased from 0.239×10^3 to 1.8×10^3 , and the uptake capacity of xylene increased from 0.73×10^3 to 1.9×10^3 . These increments are the effect of changing the TCR concentration. When the TCR concentrations are decreased, all the sorption sites should be occupied by the adsorbates, giving high uptake capacities.

4.1.6.2 Sorption of ethylbenzene, toluene and xylene in multi-component experiments

Table 4.6 shows the final concentrations and percent of removal of ethylbenzene, toluene and xylene when used in a multi-component mixture. The removal pattern was the similar for the other experiments. Xylene has the highest percent removal followed by ethylbenzene and finally toluene.

TABLE 4.6 Final (terminal) concentrations and % of removal for multi-component sorption of ethylbenzene, toluene and xylene at different concentrations of TCR.

Crumb Rubber	Ethylbenzene		Toluene		Xylene	
	Final concentration (mg/L)	Removal (%)	Final concentration (mg/L)	Removal (%)	Final concentration (mg/L)	Removal (%)
5.0 g/L	2.05 ± 0.07	78.7	3.74 ± 0.09	60.4	1.81 ± 0.08	81.3
3.3g/L	3.0 ± 0.2	69.2	4.44 ± 0.06	52.9	2.8 ± 0.2	70.9
2.0 g/L	3.5 ± 0.1	64.2	5.3 ± 0.3	44.0	3.3 ± 0.2	65.6
1.0 g/L	5.7 ± 0.3	40.9	7.0 ± 0.2	25.7	5.4 ± 0.3	44.5
0.5 g/L	6.6 ± 0.2	31.2	-	-	6.6 ± 0.2	31.6
0.33 g/L	7.51 ± 0.07	21.6	8.55 ± 0.06	9.3	7.5 ± 0.1	22.3

ND: below the GC-MS quantification level.

Init. Conc.: 10 mg/L each compound

- data not available

Table 4.7 shows the parameters for linear, Langmuir and Freundlich isotherms. The results fit the Freundlich isotherm quite well. The ‘n’ values for ethylbenzene, toluene and xylene (1.1, 0.98 and 1.03, respectively) for multi-component systems were similar to those of the single-component experiments (0.97, 1.27 and 0.99, respectively – table 4.5). These small differences suggest that there is no effect in the sorption pattern when the adsorbates are mixed in multi-component system and the TCR concentration is changed.

TABLE 4.7 Parameters of linear, Freundlich and Langmuir isotherm for multi-component sorption for ethylbenzene, toluene and xylene at pH 6.0.

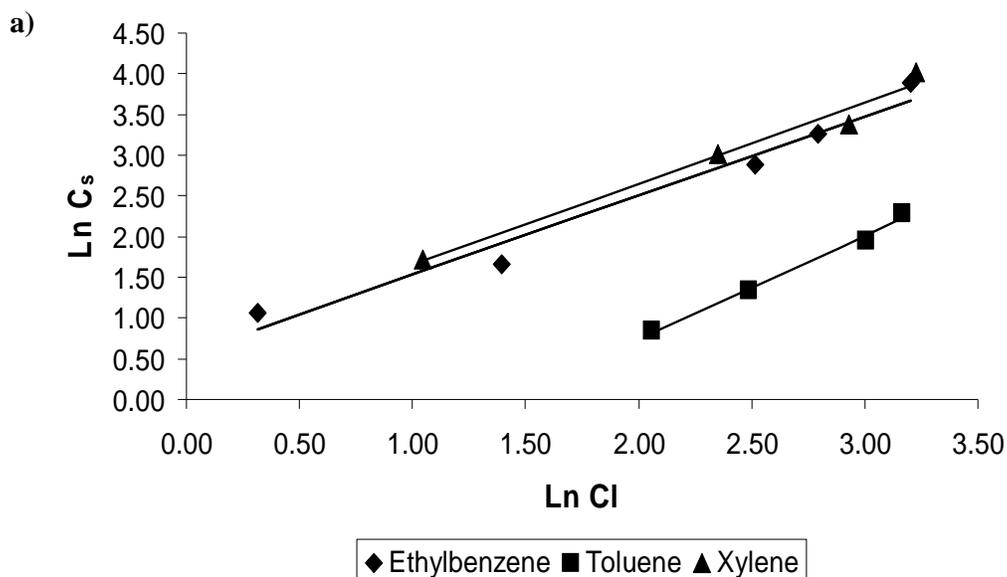
ISOTHERMS								
	Linear		Freundlich			Langmuir		
	m	r ²	n	K _f (ug/g)	r ²	b	X _m	r ²
Ethylbenzene	0.90 x 10 ³	0.951	1.1	0.67 x 10 ³	0.960	1.9 x 10 ⁻²	3.9 x 10 ⁴	0.960
Toluene	0.30 x 10 ³	0.872	0.98	0.35 x 10 ³	0.884	1.0 x 10 ⁻²	8.6 x 10 ⁴	0.899
Xylene	0.89 x 10 ³	0.970	1.03	0.81 x 10 ³	0.969	0.3 x 10 ⁻²	5.2 x 10 ⁴	0.963

m : slope
 i : intercept
 r² : R square
 n : Freundlich constant

K_f : Freundlich constant
 b : Langmuir constant
 X_m : Maximum amount adsorbed

In contrast, there are differences in the sorption capacities. The sorption capacity of ethylbenzene, toluene and xylene changed from 1.8 x10³, 0.17 x10³ and 1.9 x10³ µg/g to 0.67 x10³, 0.35 x10³ and 0.81 x10³ µg/g, respectively. These results can be explained by taking their hydrophobicity in consideration. As we discussed earlier, the compounds with high hydrophobicity or low solubility should have more affinity to the TCR than those with low hydrophobicity. Toluene has the lowest capacity removal because it has the lowest hydrophobicity and the highest solubility; however when toluene is mixed with ethylbenzene and toluene, their interactions change the hydrophobicity of the mixture. In this case, the

resulting mixture should help the removal of the compound with low hydrophobicity (toluene) but should decrease the removal of the compound with high hydrophobicity (ethylbenzene and xylene). This effect can be observed in the Freundlich isotherm plots (Figure 4.26). The isotherm for multi-component experiments (Fig 4.26b) shows a higher slope than the isotherm for single-component experiment (Fig. 4.26a), which means it possesses a higher sorption capacity.



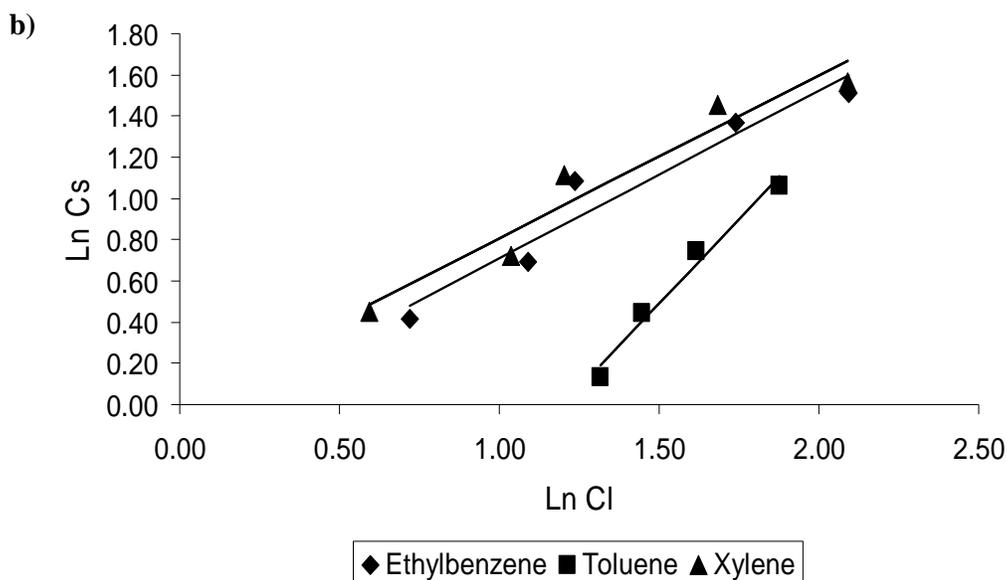


Figure 4.26 Freundlich isotherm for a) single-component and b) multi-component Linear sorption by TCR.

4.2 PAHs sorption experiments

Table 4.8 shows the average and standard deviations for the removal of acenaphthene and phenanthrene using 5 g/L of TCR, 1.5 g/L of CB and 3.0 g/L of SBP. The initial concentrations were 3.0 mg/L for acenaphthene and 1.0 mg/L of phenanthrene; these concentrations were chosen due the low solubility of these compounds. For this reason, there is no data available for phenanthrene between 1.0 and 3.0 mg/L. It was also necessary to use more concentrations for phenanthrene between 0.03 and 1.0 mg/L, so there is some data missing for acenaphthene in this range of concentrations.

The removal of both compounds was high (above 90%) at all concentrations for all sorbents. CB was the sorbent with the highest removal capacity experiencing 99.8% and 99.9% removal of acenaphthene and phenanthrene, respectively, when starting at solution

concentrations of 1.0 mg/L of each organic and contacted with 1.5 g/L of CB. On the other hand, 95.0% of acenaphthene and 97.2% of phenanthrene were removed when using 3.0 g/L of SBP.

TABLE 4.8 Removal (%) of acenaphthene and phenanthrene using 5.0 g/L TCR, 1.5 g/L CB and 3.0 g/L SBP

Init. Conc	Acenaphthene			Phenanthrene		
	TCR	CB	SBP	TCR	CB	SBP
3.0	92.5 ± 0.1	99.408 ± 0.09	96.1 ± 0.2	-	-	-
2.5	94.9 ± 0.4	99.558 ± 0.003	96.7 ± 0.2	-	-	-
2.2	96.3 ± 0.3	99.631 ± 0.003	96.0 ± 0.1	-	-	-
2.0	97.7 ± 0.1	-	95.4 ± 0.4	-	-	-
1.5	97.8 ± 0.2	99.730 ± 0.003	95.1 ± 0.2	-	-	-
1.0	97.6 ± 0.4	99.809 ± 0.002	95.0 ± 0.2	99.30 ± 0.05	99.949 ± 0.004	97.2 ± 0.1
0.90	-	-	94.8 ± 0.3	-	99.959 ± 0.003	-
0.80	-	-	95.0 ± 0.3	99.35 ± 0.01	99.959 ± 0.003	97.4 ± 0.1
0.70	-	-	94.8 ± 0.1	-	99.962 ± 0.001	-
0.50	97.5 ± 0.1	99.824 ± 0.006	-	99.45 ± 0.03	99.966 ± 0.006	97.5 ± 0.8
0.30	-	-	-	99.42 ± 0.04	~ 100	98.3 ± 0.3
0.10	97.9 ± 0.1	99.932 ± 0.007	-	98.78 ± 0.04	~ 100	97.8 ± 0.3
0.08	97.8 ± 0.1	99.934 ± 0.005	-	98.6 ± 0.1	~ 100	98.0 ± 0.1
0.05	97.9 ± 0.1	~ 100	-	98.1 ± 0.1	~ 100	97.7 ± 0.2
0.03	98.1 ± 0.2	~ 100	-	97.84 ± 0.02	~ 100	98.0 ± 0.1

- data not available

The removal of acenaphthene and phenanthrene using TCR was a rapid process. More than 85% of both compounds were removed in the first hour of contact. Under equilibrium conditions, 97.6% of acenaphthene and 99.3% of phenanthrene were removed from 1.0 mg/L starting solutions. The concentration of TCR was 5.0 g/L in both cases. No desorption of any adsorbate was observed after 5 hours of contact time.

4.2.1 Isotherms for acenaphthene and phenanthrene experiments

TCR sorbent

The data was fitted to linear, Freundlich and Langmuir type isotherms. The figures 4.27 and 4.28 show the isotherms for acenaphthene and phenanthrene respectively using TCR. The profile suggests a sorption process where the sorbent is saturated with time, i.e. the first adsorbate molecules are adsorbed quickly onto available sorption sites of the sorbent surface (exposed CB particles and SBP surface). The sorption rate slows as the sorption sites are occupied.

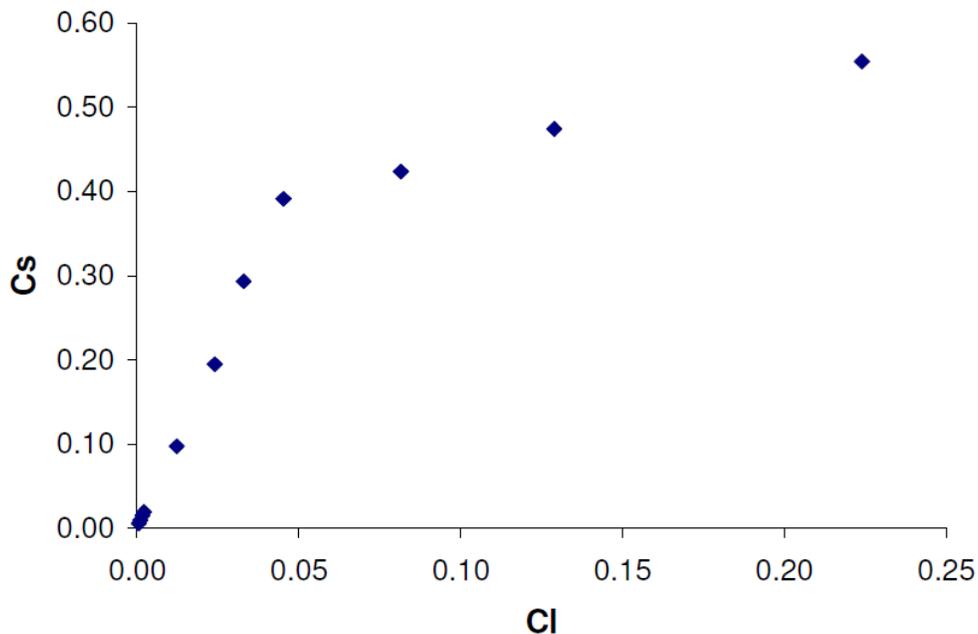


Figure 4.27 Isotherm for acenaphthene sorption by TCR.

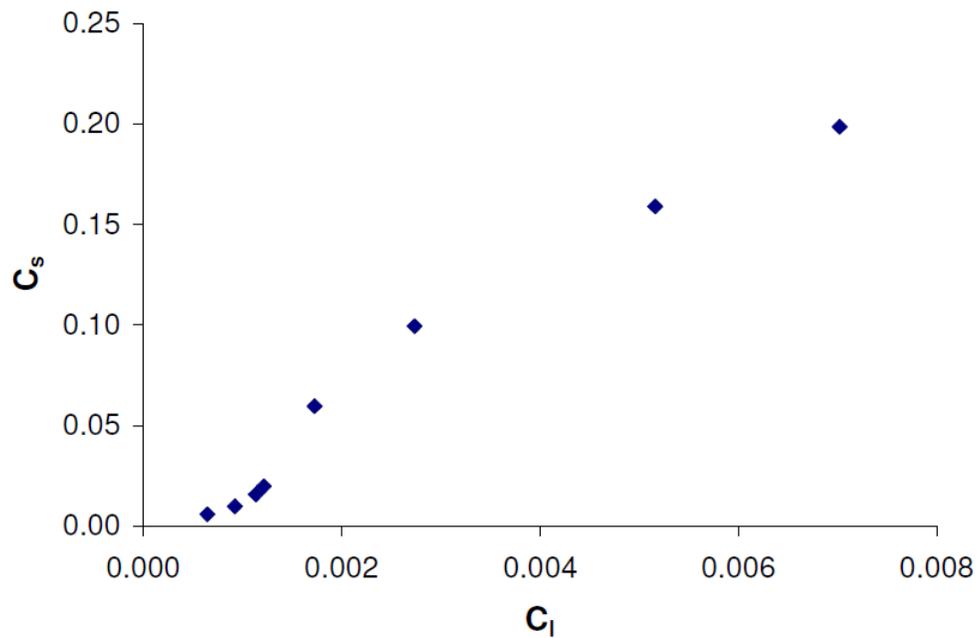


Figure 4.28 Isotherm for phenanthrene sorption by TCR.

CB sorbent

Figures 4.29 and 4.30 show the isotherms for acenaphthene and phenanthrene respectively using CB. The non-linear pattern for CB follow a trend that is typical for adsorption processes onto amorphous and carbonaceous sorbents (Carratala-Abril, Lillo-Rodenas et al. 2009; Lai, Quio Chu et al. 2009).

