Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.719350

49 (2012) 296–306
November

Taylor & Francis
Taylor & Francis Group

Use of recycled tires crumb rubber to remove organic contaminants from aqueous and gaseous phases

Luis Alamo-Nole[a,*], Oscar Perales-Perez[b], Felix R. Roman[a]

[a]*Chemistry Department, University of Puerto Rico at Mayagüez, PO Box 9000, Mayagüez, PR 00681-9000, USA*
Tel. +1 787 832 4040x2501; email: luis.alamo@upr.edu
[b]*Department of Engineering Science and Materials, University of Puerto Rico at Mayagüez, PO Box 9044, Mayagüez, PR 00681-9044, USA*

Received 3 November 2011; Accepted 28 June 2012

ABSTRACT

Tire crumb rubber (TCR) was used to remove poly-aromatic hydrocarbons (acenaphthene and phenanthrene) and gasoline components in aqueous phase and toluene in gaseous phase. The initial concentrations were below the solubility of each contaminant. To better understand the role of the main components of TCR, the removal was also evaluated using carbon black (CB) and styrene-butadiene polymer (SBP). The Scatchard plots suggested multiple interactions between adsorbates and TCR, whereas a single interaction became evident for CB and SBP. The removal of gasoline components, and toluene and o-xylene in gasoline was evaluated using total ion current mode and selective ion monitoring mode, respectively. A gas chromatographer was modified to evaluate the removal of gaseous toluene. Toluene was injected at a rate of 30 μL/h. The isotherm was elaborated using pressures between 2.5 and 40 psi. The maximum uptake capacities (K_f) for TCR calculated from Freundlich's equation for acenaphthene and phenanthrene were 3.32 and 54.6 mg/g, respectively; for total gasoline, toluene and xylene in gasoline were 4.0, 0.55 and 1.87 mg/g, respectively; and for gaseous toluene was 0.54 ± 0.04 mg/g. Its proven sorption capacity and low cost make TCR a promising sorbent for organic contaminants in aqueous and gaseous phases.

Keywords: Waste tire; Crumb rubber; Sorption; Recycling; Water treatment; Scatchard plot

1. Introduction

The US Environmental Protecting Agency (EPA) regulates the content of volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls are organic contaminants of water, air, and soil. The exposure to VOCs such as toluene, benzene, and xylene can produce damage to the central nervous system, and damage to the kidneys and liver. Long-term exposure to these pollutants is related with cancer [1]. PAHs are recalcitrant compounds and they can be carcinogenic and constitute risk for human health [1–3]. Gasoline is a complex mixture of organic volatile and semivolatile compounds. Gasoline is considered a hazardous compound by the International Agency for Research on Cancer [1].

Although these organic contaminants are poorly soluble in water, some of them can be mobilized into the aqueous phase due their solubility, e.g. the solubility of toluene and xylene in water is 515 and 200 mg/L, respectively. Leaking or spilling of these compounds into rainwater makes the pollution problem even worse [3]. PAHs can also be mobilized into the aquatic environment through discharges from industrial

---

*Corresponding author.

and domestic sewage effluents, leakages of PAHs containing materials (e.g. oils), runoff from paved roads, parking lots, and wood preservation facilities [4].

The removal of VOCs and PAHs in water by multiple sorbents has been reported in the technical literature [5,6]. The most common sorbent used to remove organic contaminants such as VOCs and PAHs from water is activated carbon [7–9]. Other sorbents such as zeolites or polymers [10] and electrochemical and photochemical techniques [11,12] can be used, but their high cost makes their applicability difficult [10]. The use of cheap material or recycled material such as tire crumb rubber (TCR) [13–16], carbon slurry [17–19], agricultural waste [20–32], algae [33,34] among others, have been investigated as an inexpensive option to remove organic and inorganic contaminants from water.

The USA generated approximately 259 million scrap tires in 2005. After markets use approximately 80% of them whereas the remainder is stockpiled or land filled [35,36]. Some uses of recycled TCR include floor mats, sound barriers, rubberized sidewalks, asphalt-rubber, among others [37]. TCR is a complex matrix that contains carbon black, styrene-butadiene polymer (SBP), zinc oxide, and extender oils, among other components [38]. Some components of the TCR have the capacity to remove VOCs. The polymeric matrix containing SBP can absorb these contaminants between its chains in an absorption process [39,40]. Carbon black (CB) has an adsorption capacity comparable to that of activated carbon [41,42]. Based on the fact that both CB and the elastomeric matrix can exhibit sorption capabilities, the removal of target species through absorption/adsorption mechanisms becomes a viable process [13,14,43,44].