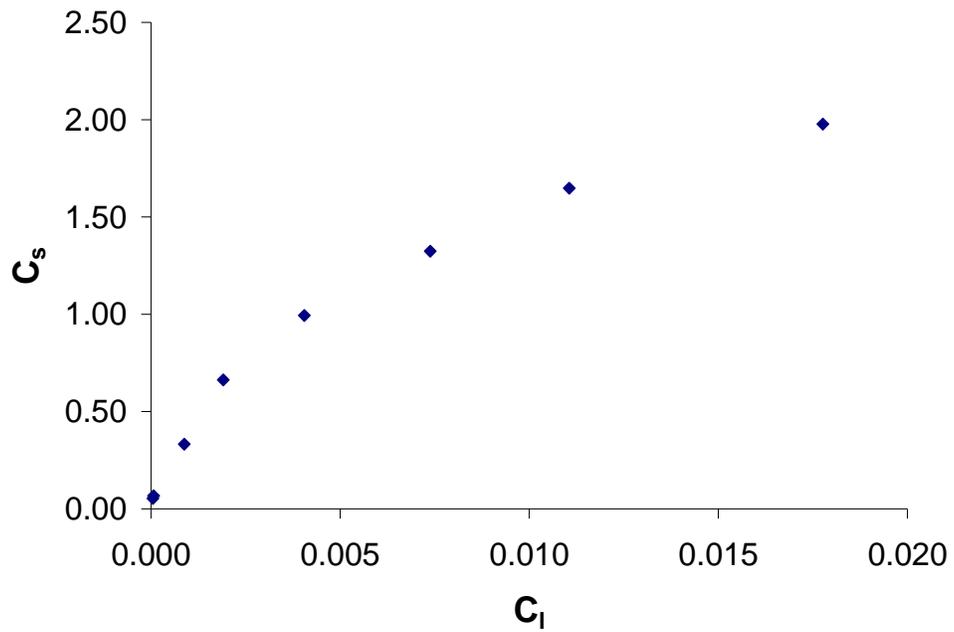


Figure 4.29 Isotherm for acenaphthene sorption by CB.

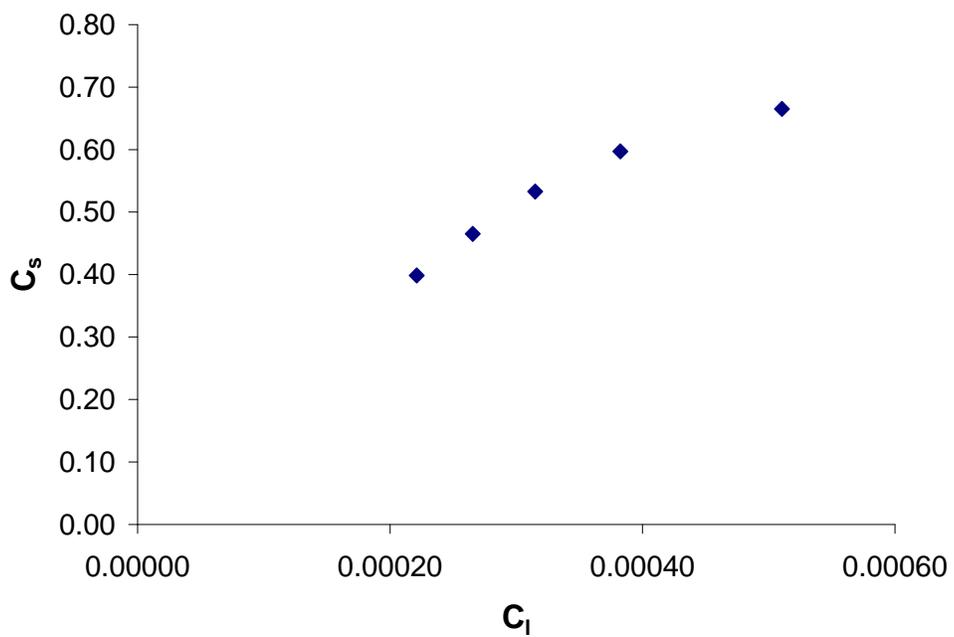


Figure 4.30 Isotherm for phenanthrene sorption by CB.

SBP sorbent

Figures 4.31 and 4.32 show the isotherms for acenaphthene and phenanthrene respectively using SBP. The linear pattern suggested an absorption process where the adsorbate is partitioned between the sorbent and water (Ceylan, Dogu et al. 2009). In typical absorption processes the removal efficiency depends on the adsorbent-water partition coefficient and not on the surface characteristics of the sorbent.

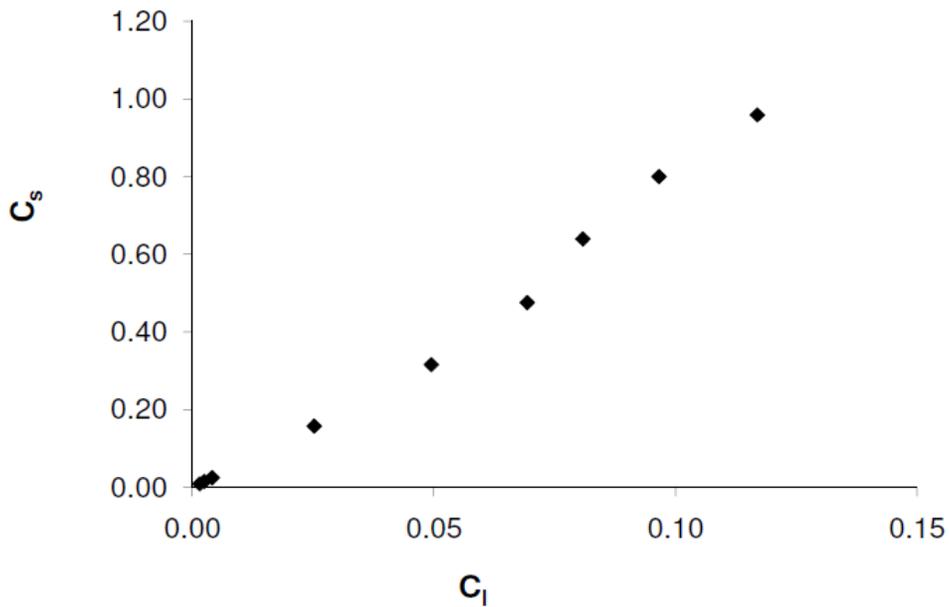


Figure 4.31 Isotherm for acenaphthene sorption by SBP.

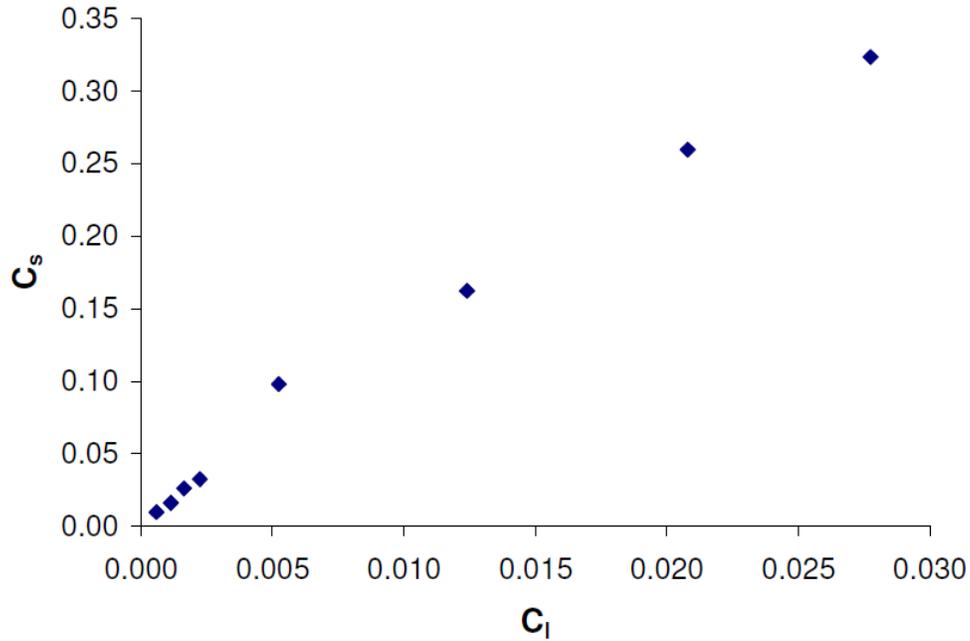


Figure 4.32 Isotherm for phenanthrene sorption by SBP.

The Langmuir equation represents a sorption process where a monolayer is formed on the sorbent and the energy of the adsorption is equal at all surface sites (Stumm and Morgan 1996). A linear relation was obtained after applying the Langmuir equation and used to calculate sorption parameters such as the sorption capacity. Figures 4.33 and 4.34 show the results adjusted to the Langmuir equation from acenaphthene and phenanthrene, respectively when using TCR.

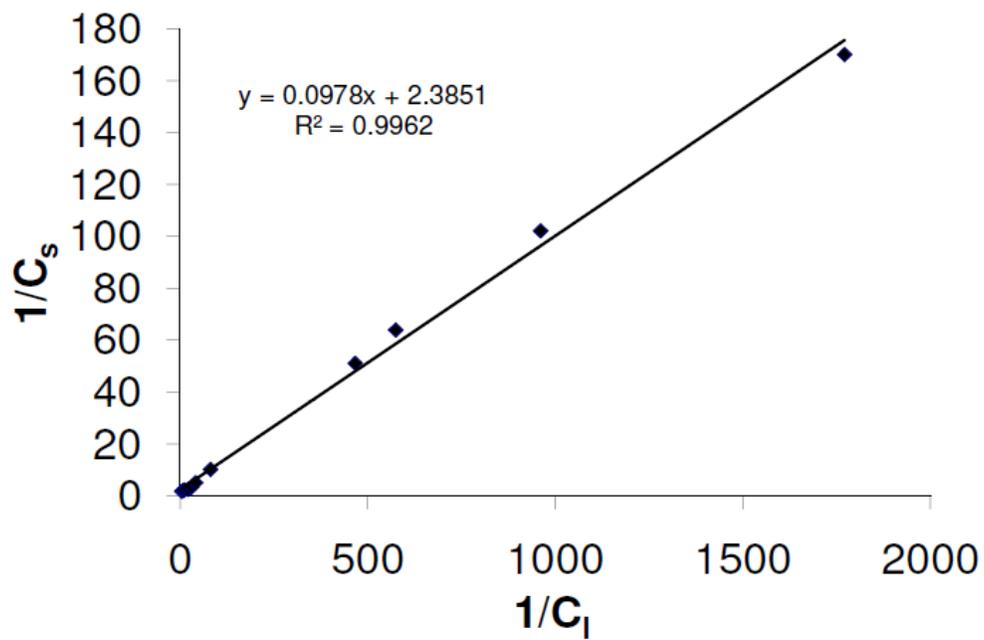


Figure 4.33 Langmuir isotherm for acenaphthene sorption by TCR.

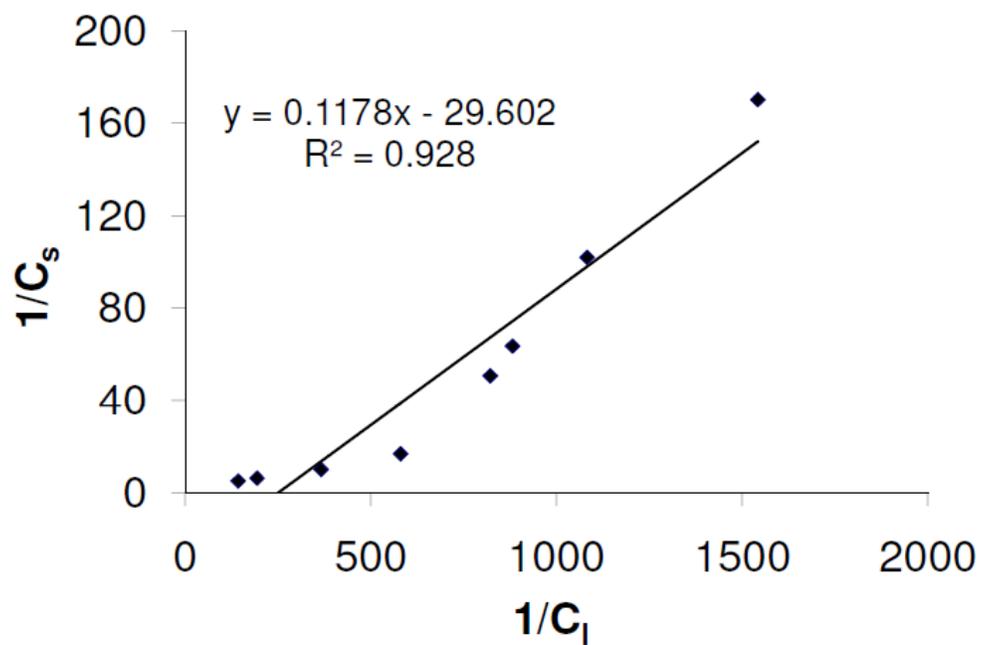


Figure 4.34 Langmuir isotherm for phenanthrene sorption by TCR.

4.2.2 Langmuir isotherms for acenaphthene and phenanthrene experiments using TCR, CB and SBP

Figures 4.35 and 4.36 show the results adjusted to the Langmuir equation from acenaphthene and phenanthrene, respectively when using CB. The isotherm for phenanthrene has fewer points than acenaphthene due to the total sorption of this adsorbate on the CB at low concentrations.

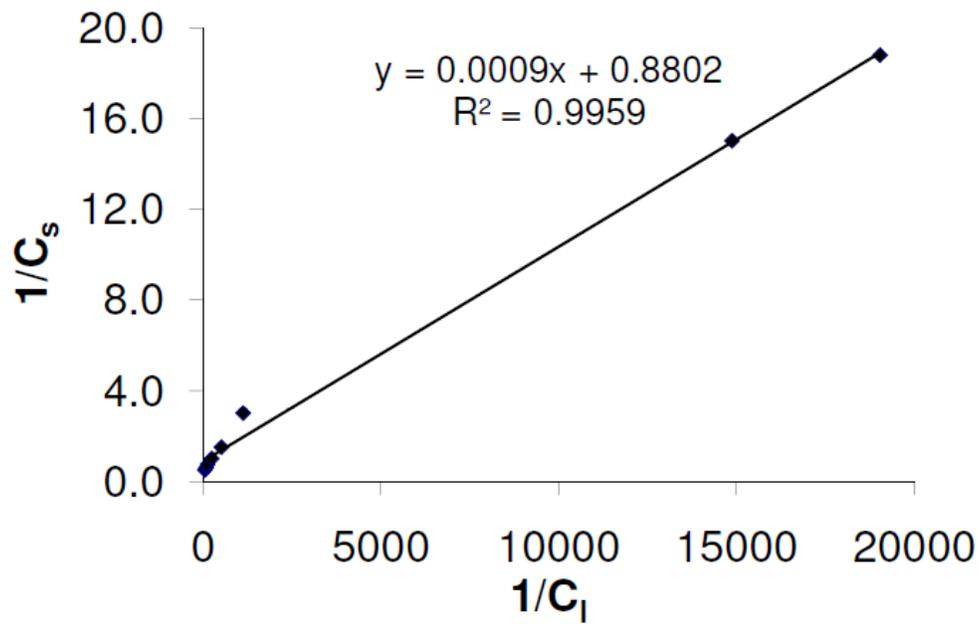


Figure 4.35 Langmuir isotherm for acenaphthene sorption by CB.

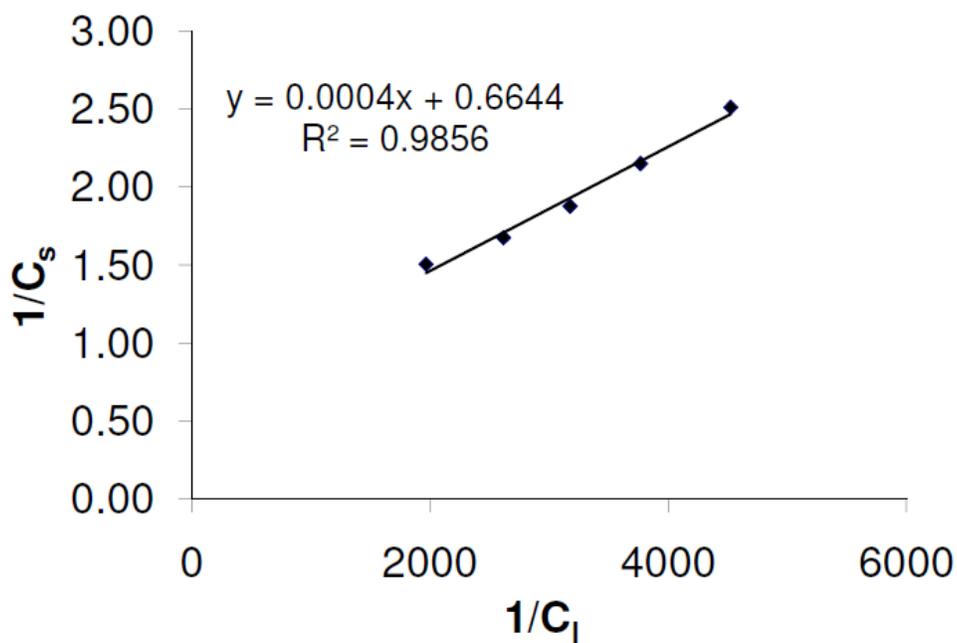


Figure 4.36 Langmuir isotherm for phenanthrene sorption by CB.

Figures 4.37 and 4.38 show the results adjusted to the Langmuir equation for acenaphthene and phenanthrene, respectively when using SBP.

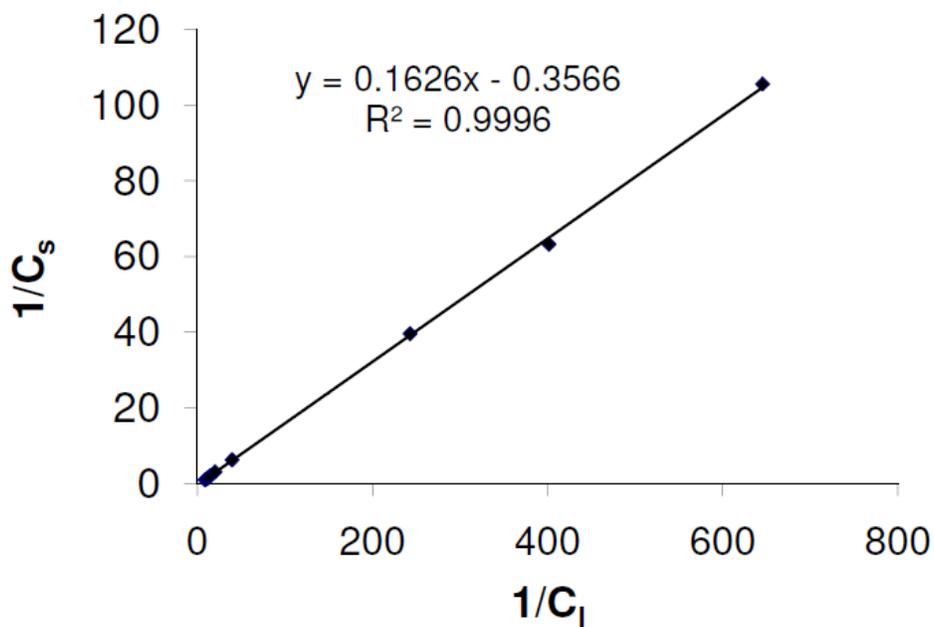


Figure 4.37 Langmuir isotherm for acenaphthene sorption by SBP.

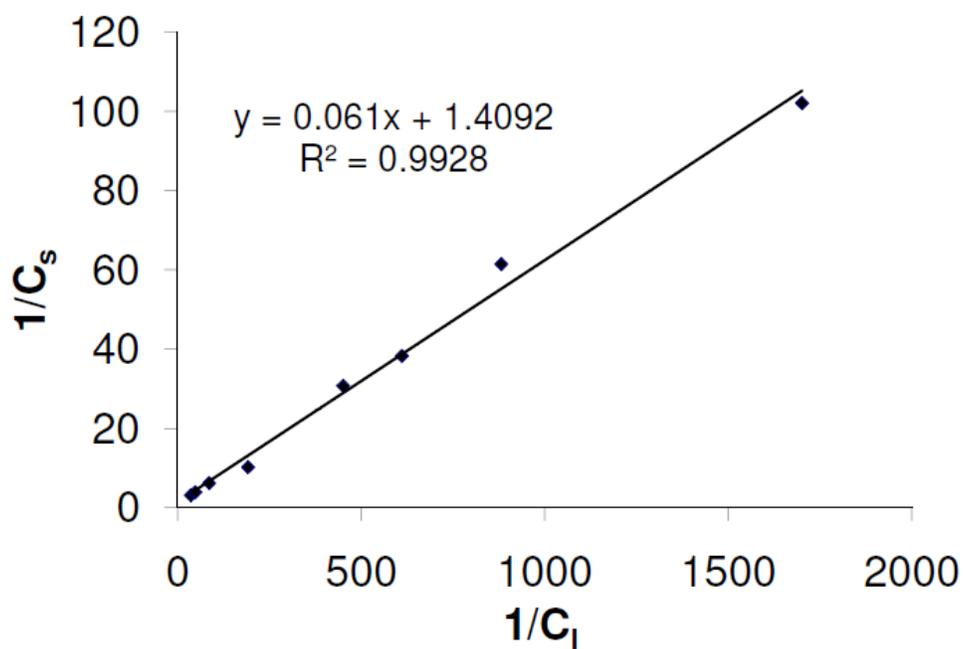


Figure 4.38 Langmuir isotherm for phenanthrene sorption by SBP.

4.2.3 Freundlich isotherms for acenaphthene and phenanthrene experiments using TCR, CB and SBP

The Freundlich isotherm fits well when the sorbent surface is heterogeneous and a monolayer is formed. The parameters obtained after the application of the logarithmic relation describe the sorption process. Figures 4.39 and 4.40 show the results adjusted to the Freundlich equation for acenaphthene and phenanthrene, respectively when using TCR.

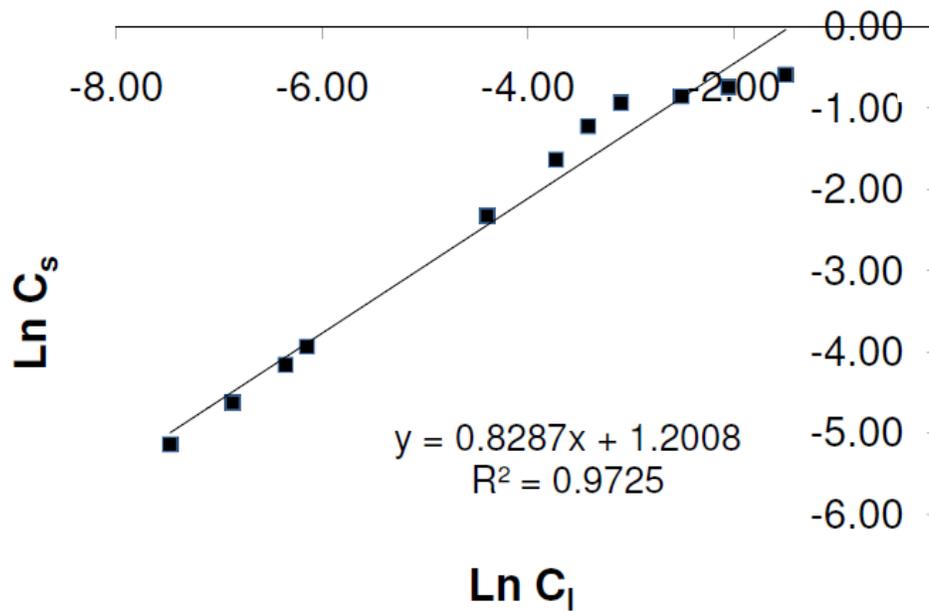


Figure 4.39 Freundlich isotherm for acenaphthene sorption by TCR.

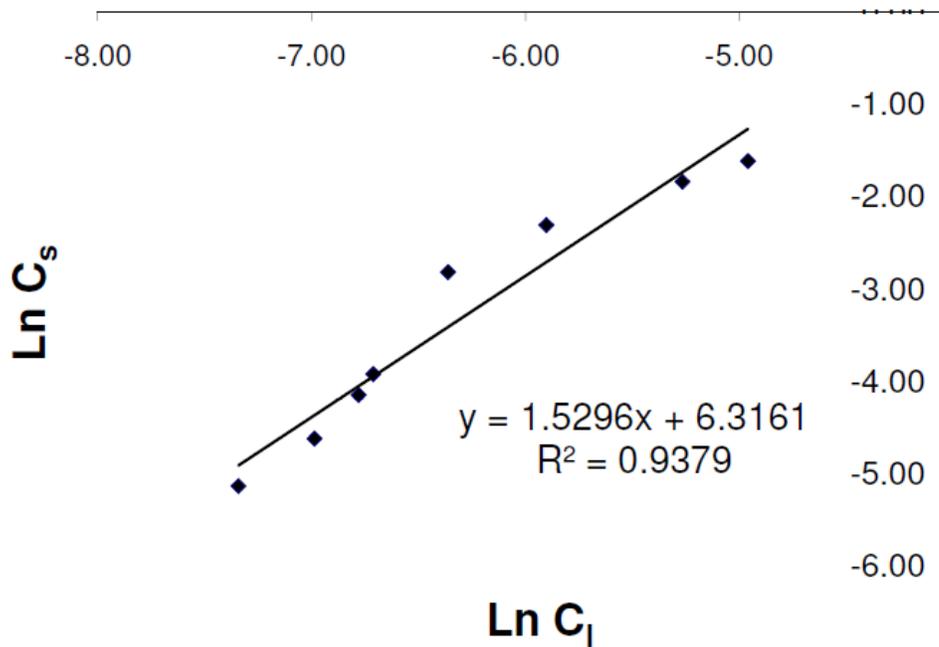


Figure 4.40 Freundlich isotherm for phenanthrene sorption by TCR.

Figures 4.41 and 4.42 show the results adjusted to the Freundlich equation for acenaphthene and phenanthrene, respectively when using CB.

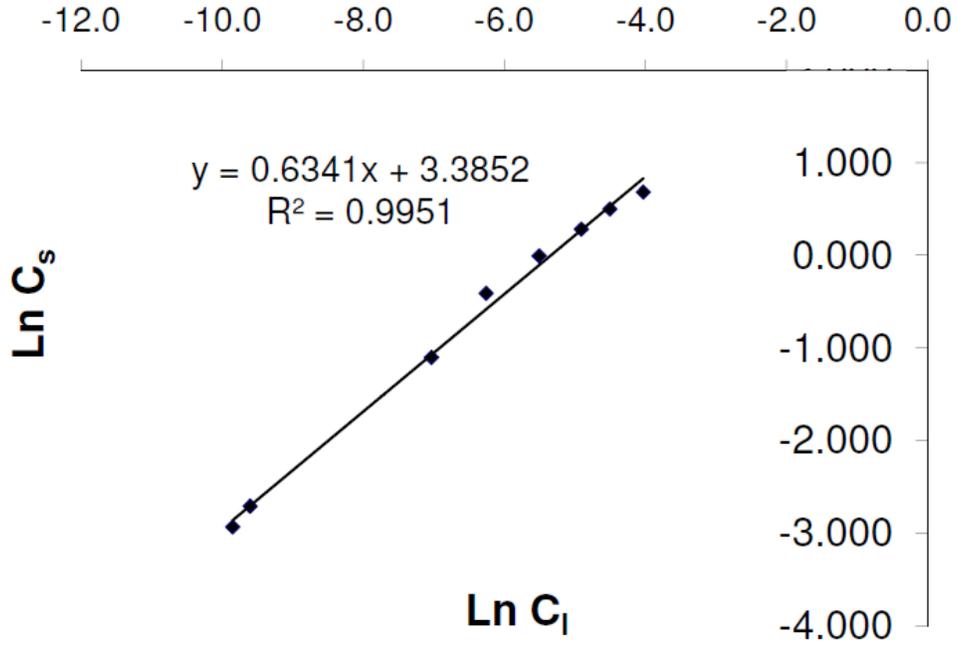


Figure 4.41 Freundlich isotherm for acenaphthene sorption by CB.

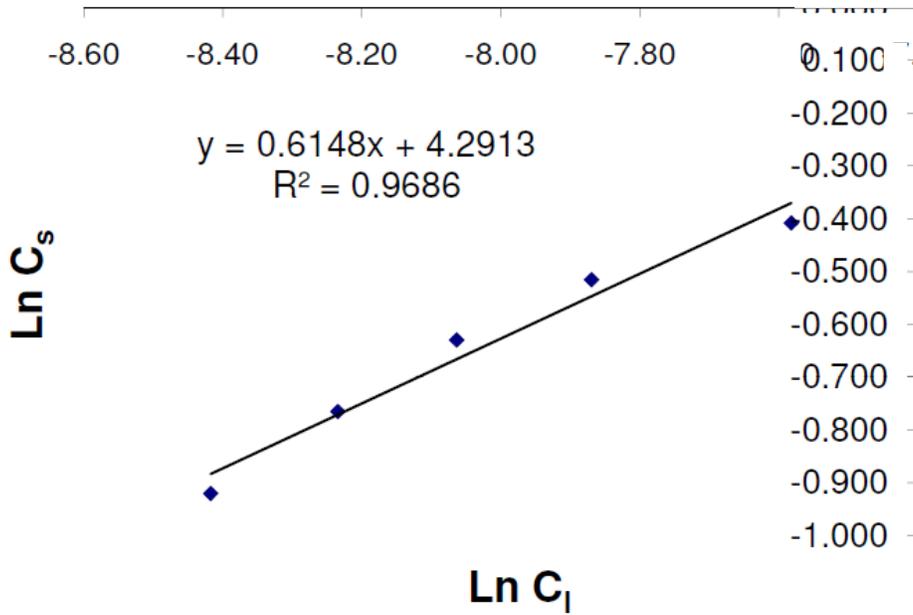


Figure 4.42 Freundlich isotherm for phenanthrene sorption by CB.

Figures 4.43 and 4.44 show the results adjusted to the Freundlich equation for acenaphthene and phenanthrene, respectively when using SBP.

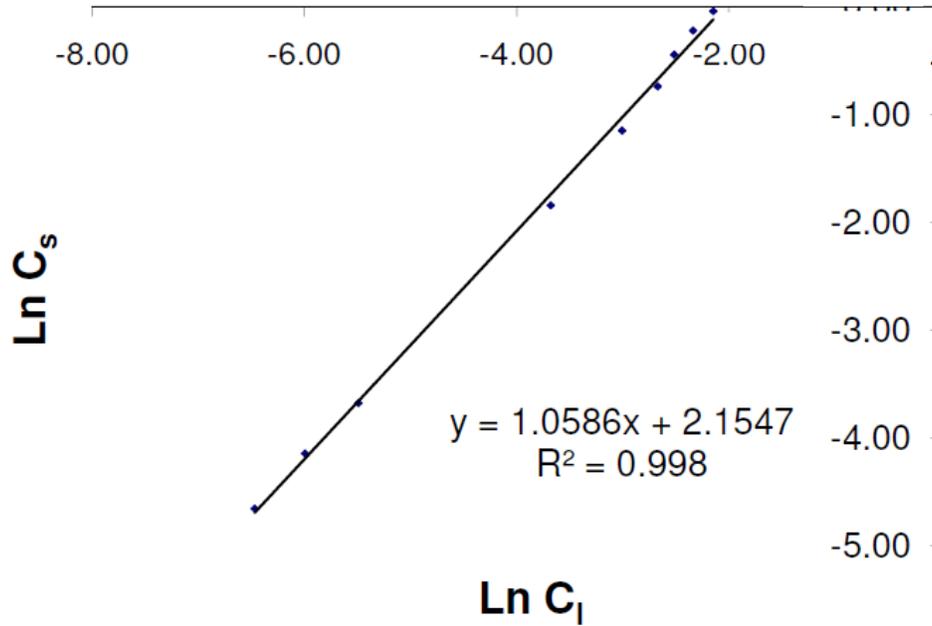


Figure 4.43 Freundlich isotherm for acenaphthene sorption by SBP.

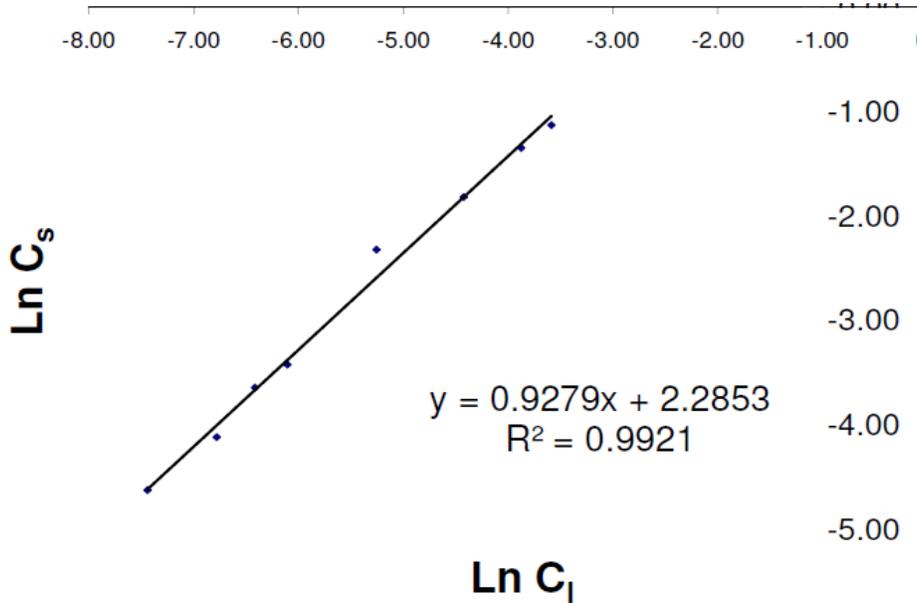


Figure 4.44 Freundlich isotherm for phenanthrene sorption by SBP.