To the best of our knowledge, this is the first study about the sorption of PAHs and gasoline components from water samples, and toluene from gaseous samples using TCR. In addition, the systematic evaluation of CB and SBP as the components responsible for the sorption behavior of vulcanized rubber has also been conducted. Total ion current mode (TIC) for gasoline and selective ion monitoring mode (SIM) for toluene and o-xylene in gasoline were used to evaluate the removal of these contaminants by TCR. The use of Scatchard type plots is proposed as a complementary tool to identify the interactions between the adsorbate and the sorbent.

2. Material and methods

TCR mesh 14–20 from REMA Inc. (Caguas, PR, USA) with an average diameter of 2.45 mm was washed with deionized water for 24 h and dried at room temperature prior to use. Acenaphthene, phenanthrene, toluene, and xylene were ACS certified grade. The gasoline used was Regular Texaco. Concentrations below their limit solubility in water were used to assure their solubility during sorption tests. Amorphous CB N330 (density 1.7–1.9 g/cm^3) was purchased from Sid Richardson Carbon Company (CAS 1333-86-4). Poly(styrene-co-butadiene) $[CH_2CH(C_6H_5)]_x(CH_2CH{=}CHCH_2)_y$ from Sigma-Aldrich (CAS 9003-55-8) was trimmed to a similar size as TCR used in this study.

2.1. Sorption experiments in aqueous phase

Stock solutions were prepared in acetonitrile. Standards dilutions in water were placed in 120 mL amber bottles leaving 10 mL of headspace, capped with septa and sealed with paraffin. Standard solutions were magnetically stirred and sampled (in triplicates) after 20 min of contact time using the solid-phase microextraction technique (SPME) [45]. A polidimethyl siloxane (10 μm) SPME fiber was introduced into the headspace of the 120 mL amber bottles followed by injection into the Hewlett Packard 5890 gas chromatography coupled to a HP 5970 mass spectrometry (GC-MS) (Palo Alto, CA, USA) with electron impact ionization of 70 eV. The column used was a J&W DB-225 capillary column (30 m × 0.25 mm × 0.3 pm). Quality controls samples were prepared at concentrations of middle calibration standard and used to evaluate both the integrity of the SPME fiber and the calibration status. The *Q*-test was used to evaluate outlier values.

2.1.1. PAHs

Aqueous solutions of acenaphthene (0.03–3.00 mg/L) and phenanthrene (0.03–1.00 mg/L) were put in contact with TCR, CB, and SBP at concentrations of 5.0, 1.5, and 3.0 g/L, respectively. Low concentrations of PAHs below solubility in water were used to assure complete solubility in aqueous phase. The concentrations of CB and SBP were selected based on their actual concentration in commercial TCR matrix (30% w/w and 60% w/w, respectively) [36]. All experiments were carried out (in triplicates) under magnetic stirring (500 rpm) at 25°C (room temperature) and pH 6.0. The SPME technique requires a constant stirring and temperature to be reproducible. Different rpm values were evaluated and 500 rpm was the optimum speed. The value of pH 6.0 was picked because PAHs do not have the capacity to change the pH of the water, so that, waste water containing these contaminants should be lightly neutral. Also, the sorption capacity of TCR was evaluated at different pH values and a small decrease (5%) in the removal was observed at pH low as 1.5 (data not showed). The components of TCR (CB and SBP) and the PAHs are nonionizable compounds which do not affect the sorption process.

SIM mode at 154 and 178 *m*/*z* were used to quantify acenapththene and phenanthrene, respectively. The calibration curve used to quantify low concentrations of phenanthrene gave a detection limit of 0.0006 mg/L and a quantification limit of 0.0020 mg/L.