4.2.4 Scatchard plots for acenaphthene and phenanthrene experiments

TCR sorbent

The plot obtained through the Scatchard relation can be used to evaluate the sorption process. The Scatchard profile of figures 4.45 and 4.46 clearly shows negative and positive slopes. Different slopes in the same plot suggest a multistage sorption process that can be due to the sorption capabilities of the main components in TCR (Ayar, Gürsal et al. 2008). Accordingly, acenaphthene and phenanthrene should have been absorbed by the TCR by combining both the adsorption by CB and absorption by SBP.

A convex curve formed between the first 2 slopes (between 0.00 and 0.20 mg/g in Figure 4.45) suggests a negative cooperativity among the different binding sites. A concave curve formed between the last 2 slopes (between 0.20 and 0.60 mg/g in Figure. 4.45) suggests a positive cooperativity among the different binding sites (Ozturk, Artan et al. 2004; Gurten, Ucan et al. 2005). The Scatchard plot for phenanthrene using TCR (Figure 4.46) also suggests more than one binding site. The concave curve suggests a positive cooperativity between the binding sites in the TCR (Gurten, Ucan et al. 2005).

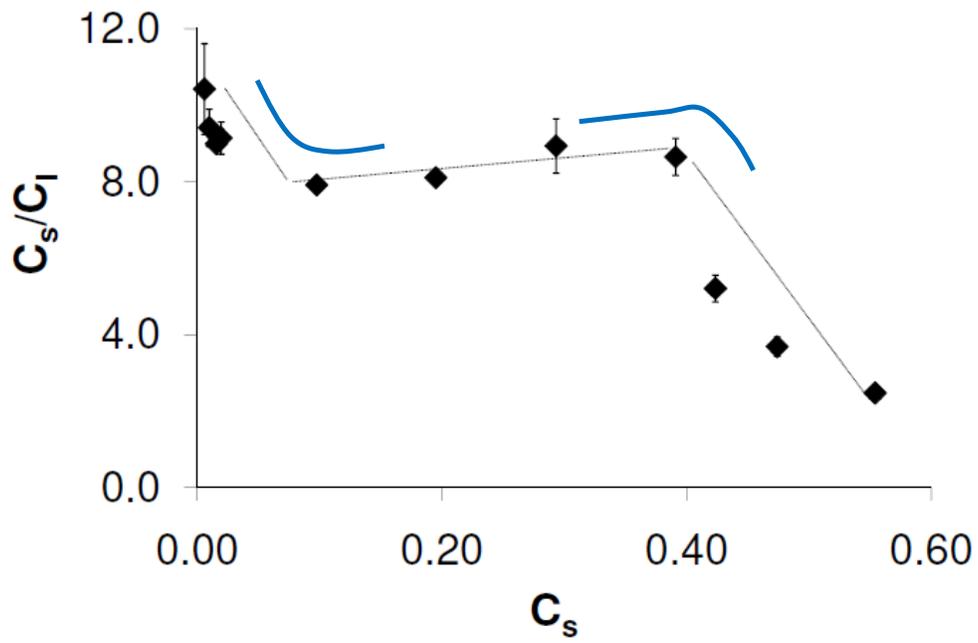


Figure 4.45 Scatchard plot for acenaphthene sorption by TCR.

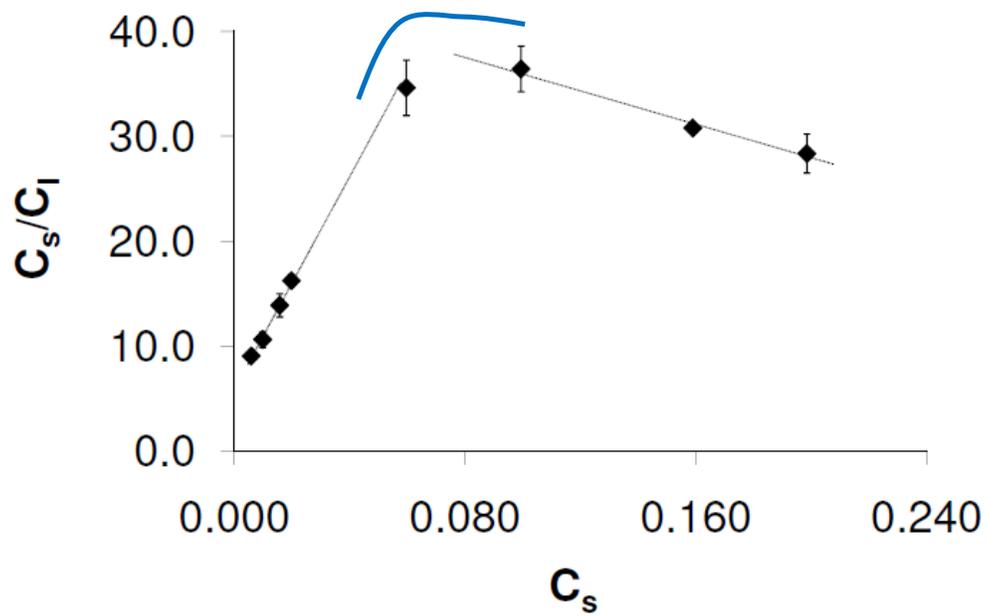


Figure 4.46 Scatchard plot for phenanthrene sorption by TCR.

CB sorbent

Figures 4.47 and 4.48 show the results adjusted to the Scatchard equation for acenaphthene and phenanthrene, respectively, using CB. The Scatchard profile with a negative slope in each plot would evidence that the sorption process took place in a single-step. Acenaphthene and phenanthrene should have been adsorbed on the CB surface through Van der Waals interactions including the London dipole-dipole interactions (Stumm and Morgan 1996). The points at the value 1000 in the acenaphthene Scatchard plot can suggest a extra step in this sorption process possibly due to the proximity of the adsorbate to the interface water/sorbent. This effect is not observed for phenanthrene because some points were missing due to total sorption of the adsorbate.

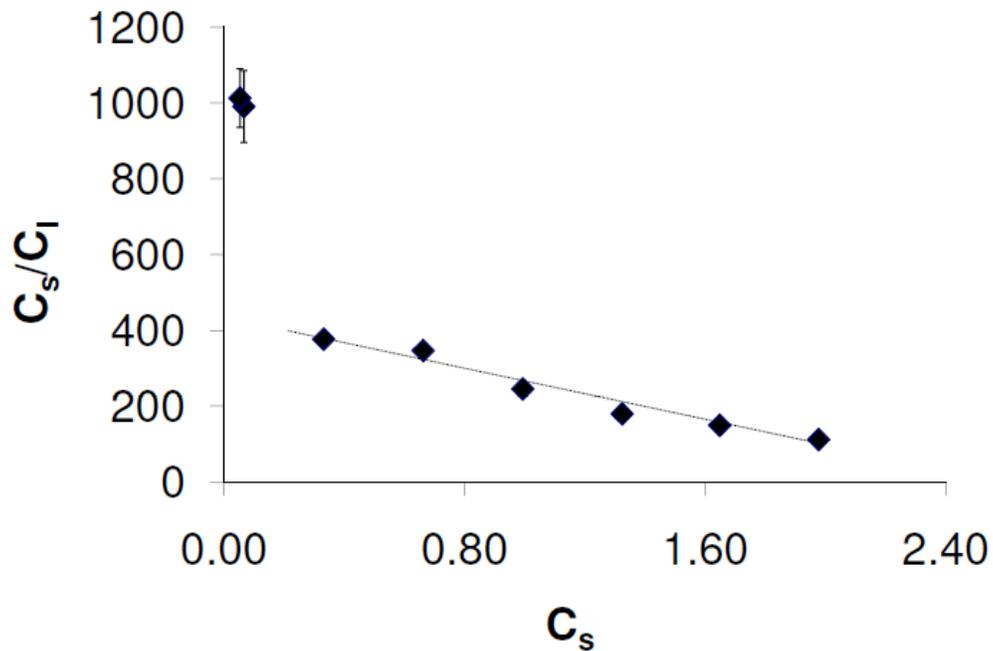


Figure 4.47 Scatchard plot for acenaphthene sorption by CB.

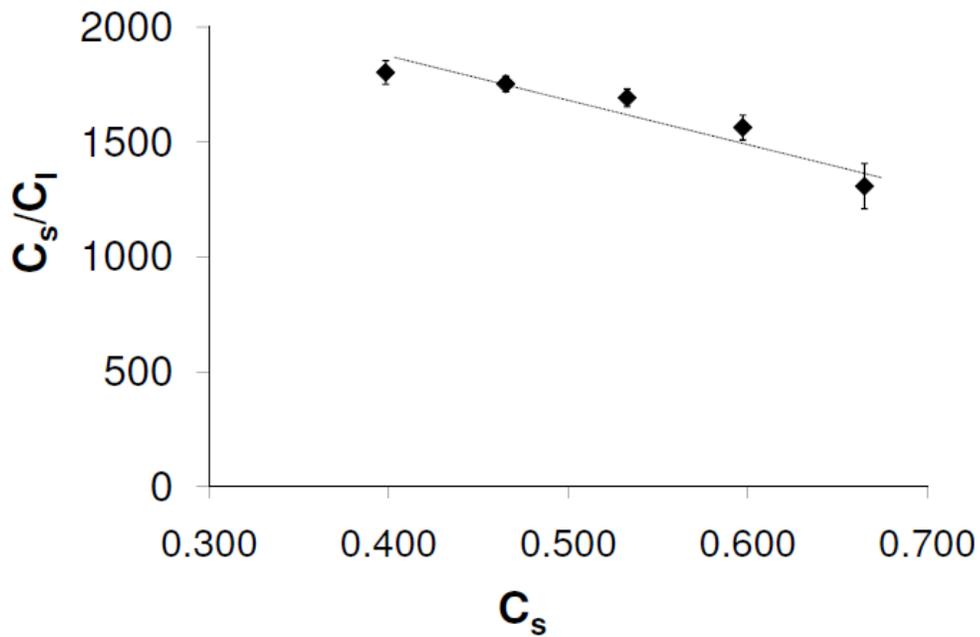


Figure 4.48 Scatchard plot for phenanthrene sorption by CB.

SBP sorbent

Figures 4.49 and 4.50 show the results adjusted to the Scatchard equation for acenaphthene and phenanthrene, respectively when using SBP. Figure 4.49 shows a positive slope and Figure 4.50 shows a negative slope. A slope in each plot suggested a one-step sorption process for each adsorbate.

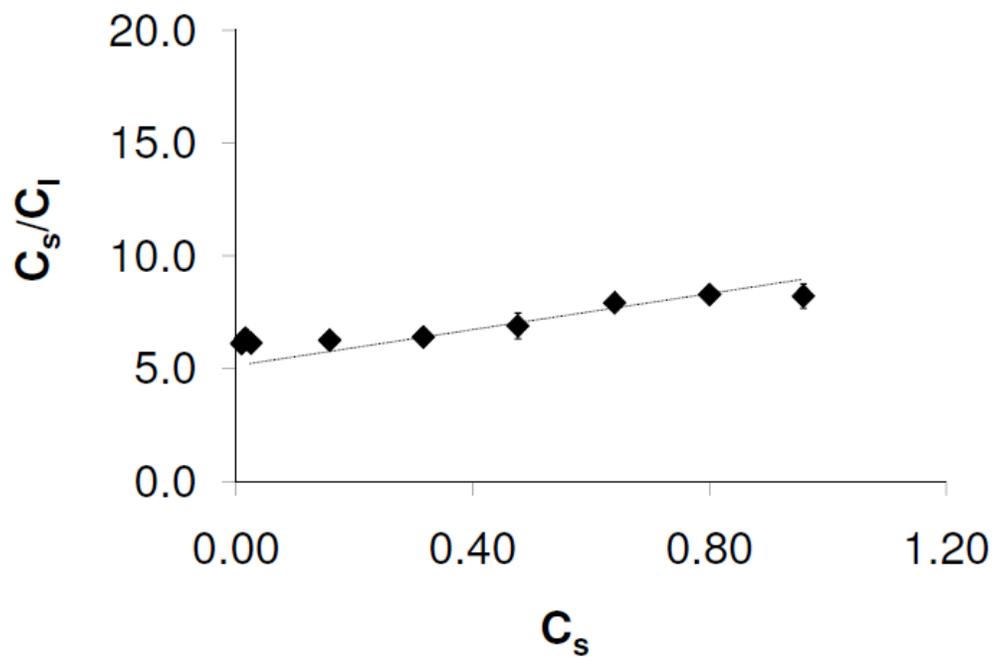


Figure 4.49 Scatchard plot for acenaphthene sorption by SBP.

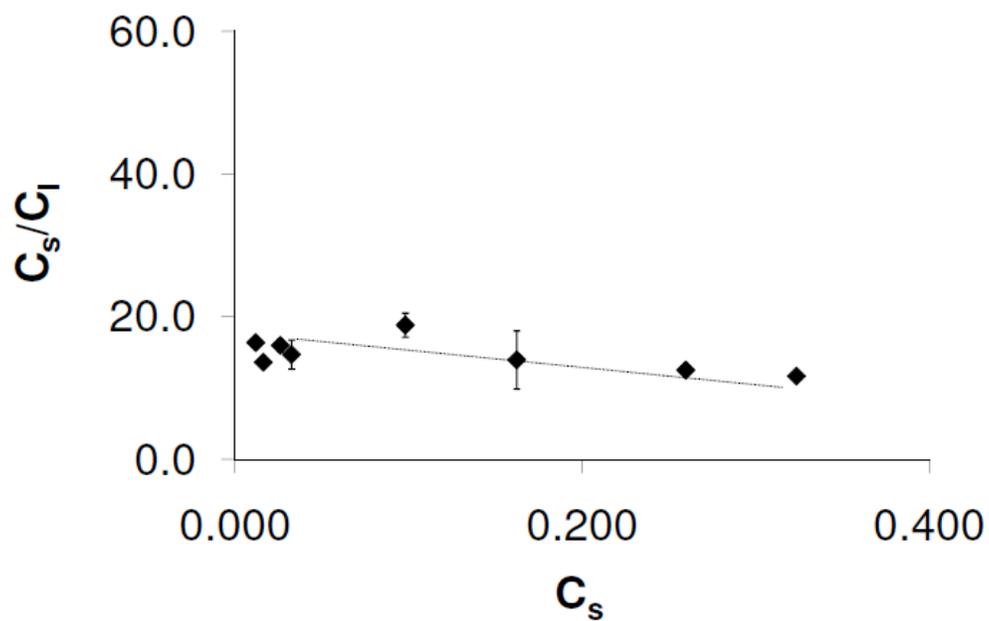


Figure 4.50 Scatchard plot for phenanthrene sorption by SBP.

4.2.5 Isotherm parameters for acenaphthene and phenanthrene experiments using TCR, CB and SBP

Tables 4.9 and 4.10 summarize the linear, Freundlich and Langmuir parameters, and the ‘P’ values corresponding to the sorption of acenaphthene and phenanthrene by TCR, CB and SBP. Low ‘P’ values indicate low dispersion of the data. In all cases, the ‘P’ values for the Freundlich isotherm were lower than those for both Langmuir’s and linear isotherms. Accordingly, only the data for Freundlich isotherms will be discussed herein.

TABLE 4.9 Isotherms parameters for the removal of acenaphthene using TCR, CB and SBP

		TCR	CB	SBP
Linear	r^2	0.756 ± 0.003	0.906 ± 0.005	0.98 ± 0.01
	K	2.59 ± 0.02	76 ± 57	8.2 ± 0.2
	P	325 ± 2	99 ± 12	52 ± 17
Langmuir	r^2	0.993 ± 0.005	0.9954 ± 0.0003	0.999 ± 0.001
	b	26 ± 18	932 ± 88	2 ± 1
	X_m	0.7 ± 0.6	1.13 ± 0.02	4 ± 4
	P	39 ± 23	23.6 ± 0.05	24 ± 8
Freundlich	r^2	0.972 ± 0.001	0.9951 ± 0.0005	0.998 ± 0.002
	n	1.207 ± 0.004	1.58 ± 0.02	0.945 ± 0.006
	K_f (mg/g)	3.32 ± 0.02	30 ± 1	8.6 ± 0.2
	P	22 ± 1	7.8 ± 0.4	9 ± 3

m : slope
i : intercept
 r^2 : R square
n : Freundlich constant

K_f : Freundlich constant
b : Langmuir constant
 X_m : Maximum amount adsorbed
P: Probability of the model

The 'n' and K_f coefficients are related to sorption behavior and loading factor of the sorbent, respectively. While 'n' values lower than one ($n < 1$) suggests the removal capacity of the sorbent increases at high adsorbate concentrations, an 'n' value close to one ($n \sim 1$) indicates that the removal capacity of the sorbent is independent of the adsorbate concentration. The 'n' values for the sorption of acenaphthene and phenanthrene by TCR were 1.207 ± 0.004 and 0.655 ± 0.004 respectively, which suggest that the removal capacity of TCR increases at low concentrations of acenaphthene and at high concentrations of phenanthrene.

The corresponding 'n' values for the sorption of acenaphthene and phenanthrene using CB were 1.58 ± 0.02 and 1.6 ± 0.2 , respectively. The similarity between these values suggests analogous sorption behaviour of these adsorbates onto this sorbent. The data is also in agreement with other carbonaceous sorbents used to remove PAHs (Lai, Quio Chu et al. 2009). As tables 4.09 and 4.10 also show, the 'n' values for the sorption of acenaphthene and phenanthrene by SBP were close to unity (0.945 ± 0.006 and 1.08 ± 0.03 , respectively), which suggests that the sorption process is independent of adsorbate concentration and dependent on the partition coefficient only.

TABLE 4.10 Isotherms parameters for the removal of phenanthrene using TCR, CB and SBP

		TCR	CB	SBP
Linear	r^2	0.97 ± 0.01	0.94 ± 0.03	0.98 ± 0.01
	K	32 ± 2	914 ± 133	11.5 ± 0.4
	P	34 ± 3	4 ± 1	26 ± 8
Langmuir	r^2	0.925 ± 0.009	0.98 ± 0.1	0.990 ± 0.07
	b	250 ± 12	1686 ± 340	25 ± 15
	X_m	0.034 ± 0.001	1.5 ± 0.2	1.0 ± 0.9
	P	79 ± 4	2 ± 1	12 ± 4
Freundlich	r^2	0.94 ± 0.01	0.97 ± 0.02	0.987 ± 0.001
	n	0.655 ± 0.001	1.6 ± 0.2	1.08 ± 0.03
	K_f (mg/g)	55 ± 5	80 ± 38	10 ± 2
	P	7.8 ± 0.5	5 ± 1	4.2 ± 0.7

m : slope
 i : intercept
 r^2 : R square
 n : Freundlich constant

K_f : Freundlich constant
 b : Langmuir constant
 X_m : Maximum amount adsorbed
 P: Probability of the model

The uptake capacity (K_f) for phenanthrene (54.6 mg/g) was much larger than acenaphthene (3.32 mg/g) when TCR was used as sorbent. The uptake capacity (K_f) for acenaphthene and phenanthrene using CB were 30 ± 1 mg/g and 80 ± 38 mg/g, respectively. The corresponding K_f values when SBP was used as sorbent were 8 ± 2 mg/g and 10 ± 2 mg/g respectively. The low solubility in water of phenanthrene (1.002 mg/L) compared to acenaphthene (3.8 mg/L) could explain the obtained differences in K_f values for the two adsorbates. Alamo et al. (Alamo-Nole, Perales-Perez et al. 2010) have proposed that the low affinity of the adsorbate species for the solvent molecules should favour the displacement of the adsorbate from the aqueous into the solid phase (the sorbent). On the other hand, the

larger uptake capacities obtained for acenaphthene and phenanthrene using CB when compared to SBP supports our claim that adsorption onto CB surface will be the main mechanism involved with the removal of acenaphthene and phenanthrene using TCR. Although, nanosize CB and SBP exhibit higher uptake capacities than TCR, the advantage of using TCR is based on the extremely low cost (\$0.15/lb in Puerto Rico), in addition to its simpler handling as a granular sorbent material. The demonstrated possibility of expanding the recycling options for waste tire rubber is also an additional asset.

4.2.6 Effect of TCR concentration for PAHs sorption experiments

4.2.6.1 Sorption of acenaphthene, acenaphthylene and phenanthrene in single-component experiments

The removal of PAHs was evaluated as a function of TCR concentrations. The removal of acenaphthene, acenaphthylene and phenanthrene was highly efficient and rapid. The order of affinity of the adsorbates by TCR was phenanthrene followed by acenaphthene and lastly acenaphthylene.

As we discussed earlier phenanthrene has the lowest solubility in water (1.0 mg/L), thus the partition between the TCR and water is expected to be significantly different from the observed for acenaphthene and acenaphthylene with solubilities of 3.8 mg/L and 2.6 mg/L respectively. Acenaphthene and acenaphthylene are less hydrophobic and are expected to be less absorbed into the TCR (Alamo-Nole, Perales-Perez et al. 2010).

Table 4.11 shows the terminal concentrations and removal percentage for single-component sorption of acenaphthene, acenaphthylene and phenanthrene using initial

concentration of 900 µg/L, 900 µg/L and 500 µg/L respectively and at pH 6.0. After 5 hours of contact time and using 10 g/L of TCR all adsorbates were almost completely removed. On the other hand, 90% of phenanthrene, 83.3% of acenaphthene and 71.8% of acenaphthylene were removed using 0.5 g/L of TCR. This represents 20 times less TCR than 10 g/L which is the concentration of sorbent usually used in commercial sorbent processes (Alamo-Nole 2006).

TABLE 4.11 Final (terminal) concentrations and % of removal for single-component sorption of acenaphthene, acenaphthylene and phenanthrene at different concentrations of TCR.

TCR (Conc.)	Acenaphthene		Acenaphthylene		Phenanthrene	
	Final concentration (ug/L)	Removal (%)	Final concentration (ug/L)	Removal (%)	Final concentration (ug/L)	Removal (%)
10 g/L	6.2 ± 0.3	99.3	20.7 ± 0.9	97.7	4.2 ± 0.3	99.2
5.0 g/L	16.9 ± 0.6	98.0	61 ± 4	93.3	5.8 ± 0.6	98.8
2.8 g/L	33 ± 1	96.1	68 ± 4	92.5	10.7 ± 0.7	97.9
1.0 g/L	74 ± 5	91.9	161 ± 5	82.3	19 ± 2	96.2
0.7 g/L	114 ± 8	87.7	190 ± 8	79.1	23 ± 3	95.5
0.5 g/L	144 ± 17	83.3	257 ± 1	71.8	52 ± 7	90.0
0.3 g/L	197 ± 2	78.7	408 ± 9	55.1		

Init. Conc. of acenaphthene 900 ug/L, acenaphthylene 900 ug/L y phenanthrene 500 ug/L

The results were linearized using Freundlich equation. The experimental data fits the Freundlich model very well (Table 4.12).

TABLE 4.12 Parameters of linear, Freundlich and Langmuir isotherm for single-component sorption for acenaphthene, acenaphthylene and phenanthrene at pH 6.0.

	ISOTHERM							
	Linear		Freundlich			Langmuir		
	m	r ²	n	K _f (mg/g)	r ²	b	X _m	r ²
Acenaphthene	11.6	0.977	1.03	10.2	0.987	6.77	2.13	0.976
Acenaphthylene	4.54	0.984	0.97	5.02	0.995	0.60	9.65	0.998
Phenanthrene	18.9	0.894	0.84	46.9	0.946	22.8	0.55	0.946

m : slope
i : intercept
r² : R square
n : Freundlich constant

K_f : Freundlich constant
b : Langmuir constant
X_m : Maximum amount adsorbed

The Freundlich relation gives good fitting for heterogeneous sorbents such as TCR. The ‘n’ values for acenaphthene, acenaphthylene and phenanthrene were 1.03, 0.97 and 0.84. These values are slightly different from the values obtained in tables 4.9 and 4.10. The ‘n’ values for acenaphthene decreased from 1.207 ± 0.004 to 1.03 ± 0.05 and the ‘n’ values for phenanthrene increased from 0.655 ± 0.001 to 0.84 ± 0.02 . The uptake capacity for acenaphthene also increased from 3.32 ± 0.02 to 10.2 ± 0.3 and the uptake capacity of phenanthrene decreased from 55 ± 5 to 46.9 ± 0.4 . These changes correspond to the effect of change in TCR concentration.

4.2.6.2 Sorption of acenaphthene, acenaphthylene and phenanthrene in multi-component experiments

Table 4.13 shows the final concentrations and percent of removal of acenaphthene, acenaphthylene and phenanthrene when they were mixed in a multi-component mixture and the concentration of TCR was changed. The removal pattern was the same for the other

experiments. Phenanthrene has the highest removal followed by acenaphthene and finally acenaphthylene. The high removal of phenanthrene was expected due to its low solubility in water (1.0 mg/L); however acenaphthene has the highest solubility (3.8 g/L) and was the second with the highest removal suggesting other considerations besides solubility.

TABLE 4.13 Final (terminal) concentrations and % of removal for multi-component sorption of acenaphthene, acenaphthylene and phenanthrene at different concentrations of TCR.

TCR (conc.)	Acenaphthene		Acenaphthylene		Phenanthrene	
	Final concentration (ug/L)	Removal (%)	Final concentration (ug/L)	Removal (%)	Final concentration (ug/L)	Removal (%)
10 g/L	2.2 ± 0.3	99.3	5.0 ± 0.4	98.5	ND	~100
5.0 g/L	4.6 ± 0.6	98.6	9.0 ± 0.9	97.3	ND	~100
2.8 g/L	13.3 ± 0.4	96.0	23.8 ± 0.7	92.8	3.1 ± 0.6	99.1
1.0 g/L	37 ± 2	88.9	61 ± 5	81.8	12.4 ± 0.8	96.4
0.7 g/L	42 ± 2	76.8	65 ± 4	79.3	16 ± 1	95.3
0.5 g/L	62 ± 3	81.2	98 ± 5	69.9	21 ± 1	93.8
0.3 g/L	84 ± 2	74.6	122 ± 4	63.7	41 ± 2	87.8
0.18 g/L	125 ± 8	62.0	165 ± 9	50.6	78 ± 9	76.9

Init. Conc.: 330 ug/L of each component

Table 4.14 shows the parameters for linear, Langmuir and Freundlich isotherms. The results fit the Freundlich isotherm quite well. The 'n' value for acenaphthylene in multi-component (1.08 ± 0.04) was quite similar to that in single-component (0.97 ± 0.06) which means that there is no change in sorption patterns for this adsorbate. The 'n' value for

acenaphthene in multi-component (1.15 ± 0.03) was slightly higher than in single-component (1.03 ± 0.02) which means the removal should increase at low concentrations of the adsorbate. Also, the 'n' value for phenanthrene in multi-component (1.28 ± 0.04) was higher than in single-component (0.84 ± 0.02), which should indicate changes in the removal pattern. In this case, the removal of acenaphthene changes from high removal at high concentrations of adsorbate in single-component to high removal at low concentrations of adsorbate in multi-component.

TABLE 4.14 Parameters of linear, Freundlich and Langmuir isotherm for multi-component sorption for acenaphthene, acenaphthylene and phenanthrene at pH 6.0.

	ISOTHERM							
	Linear		Freundlich			Langmuir		
	m	r ²	n	K _f (mg/g)	r ²	b	X _m	r ²
Acenaphthene	8.74	0.989	1.15	6.23	0.987	18.8	0.89	0.984
Acenaphthylene	5.42	0.984	1.08	4.38	0.985	5.32	1.47	0.985
Phenanthrene	19.0	0.994	1.28	11.1	0.995	31.2	1.56	0.988

m : slope
i : intercept
r² : R square
n : Freundlich constant

K_f : Freundlich constant
b : Langmuir constant
X_m : Maximum amount adsorbed

The sorption capacity of acenaphthene, acenaphthylene and phenanthrene changed from 10.2, 5.02 and 46.9 mg/g for single-component to 6.23, 4.38 and 11.1 mg/g for multi-component, respectively. As we discussed earlier, the hydrophobicity is the key for the change in the sorption capacity. In multi-component, the hydrophobicity of each component can change. This change should increase the removal of adsorbates with low hydrophobicity (acenaphthene and acenaphthylene) but should decrease the removal of adsorbates with high hydrophobicity (phenanthrene).

4.3 Sorption of gasoline components

4.3.1 Sorption of total gasoline components in aqueous samples

The total ion chromatogram (TIC) mode in a GC-MS system can provide structural information of the compounds present in a sample. It can also be used to determine the number of compounds present in a complex mixture such as gasoline. The TIC-chromatogram of figure 4.51 gives an idea of the complexity of gasoline samples. Each peak in the chromatogram represents at least one compound present in gasoline. The expanded part in the figure 4.51 shows the chromatogram after 11 minutes of retention time and represents compounds with a high boiling point, low volatility and a high molecular weight (including poly aromatic hydrocarbons). The complexity of the gasoline chromatogram is evidence of the co-existence of volatile and semi volatile organic compounds including alkanes, alkenes, isoalkanes, cycloalkanes, cycloalkenes and aromatics (IARC 1998).

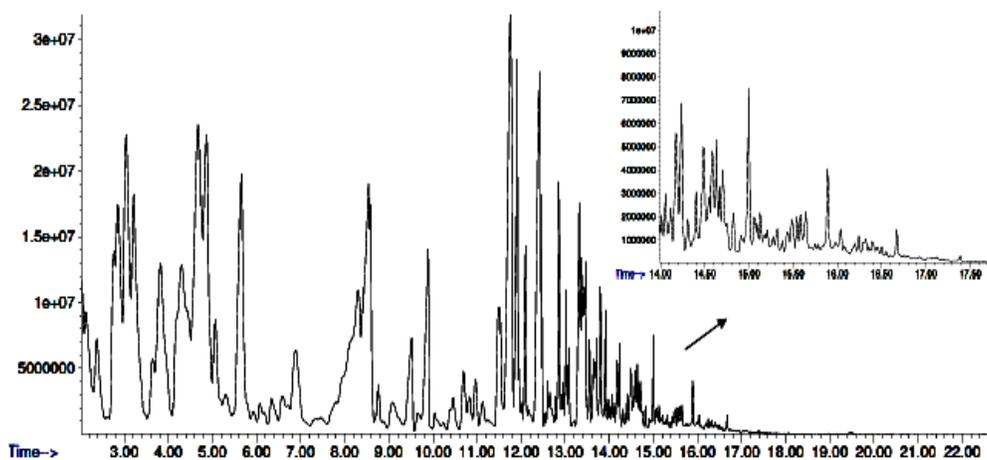


Figure 4.51 TIC-chromatogram for gasoline (regular Texaco) aqueous solution (30 mg/L).

Figure 4.52 shows the TIC-chromatogram of the aqueous dilution of gasoline after 6 hours of contact with 5.0 g/L of TCR. It can be observed that the intensity of all peaks decreased significantly when compared with the chromatograms of figure 4.51, which suggests that all gasoline components were partially removed. The removal of gasoline components from a gasoline water solution with an initial concentration of 30 mg/L was $95.6 \pm 0.4\%$ when using 5.0 g/L of TCR (Table 1).

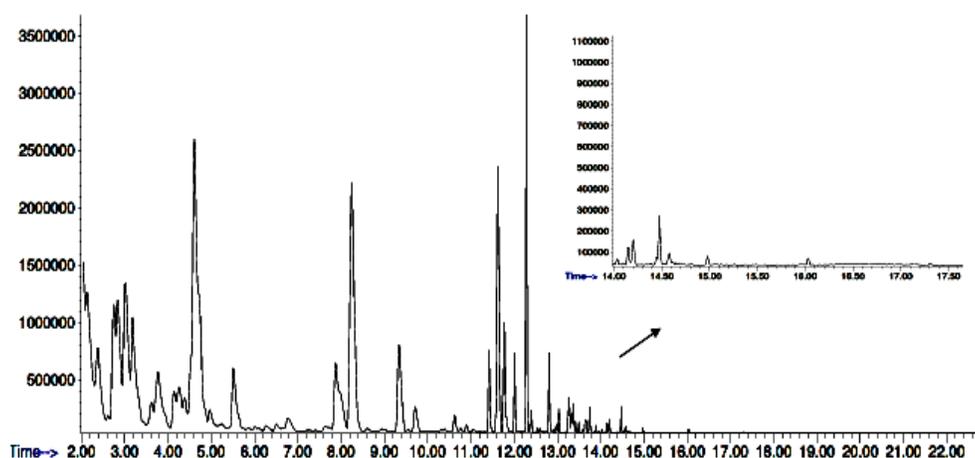


Figure 4.52 TIC-chromatogram for gasoline aqueous solution after 6 hours of contact with 10 g/L of TCR.

The almost complete elimination of gasoline components after 11 minutes of retention time (expanded areas in Figures 4.51 and 4.52) using 5.0 g/L of TCR suggest that compounds with high molecular weight and low solubility are better removed by TCR. Alamo suggested that less soluble compounds, i.e. those possessing high hydrophobicity or large molecular weight, should be efficiently removed using TCR as a sorbent (Alamo-Nole, Perales-Perez et al. 2011). Low solubility of those gasoline compounds should increase their removal through the increment of contact between adsorbates and sorbent which enhances the sorption through van der Waals forces (Stumm and Morgan 1996).