2.1.2. Gasoline

The concentration of gasoline standards ranged between 0 mg/L and 40 mg/L and the concentrations of toluene and xylene standards ranged between 0 and 5 mg/L. The removal of gasoline components was performed using the TIC mode and the area obtained from the sum of all integrated peaks was considered. TIC mode involves the monitoring of all ions generated during electron impact ionization. The removal of toluene and o-xylene contained in actual aqueous dilutions of gasoline was determined using SIM mode. SIM allows monitoring of specific ions formed during the ionization step, which facilitates the elimination of peaks that may interfere with the quantification of the analytes. The ions monitored for toluene were 65, 91, and 92 *m*/*z* and for xylene were 72, 91, and 106 *m*/*z*. All experiments were done in triplicates.

The removal of gasoline and its components by TCR was compared to the removal by TCR principal components: CB and 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. Finally, the removal of toluene and xylene in the gasoline water solutions was evaluated using SIM.

2.2. Sorption experiments in gaseous phase

2.2.1. Instrument configuration

A gas chromatographer Hewlett Packard 5890 series II (Palo Alto, CA, USA) was modified to conduct the experiments. Fig. 1 shows the system configuration. Compressed air was used as the mobile phase. The inlet pressure (60 psi) was regulated by an external gas regulator. The flow was regulated using a control valve located 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 μL/h) that was connected to the injector. An aluminum column with a length of 14.1 cm (5½″), a diameter of 3.3 cm (1¼″), and a volume of 60.8 ± 0.1 mL was used. The column was filled with approximately 25.0 g of TCR and placed inside the modified GC. It was connected to the injector and sampling port using copper lines. The oven, injector, and sampling port temperatures were set to 40, 250, and 180°C, respectively. The pressure of the system was monitored using the GC system display and this parameter was changed to elaborate the isotherm.

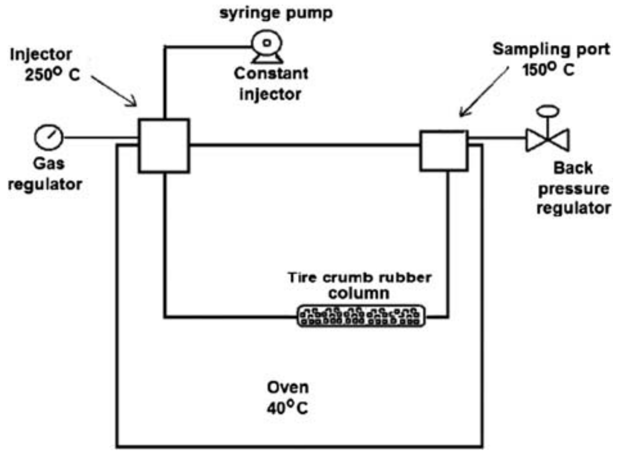

Fig. 1. System configuration. Modified Gas Chromatographer Hewlett Packard 5890 series II.

2.2.2. Gaseous toluene

The calibration curves were elaborated changing the injection rate of toluene between 0 (blank) and 30 μL/h for the pressures of 2.5, 10, 20, 25, 30, and 40 psi. Gas samples were collected at the sampling port (Port B) using a gas tight syringe (0.1 mL) and were analyzed by direct injection in a Hewlett Packard 5,890 gas chromatography coupled to a HP 5970 mass spectrometry (GC-MS) with electron impact ionization of 70 eV.

The column was heated in the GC system for 2 h to condition it and eliminate gases adsorbed onto TCR from the laboratory environment. Toluene was injected at a rate of 30 μL/h and 0.1 mL gas samples using a gas tight syringe were taken at specific times. The isotherm was elaborated using pressures of 2.5, 10, 20, 25, 30, and 40 psi. The flows generated at different pressures were measured using a digital flow meter and were used to calculate the toluene concentration. All experiments were done in triplicates.

2.3. Adsorption isotherms

The results from the sorption tests were fitted to Freundlich's isotherm (Eq. (1))

$$q = K_f C^{1/n} \quad \text{or} \quad C_s = K_f C_l^{1/n} \tag{1}$$

where q (C_s) is the weight of solute per unit weight of sorbent; "C" (C_l) is the concentration of the solute; and "n" and K_f (mg adsorbate/g sorbent) are Freundlich parameters.

Scatchard relationship (Eq. (3)), derived from Langmuir's equation (Eq. (2)), provided 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 sorption process would be suggested by a linear trend with one slope, whereas multiple slopes imply a multistage sorption process [46].

$$q = q_m \frac{K_b C}{1 + K_b C} \quad \text{or} \quad C_s = q_m \frac{K_b C_l}{1 + K_b C_l} \tag{2}$$

$$\frac{q}{C} = q_m K_b - q K_b \quad \text{or} \quad \frac{C_s}{C_l} = q_m K_b - C_s K_b \tag{3}$$

where, q_m is the number of binding sites in the sorbent and K_b is the association (affinity) constant.