4.3.2 Sorption of toluene and xylene in gasoline aqueous samples

Figure 4.53 shows the mass spectra for toluene and o-xylene using electron impact ionization of 70 eV. At least three peaks with high intensities must be selected for the SIM mode measurements. Based on the retention times (Rt) provided by injection of toluene (Rt: 4.72 ± 0.08) and xylene (Rt: 8.66 ± 0.06) standards and the information in the figure 4.53, the ions with 65, 91 and 92 m/z (toluene fragment ions) were monitored for the first 5.5 minutes. Subsequently, the ions with 72, 91 and 106 m/z (o-xylene fragments ions) were monitored.

The relative abundances for the fragments ions of toluene standards 65, 91 and 92 m/z were $8.4 \pm 0.1\%$, $56.7 \pm 0.2\%$ and $34.9 \pm 0.2\%$ respectively. The relative abundance in the standards for o-xylene fragment ions 72, 91 and 106 m/z were $0.087 \pm 0.003\%$, $68.8 \pm 0.1\%$ and $31.1 \pm 0.2\%$. The content of toluene and xylene in gasoline samples were analyzed using the retention time (Rt) and the relative abundance of each fragment ions.

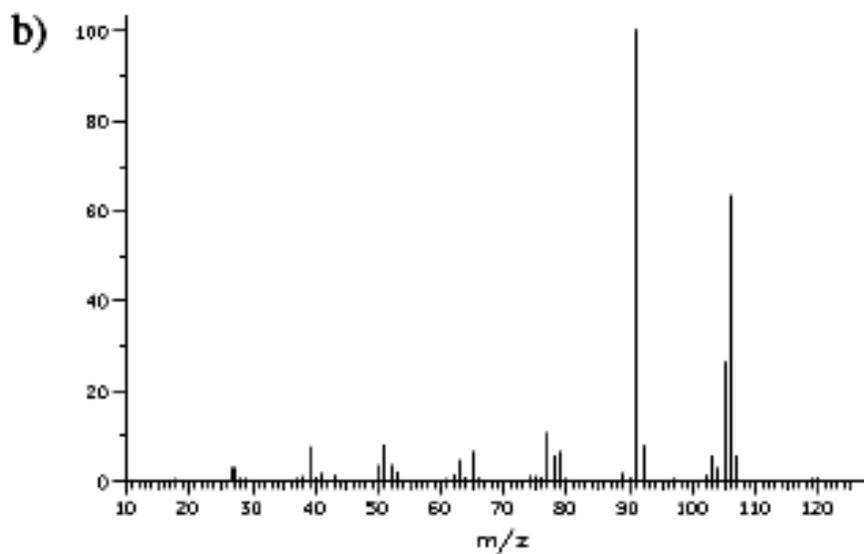
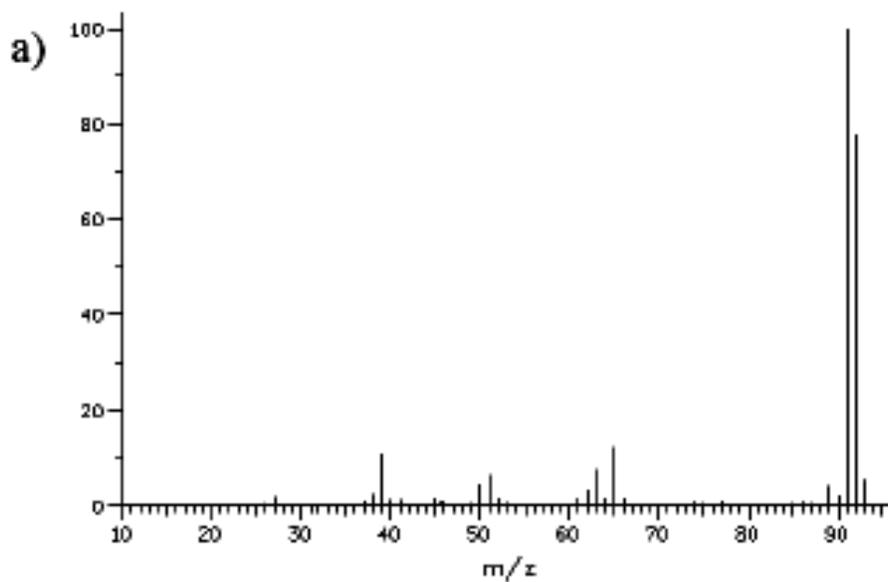


Figure 4.53 S Mass spectra of a) toluene and b) o-xylene

Figure 4.54 shows the chromatogram of gasoline water sample (30 mg/L) using SIM mode. There are only a few components of gasoline with the selected fragment ions, which allows quantification without any modifications to the method.

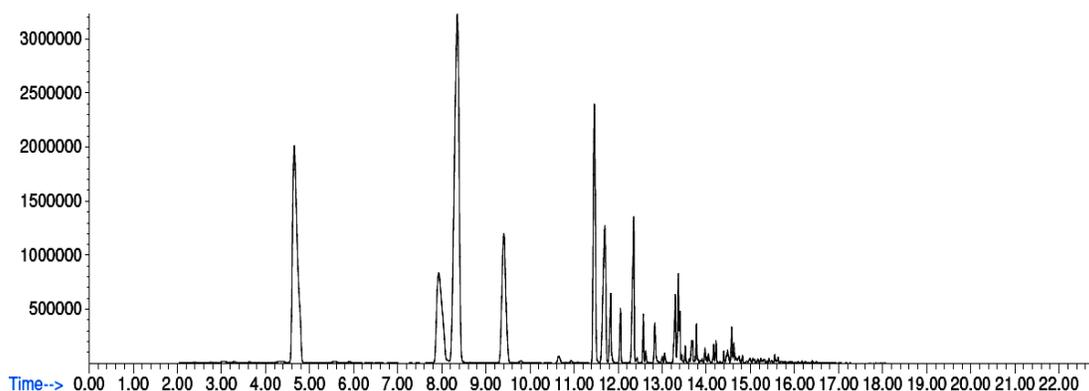


Figure 4.54 SIM-chromatogram of gasoline aqueous solution (30 mg/L)

After 6 hours of contact with 5 g/L of TCR, the removal for toluene and o-xylene in a gasoline aqueous sample (30 mg/L) were $73 \pm 2\%$ and $86.4 \pm 0.6\%$, respectively (table 4.15). These results confirm that compounds with low solubility or high hydrophobicity (o-xylene) are more efficiently removed by TCR than compounds with low hydrophobicity (toluene) (Alamo-Nole, Perales-Perez et al. 2011).

TABLE 4.15 Removal (%) of gasoline, toluene and xylene in aqueous solution using TCR (5g/L), CB (1.5 g/L) and SBP (3.0 g/L). The initial concentration of gasoline was 30 mg/L.

	Gasoline	Toluene	Xylene
TCR	95.6 ± 0.4	73 ± 2	86.4 ± 0.6
CB	97.3 ± 0.5	67 ± 2	86.8 ± 0.8
SBP	96.4 ± 0.4	89.5 ± 0.1	88.6 ± 0.1

The removal of gasoline components by TCR due to its components like CB and SBP has been reported (Alamo-Nole, Perales-Perez et al. 2011). CB as activated carbon has the

capacity to remove inorganic and organic contaminants through adsorption mechanisms (Valderrama, Cortina et al. 2007; Carratala-Abril, Lillo-Rodenas et al. 2009). SBP is an organic polymer that can absorb or incorporate organic contaminants between its polymeric chains in an absorption mechanism (Soney, Sabu et al. 1996). The removal of total gasoline components by TCR is almost the same as the removal by its components (Table 4.15) which could suggest the removal by TCR (95.6%) is due to the removal of CB (97.3%) and SBP (96.4%) at the same proportion. Instead, the removal of toluene by TCR (73%) could be principally due to the absorption by SBP (89.5%) followed by the adsorption by CB (67%). Finally, the removal of xylene by TCR (86.4%) should be due to the removal by CB (86.8%) and SBP (88.6%) at the same proportion.

4.3.2 Sorption Isotherms for gasoline, toluene and xylene

Table 4.16 shows the parameters for linear, Langmuir and Freundlich isotherms for gasoline aqueous samples and for toluene and xylene in gasoline aqueous samples. The r^2 and the P values (probability of the model) indicate that the results fit the linear isotherm quite well, which could suggest the partition mechanism between the solvent and the sorbent is the principal sorption process. The r^2 and P values obtained for Freundlich isotherms (figure 4.54) were better than the values for Langmuir isotherm. The 'n' value in Freundlich's relationship is related to the sorption behavior. The 'n' values for the sorption of gasoline, toluene and xylene using TCR were 0.74 ± 0.01 , 0.85 ± 0.05 and 0.70 ± 0.02 , respectively. These values are lower than 1 which would indicate the sorption process is favored at high starting concentrations of the adsorbate. In addition, the small differences among 'n' values would suggest similar sorption mechanisms for gasoline and its components (toluene and xylene) in aqueous solutions.

TABLE 4.16 Linear, Langmuir and Freundlich parameters for gasoline, toluene and xylene sorption by TCR.

		Gasoline	Toluene	Xylene
Linear	r^2	0.99 ± 0.01	0.99 ± 0.01	0.98 ± 0.01
	K	5.07 ± 0.07	0.58 ± 0.05	1.54 ± 0.07
	P	5 ± 2	4 ± 1	7 ± 1
Langmuir	r^2	0.97 ± 0.02	0.952 ± 0.003	0.84 ± 0.02
	K_b	0.39 ± 0.04	0.44 ± 0.09	1.38 ± 0.03
	q_m	6.0 ± 0.8	0.8 ± 0.2	0.43 ± 0.02
	P	7 ± 2	10 ± 1	16.1 ± 0.2
Freundlich	r^2	0.991 ± 0.004	0.980 ± 0.002	0.941 ± 0.007
	n	0.74 ± 0.01	0.85 ± 0.05	0.70 ± 0.02
	K_f	4.0 ± 0.1	0.55 ± 0.05	1.87 ± 0.08
	P	12 ± 7	3.0 ± 0.3	6 ± 1

K: Linear parameter (Uptake capacity mg/g) r^2 : Linearity of the model P: Probability of the model
 K_b : Langmuir parameter (Uptake capacity mg/g) q_m : Langmuir model parameter
 K_f : Freundlich parameter (Uptake capacity mg/g) n: Freundlich parameter (Sorption behavior)

The K_f (mg adsorbate/g sorbent) in Freundlich's relationship represent the loading factor or uptake capacity of the sorbent. The K_f for gasoline in water samples using TCR as sorbents was 4.0 ± 0.1 mg/g. And, the K_f for toluene and xylene contained in the gasoline aqueous samples were 0.55 ± 0.05 mg/g and 1.87 ± 0.08 mg/g (table 2 and figure 4.55). The uptake capacity for gasoline is higher than the values for toluene and xylene because it represents the sorption of all components present in the gasoline. The K_f values for toluene

and xylene in gasoline water samples are close to the reported values (Kim, Park et al. 1997; Guanasekara, Donovan et al. 2000; Alamo-Nole, Perales-Perez et al. 2011). The organic molecules can be adsorbed onto the carbon black and they also have the ability to migrate between polymeric chains in adsorption and absorption processes respectively (Iwai, Ishidao et al. 1991; Soney, Sabu et al. 1996; Ranimol, Kuruvilla et al. 2007). The advantage of using TCR compared to commercial sorbents is the extremely low cost (\$0.15/lb in Puerto Rico). The used granular recycled TCR can also be packed in columns for continuous systems.

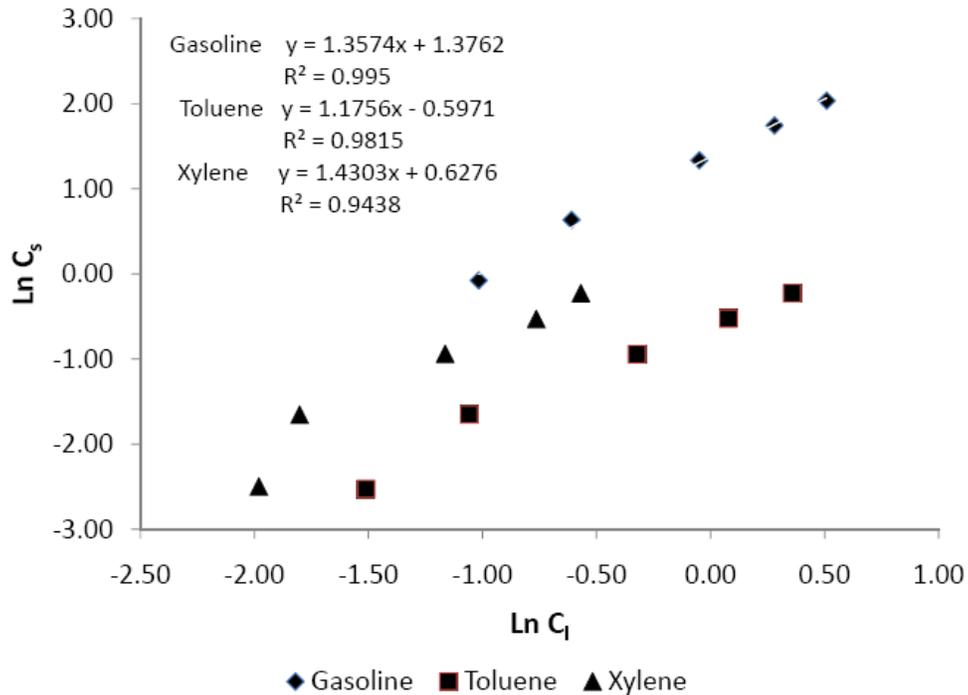


Figure 4.55 Freundlich isotherms for gasoline, toluene and xylene sorption by TCR

4.4 Sorption experiments in air

4.4.1 Kinetic, Isotherms and Scatchard plots for toluene sorption experiments

The isotherm was plotted using the concentration of toluene that was sorbed by TCR at different pressures. Figure 4.56 shows the isotherm for toluene using TCR as sorbent.

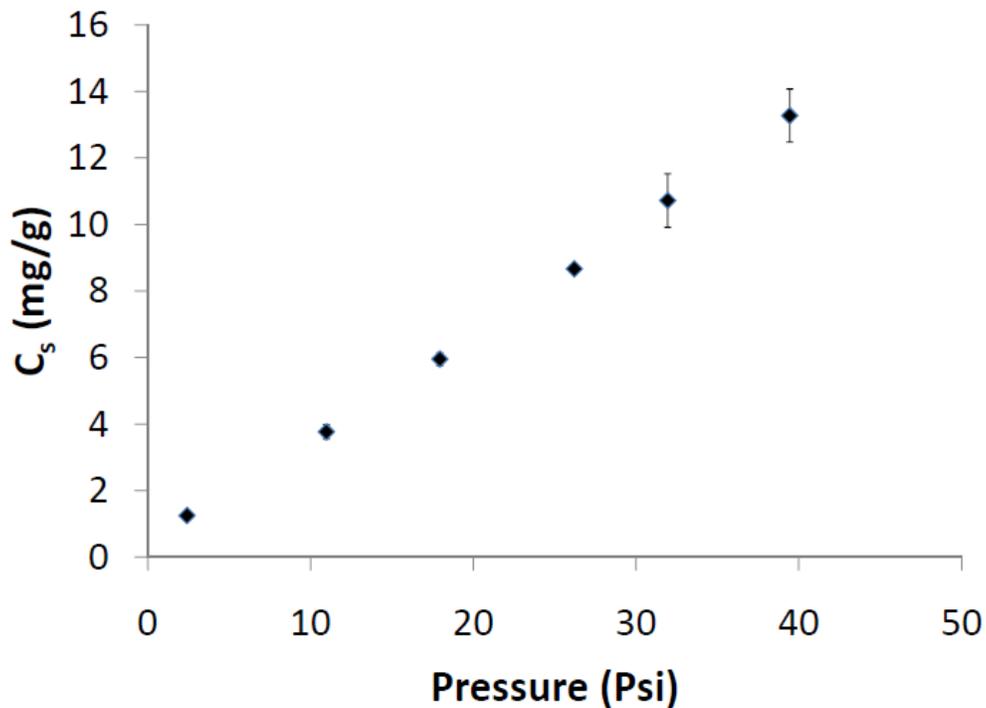


Figure 4.56 Isotherm for toluene sorption in gas phase by TCR.

The Langmuir isotherm assumes that the adsorption sites are occupied by the adsorbates forming a monolayer. The equation generated gives some parameters that describe the sorption process (Stumm and Morgan 1996). Figures 4.57 shows the results adjusted to

Langmuir equation. The high dispersion in the highest point in the isotherm is due to the fact that these values correspond to the lowest real values.

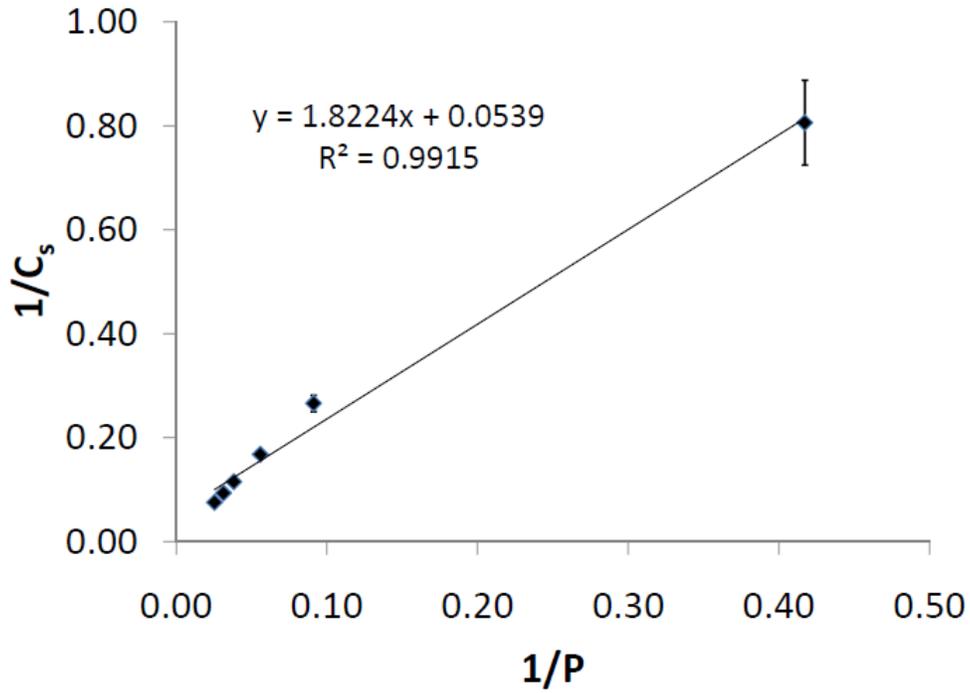


Figure 4.57 Langmuir isotherm for toluene sorption in gas phase by TCR.

The Freundlich equation uses a logarithmic relation to obtain information about the sorption process. This isotherm assumes that the sorbent has a heterogeneous solid surface (Stumm and Morgan 1996). Figure 4.58 shows the Freundlich isotherm for toluene using TCR.

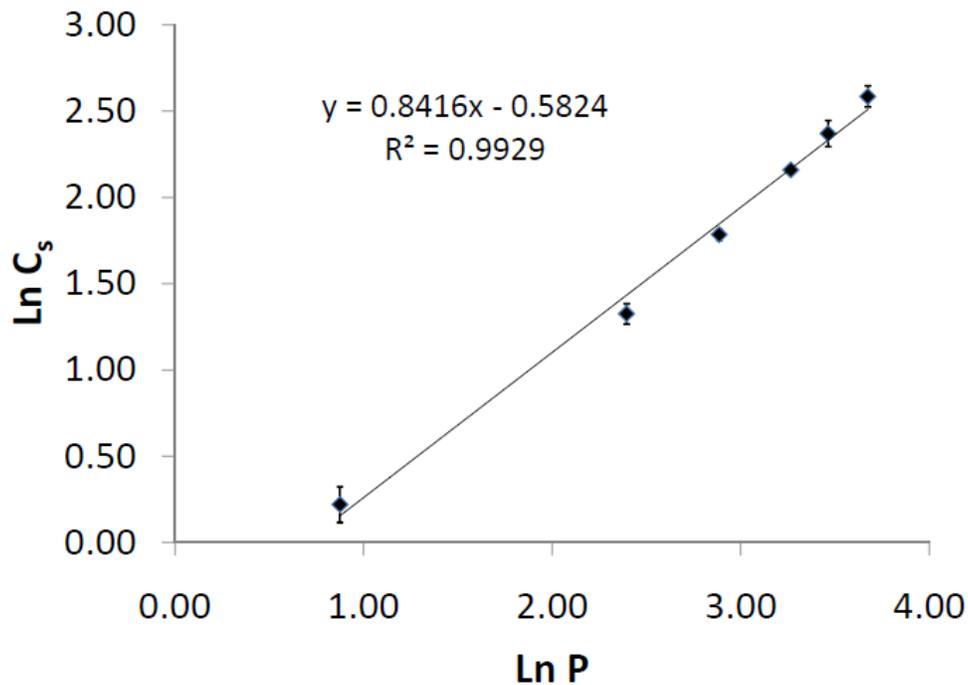


Figure 4.58 Freundlich isotherm for toluene sorption in gas phase by TCR.

The plot obtained through Scatchard relation can be used to evaluate the sorption process. The Scatchard profile of figure 4.59 clearly shows a plot with only one negative slope. According to Alamo (Alamo-Nole, Perales-Perez et al. 2010), toluene should have been absorbed by the TCR by combining both the adsorption by CB and absorption by SBP. Although a plot with different slopes was expected, the one obtained suggests that the toluene sorption in gas phase is a process where one process (adsorption or absorption) was the most dominant.

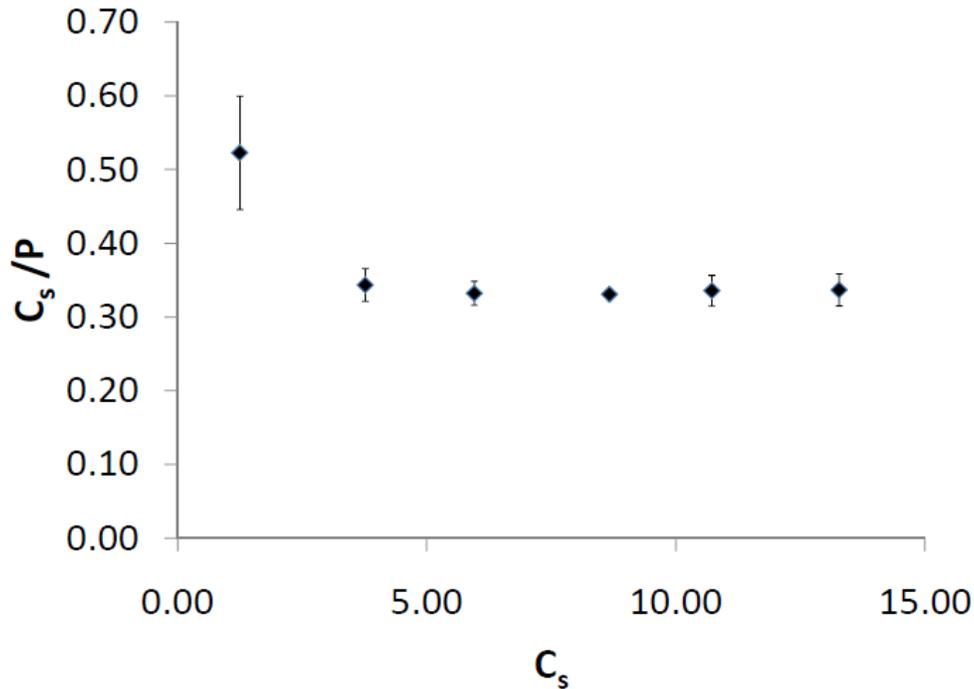


Figure 4.59 Scatchard plot for toluene sorption in gas phase by TCR.

4.4.2 Freundlich isotherms parameters for toluene sorption experiments

Table 4.17 show the parameters for linear, Langmuir and Freundlich isotherms and the P values (probability of the model) for toluene sorption by TCR in gas phase. The P values obtained for Freundlich isotherm was lower than the P values obtained for Langmuir isotherm which means the results fitted quite well the Freundlich relation. There are two Freundlich parameters related to sorption process. The ‘n’ parameter is related to the sorption behavior at different concentrations of the adsorbates. A sorption process that is more favorable at high adsorbate concentrations should show an ‘n’ value lower than 1. The K_f (mg adsorbate/g sorbent) parameter is related to the sorption capacity of the sorbent. High K_f values should represent high sorption capacity.

The 'n' value for the sorption of toluene in gas phase by TCR was 1.19 ± 0.08 . This value is slightly higher than 1, which means the sorption is slightly higher at low concentrations of toluene than at high concentrations. This value close to 1 should indicate that absorption processes could be the most dominant as discussed above. An 'n' value of 1 indicates that the process does not depend on adsorbate concentration but it depends on a partition coefficient which represents an absorption process.

The K_f (uptake capacity) for toluene in the gas phase using TCR was 0.54 ± 0.04 mg/g. This K_f value is higher than the K_f value (0.239 ± 0.004 mg/g) for the sorption of toluene in aqueous phase using TCR. The presence of water in the system should increase the hydrophobic repulsions between the water film on the TCR and the toluene molecules. In the gas phase there is no water therefore the sorption process only depends on the partition coefficient of toluene between the solid and the gas (Stumm and Morgan 1996). The CB nanoparticles in the TCR are confined in the polymeric matrix and only a fraction of them would be accessible, therefore the organic molecules should have to migrate between polymeric chains in an absorption process (Iwai, Ishidao et al. 1991; Soney, Sabu et al. 1996; Ranimol, Kuruvilla et al. 2007).

TABLE 4.17 Isotherms parameters for the removal of toluene in gas phase using TCR

Isotherm	Parameters	Toluene
Linear	r^2	0.996 ± 0.003
	m	0.33 ± 0.03
	P	5 ± 5
Langmuir	r^2	0.990 ± 0.006
	X_m	19 ± 4
	B	0.03 ± 0.01
	P	14 ± 4
Freundlich	r^2	0.991 ± 0.06
	K_f (mg/g)	0.54 ± 0.04
	n	1.19 ± 0.08
	P	8 ± 3

m : slope
i : intercept
 r^2 : R square
n : Freundlich constant

K_f : Freundlich constant
b : Langmuir constant
 X_m : Maximum amount adsorbed

4.5 Sorption and biodegradation of phenanthrene with modified crumb rubber

4.5.1 Sorption and biodegradation of phenanthrene

Figure 4.60 shows the blank for phenanthrene in the bioreactors used. The experiment evaluated the volatility of phenanthrene under the working conditions. The volatility of phenanthrene was low. The initial concentration was 0.965 ± 0.007 mg/L (2.89 ± 0.02 mg) and the volatility after 4 days was $64 \pm 4\%$ which means the concentration decreased to 0.62 ± 0.04 mg/L (1.8 ± 0.1 mg).

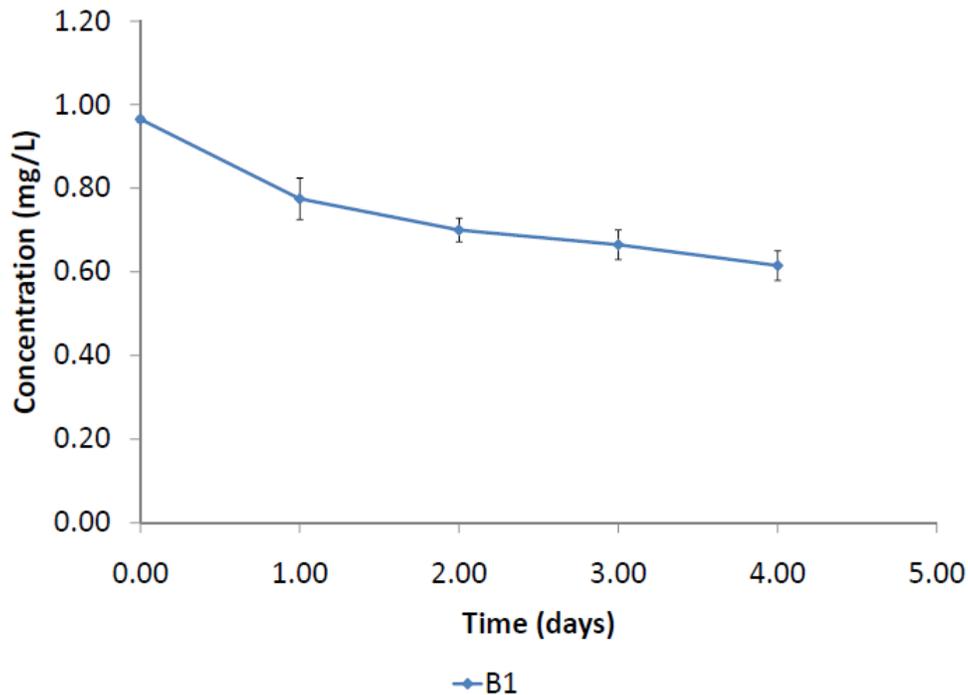


Figure 4.60 Blank for phenanthrene (B1). Air flow 300 mL/min, 30° C and pH 7.0.

Figure 4.61 shows the blank for the removal of phenanthrene by TCR in the bioreactors under the working conditions. The experiment allowed determining the saturation of TCR by phenanthrene at 30° C, pH 7.0 and a flow of 300 mL/min. Phenanthrene was added at different time intervals trying to maintain the concentration of phenanthrene around 1.0 mg/L. In this case it was necessary to add 8 times phenanthrene to maintain the concentration constant. After 4 days, 24 ± 2 mg of phenanthrene were added and the TCR adsorbed 21.3 ± 0.8 mg which represent 88 ± 4 % of phenanthrene removal.

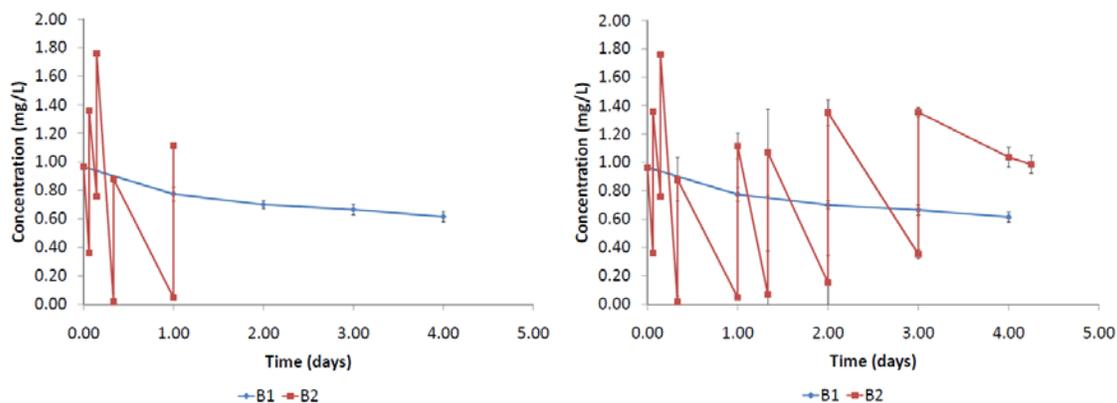


Figure 4.61 Blank for (B1) phenanthrene and removal of phenanthrene by TCR (B2) after 1 and 4 days of contact time. Air flow 300 mL/min, 30° C and pH 7.0.

Figure 4.62 shows the sorption and the degradation of phenanthrene by the TCR modified at 30° C, pH 7.0 and a flow of 300 mL/min. In the experiments the pH value was maintained constant at 7.0 using 5% HCl. After 4 days, 25 ± 2 mg of phenanthrene were added and the TCR modified adsorbed and degraded 25 ± 1 mg which represents 99 ± 1 % of phenanthrene removal. These results evidenced that the microorganism degraded approximately 10% of the phenanthrene removed in the first 4 days. The figure 4.64 also shows that the degradation continued for 3 more days. After 7 days, 38 ± 4 mg of phenanthrene were added and the TCR modified adsorbed and degraded 35 ± 5 mg. These results evidenced that the microorganism degraded around 10 mg between the 4th and 7th day.

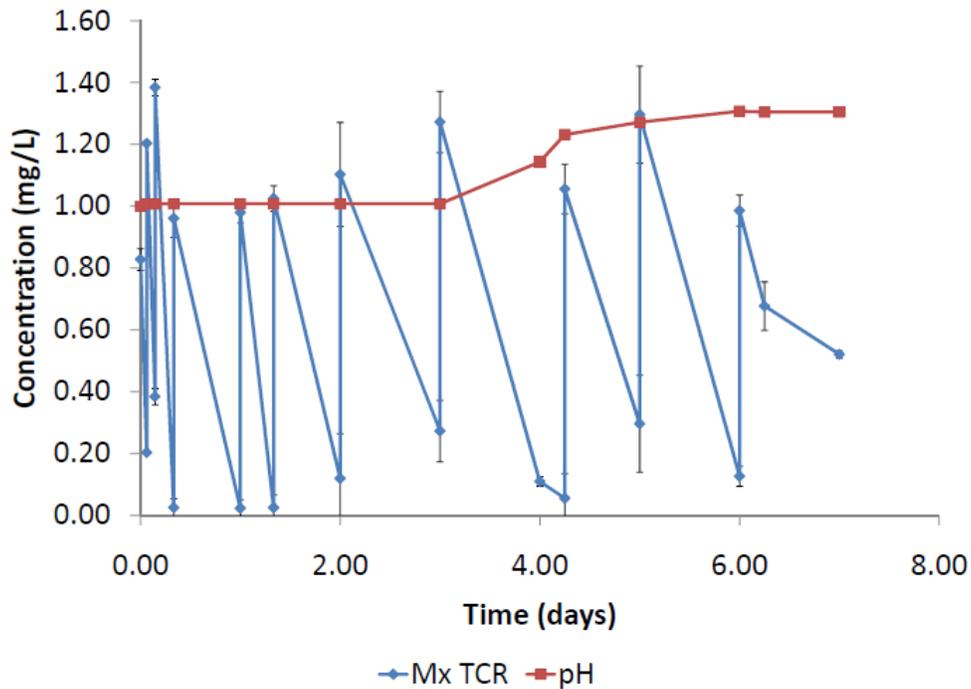


Figure 4.62 Removal and biodegradation of phenanthrene (Mx TCR) by TCR after 7 days of contact time. Air flow 300 mL/min, 30° C and pH 7.0.