The linearity of the isotherms was evaluated using the factor P (Eq. (4)), which indicates the probability that the experimental results fit the considered model, i.e. low P values indicates that the results fit the model [46].

$$P = \left(\frac{100}{N}\right) \sum_{i=1}^{i=N} \left[\frac{|q_{i(\exp)} - q_{i(\text{pred})}|}{q_{i(\exp)}}\right] \tag{4}$$

where, P is the probability, $q_{i(\exp)}$ is the experimental value, $q_{i(\text{pred})}$ is the calculated value for the model, and N is the number of replicates.

3. Results and discussion

3.1. Sorption experiments in aqueous phase

3.1.1. Sorption of PAHs

Under equilibrium conditions, 98.0% of acenaphthene was removed from 3.0 mg/L starting solutions whereas 99.4% of phenanthrene was removed from 1.0 mg/L starting solutions. The concentration of TCR was 5 g/L in both cases. No desorption of any adsorbate was observed after five hours of contact time. Acenaphthene (99.5%) and phenanthrene (99.%), respectively, were removed when starting 1.0 mg/L solutions of each organic were contacted with 1.5 g/L of CB. On the other hand, 96% of acenaphthene and 97% of phenanthrene were removed using 3.0 g/L of SBP. The sorption of PAHs by CB was slightly higher than the sorption by TCR. The CB in the TCR should be on the surface and in the polymeric matrix. This confinement could produce a decrease in the binding sites of the CB in the TCR which is reflected in a decrease in the removal.

The Scatchard plots corresponding to the three evaluated sorbents can be used for a qualitative assessment of the sorption process. The Scatchard profile for acenaphthene using TCR (Fig. 2(a1)) clearly shows both negative and positive slopes, which suggests more than one binding sites [47] due to the sorption capabilities of the main components of TCR. The different slopes also indicate that the results do not follow Langmuir relation [48]. Also, a convex curve formed between the first two slopes (between 0.00 and 0.20 mg/g in Fig. 2(a1)) suggests a negative cooperativity among the different binding sites. A concave curve formed between the last two slopes (between 0.20 and 0.60 mg/g in Fig. 2(a1)) suggests a positive cooperativity among the different binding sites [47,48]. The Scatchard plot for phenanthrene using TCR

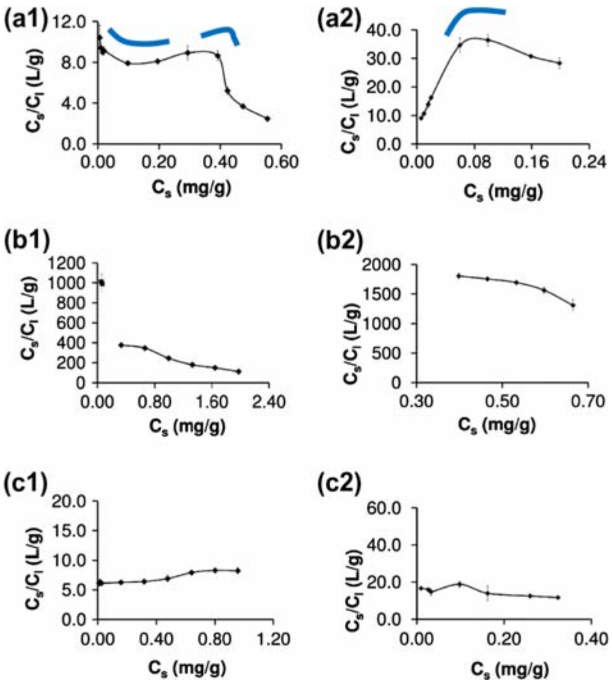

Fig. 2. Scatchard plots for acenaphthene (a1: TCR, b1: CB, and c1: SBP) and phenanthrene (a2: TCR, b2: CB, and c2: SBP).

(Fig. 2(a2)) also suggests more than one binding site. The concave curve suggests a positive cooperativity between the binding sites in the TCR [48].