Figure 4.63 shows the sorption and the degradation of the TCR modified day by day. There is a tendency that the TCR modified remove lightly more phenanthrene in the first 3 days. There is an evident difference between the removal of modified TCR and unmodified TCR at the 4th day. These results showed that the sorption of phenanthrene by TCR is the principal mechanism in the first 3 days, however the degradation by the bacteria at the day 4th becomes evident. It is also evident that the blank or volatility of the phenanthrene (green bars) is very low.

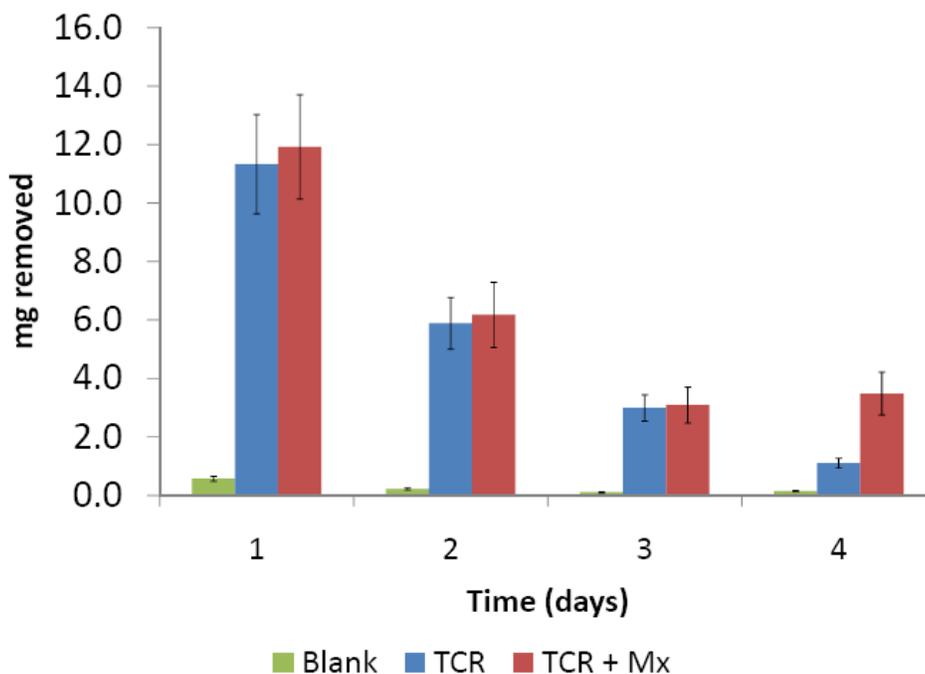


Figure 4.63 Phenanthrene (mg) removed by TCR and microorganism immobilized onto TCR (TCR + Mx).

Also, after the day 4th the solution turned a light yellow (figure 4.64), which indicated that the bacteria were released to the water solution. The release of the bacteria could occur because it covered the entire TCR surface and the posterior growth continued in the aqueous phase. When the pH value was monitored (figure 4.62, red line), the pH value (normalized) was stable for 4 days, after this time the pH increased probably as a result of bacteria metabolites in solution.



Figure 4.64 Removal and Biodegradation of phenanthrene by TCR. Air flow 300 mL/min, 30° C and pH 7.0.

CONCLUSIONS

- The excellent capability of waste tire crumb rubber (TCR) as a sorbent for organic contaminants such as VOCs and PAHs in aqueous solutions at pH 6.0 has been verified.
- The sorption of VOCs and PAHs onto TCR is due to its principal components: CB and SBP. The Scatchard plots for TCR suggest multi-interactions between the adsorbates and the sorbent, which is due to negative and positive cooperativities among its components. The Scatchard plots for CB and SBP suggest one kind of interaction between the adsorbate and the sorbent. An extra interaction can be due to the proximity of the adsorbates to the solid/liquid interface.
- The removal by CB and SBP were higher than that by TCR. The confinement of the CB in the polymeric matrix could reduce the available sorption sites of the CB. The polymerization of the matrix during the vulcanization process could modify the sorption sites of the SBP. These two processes should decrease the sorption capability of the TCR.
- The removal efficiency for VOCs was xylene, ethylbenzene and finally toluene. The removal efficiency for PAHs was phenanthrene, acenaphthene and finally acenaphthylene. This pattern may be due to the hydrophobicity of the contaminants. Compounds with high solubility should remain more stable in the aqueous phase than compounds with low solubility.
- The sorption processes for VOCs and PAHs are not affected by the change of TCR concentration in single-component system.

- The results of VOCs and PAHs fit the Freundlich isotherm. The r^2 values obtained from the regression analyses were supported by low P values.
- TCR has the capacity to remove gasoline components from aqueous solutions. The single ion monitoring mode in the GC-MS analysis allowed quantification of toluene and xylene in the gasoline samples.
- TCR was modified with *Pseudomonas* sp. This modified sorbent showed the capacity to remove and biodegrade phenanthrene in aqueous samples.
- The low cost of TCR (\$0.15/lb in Puerto Rico) compared to CB (\$64/lb), activated carbon (\$ 80/lb) and SBP (\$40/lb), and its capability to remove VOCs and PAHs support the idea of using TCR as a sorbent to remove organic contaminants form aqueous effluents.

RECOMENDATIONS

- The addition of points among the first minutes of the kinetic experiments is desirable to evaluate and calculate kinetic parameters.
- A mixture of CB and SBP at the actual concentrations of the TCR should confirm if the sorption by TCR is not the addition of the sorption by CB and SBP. The sorption process by TCR is due to CB and SBP but the processes during the tire fabrication reduce its sorption capacity.
- Although desorption of VOCs was observed during the experiments of the removal of toluene in the gas phase, a methodology to quantify this desorption in aqueous and gas phase is necessary.

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APPENDIX A QUALITY CONTROLS

The equation used to calculate the % error was:

$$\%error = \frac{(practical\ value - theoretical\ value)}{theoretical\ value} * 100$$

APPENDIX B BIOCHEMICAL ASSAYS APPLIED TO THE ISOLATED BACTERIA

TABLE 0.1 Biochemical assays for the isolated microorganism.

Essay	Result	Essay	Result
Lactose	(-)	Methyl red - VP	(-)
Dextrose	(-)	Urea	(-)
Manitol	(-)	Nitrate	(+)
TSIA	(-)	Gelatin	(-)
Indole	(-)	Motility	(+)

The lactose, dextrose and manitol assays evaluated the capacity of the bacteria to ferment these carbon sources. Triple sugar iron agar (TSIA) evaluates the capacity of the bacteria to ferment sugars. The indole test evaluates the production of indole through the tryptophanase enzyme. Methyl red VP differentiates between enterobacteriaceae species. The urea assay determines the ability of the bacteria to hydrolyze urea and produce ammonia. The nitrate assay evaluates the capacity to degrade nitrate. Gelatin assay views the capacity to degrade the protein gelatin. The motility test uses a semisolid media to evaluate the mobility of the bacteria.

APPENDIX C ASSAY OF SALT WATER RESISTANCE APPLIED TO THE PSEUDOMONA SP.

Figure 0.1 shows the results of the resistant of the bacteria to salt water medium (SWM). The concentration of the SWM was diluted at 50% with different solutions: A: blank (MM), B: 50% SWM in MM, C: 50% SWM in MM without micronutrients and D: 50% SWM in distilled water. The presence of salts and micronutrients should modify the degradation and production of pigments. This experiment is the first step to isolate bacteria which can tolerate 100% SWM that can be used in the degradation of phenanthrene in sea water.

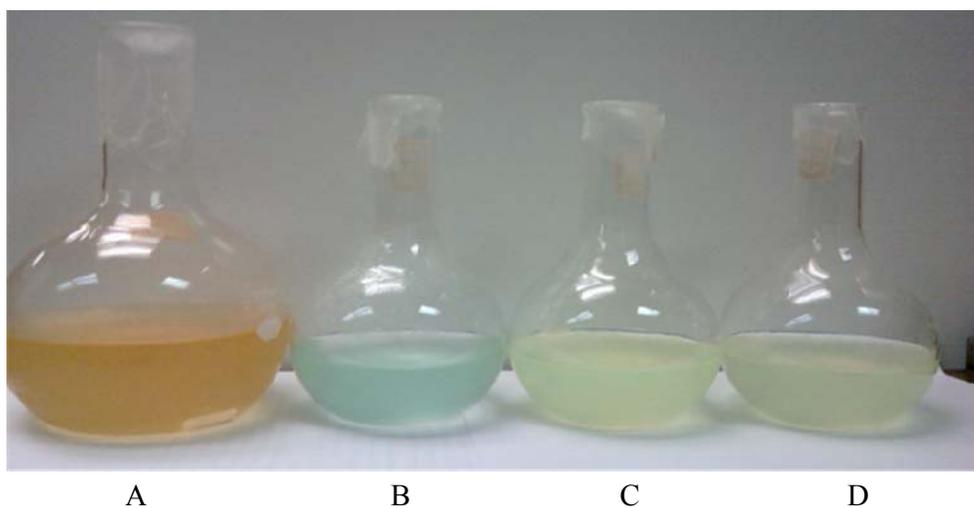


Figure 0.1 Microorganism at different concentrations of salt water medium (SWM). A MM, B 50% SWM in MM, C 50% SWM in MM without micronutrients, and D 50% SWM in distilled water.

APPENDIX D CHARACTERIZATION OF FLUORESCENT COMPOUND PRODUCED BY *PSEUDOMONA SP.*

The pigment produced during the fermentation was analyzed before and after HPLC separation using optic methods such as a UV-VIS spectrophotometer and spectrofluorometer. The grown media (figure 0.2a) was filtered using a 0.2 μm membrane and was analyzed. The filtered media was separated in an 1100 HPLC Agilent with a FLD detector using the excitation and emission wavelength obtained in the prior experiments. The figure 0.2b shows the emission of the pigment excited at 407 nm.

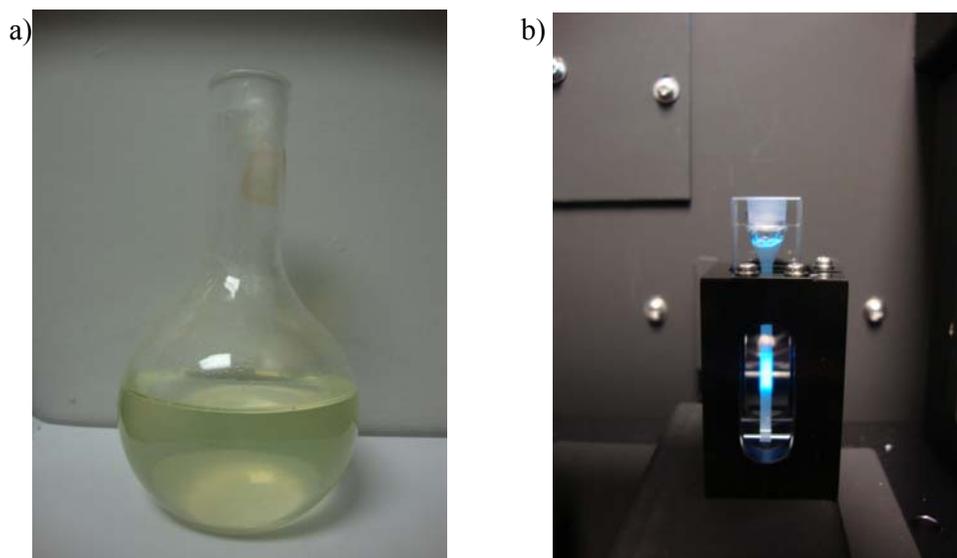


Figure 0.2 Grown medium a) after 72 hours of inoculation and b) irradiated at 407 nm.

The Figure 0.3 shows the UV-VIS spectrum for the pigment separated in the HPLC. The peak at 407 nm was used as an excitation wavelength in fluorescence experiments. Figure 0.4 shows the spectra for the pigment separated in the HPLC (sample) and a 100 mg/L standard

of fluorescein (blue line). These results confirmed that the compound is not fluorescein.

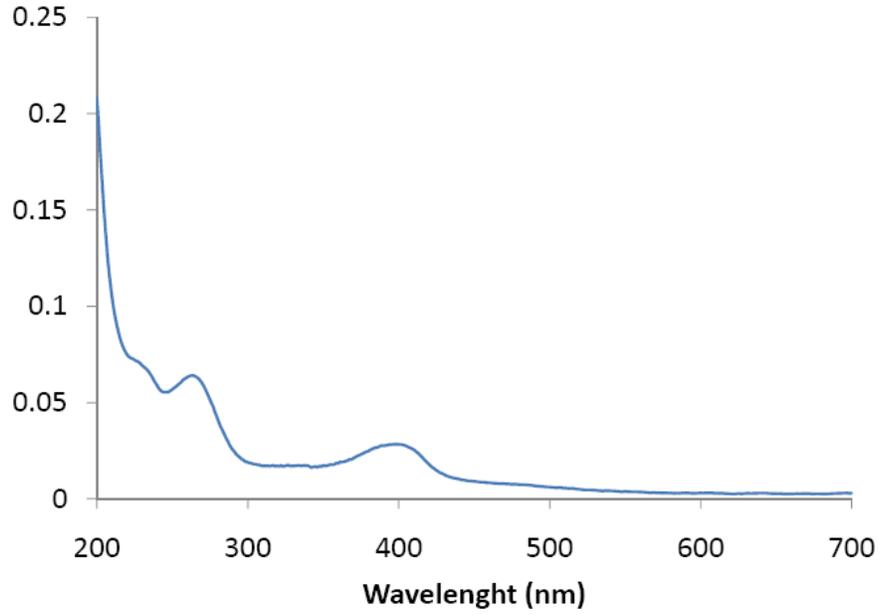


Figure 0.3 Spectrum UV-VIS of pigment separated by HPLC.

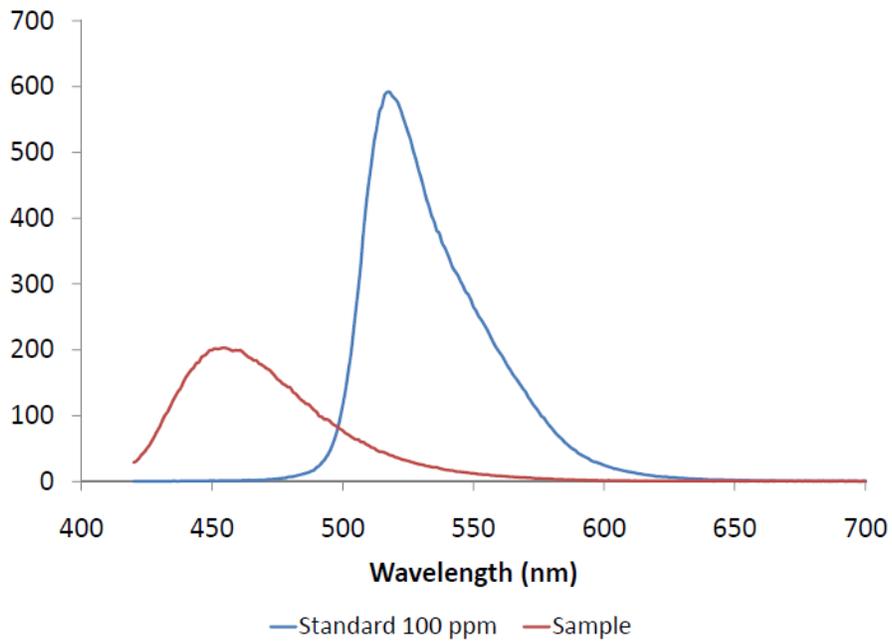


Figure 0.4 Emission spectra of 100 mg/L standard of fluorescein (blue line) and pigment separated by HPLC (red line). Excitation at 407 nm and emission at 455 nm.