The Scatchard plots suggest different interactions (cooperativities) between PAHs 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 (Fig. 3(b)). The molecules that are absorbed in the polymeric matrix near a CB particle could be adsorbed mainly on the surface of the CB, preventing the molecules from going inside the polymeric matrix in a negative cooperativity (Fig. 3(c)). 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 (Fig. 3(d)). Also, some molecules of the adsorbate can be adsorbed on the saturated CB (located on the surface) which can cause other molecules to be released rather quickly into the polymeric matrix in a positive cooperativity (Fig. 3(e)). These interactions can occur near CB particles inside the TCR, producing both negative and positive cooperativities.

The Scatchard plots suggest that these interactions could occur during the sorption process, but not necessary in a particular order. Accordingly, acenaphthene and phenanthrene should have been sorbed by the TCR by combining both the adsorption by CB and absorption by SBP. The absorption process 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. In addition, CB particles on the TCR surface should have adsorbed most of the acenaphthene at early contact times, whereas SBP would absorb the remaining adsorbate through the incorporation of these molecules within the chains of the crumb rubber polymeric matrix at prolonged contact times [15].

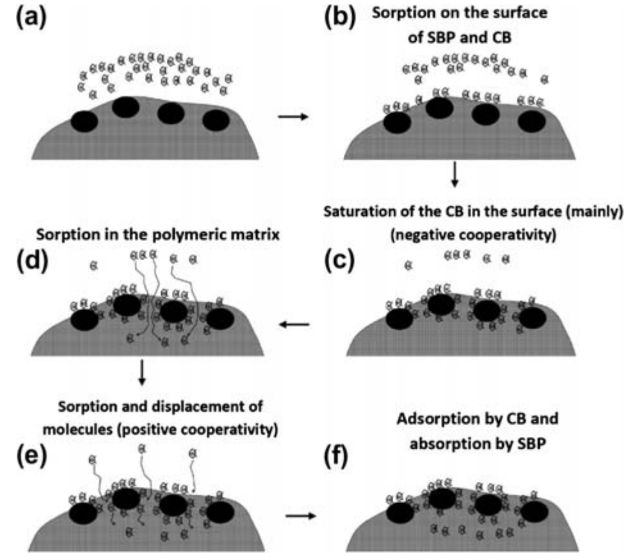

Fig. 3. Cooperativities produced during the sorption process by TCR components.

The Scatchard profiles for acenaphthene (Fig. 2 (b1)) and phenanthrene (Fig. 2(b2)) using CB shows negative slope in both cases. A plot with a negative slope indicates the interaction between the adsorbate and a simple binding site of the sorbent [48]. Acenaphthene and phenanthrene should have been adsorbed on the CB surface through van der Waals interactions including the London dipole–dipole interactions [49]. The points around 1,000 C_s/C_l in the Scatchard plot of acenaphthene (Fig. 2(b1)) could suggest an additional stage sorption process due to the diffusion of PAHs species through the water/solid interface.

A linear Scatchard profile, although exhibiting a positive slope, was observed for the absorption of acenaphthene by SBP (Fig. 2(c1)). An interaction between acenaphthene and a simple binding site of the SBP can be proposed in this case. The positive slope indicates that the interactions between sorbent and the adsorbate are inversely dependent at the used adsorbate concentrations [50]. The Scatchard plot for phenanthrene (Fig. 2(c1)) using SBP shows a linear profile with a negative slope which suggests a simple binding site of the SBP.

Table 1 summarizes the Freundlich parameters corresponding to the sorption of acenaphthene and phenanthrene by TCR, CB, and SBP. The "*P*" values indicate the 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 (not show here). Accordingly, only the data for Freundlich isotherms will be discussed herein.

The "*n*" and K_f coefficients are related to sorption behavior and loading factor of the sorbent, respectively. While "*n*" values lower than one suggest the removal capacity of the sorbent increases at high adsorbate concentrations, an "*n*" value close to one indicates that the removal capacity of the sorbent is independent of the adsorbate concentration. The sorption data obtained by using TCR, CB, and SBP sorbents fit the Freundlich's relationship quite well (Table 1 and Fig. 4). The "*n*" values for the sorption of acenaphthene and phenanthrene by TCR were 1.207 ± 0.004 and 0.655 ± 0.004, respectively. These "*n*" values suggest different sorption behaviors between these adsorbates. The sorption by TCR is increased at high concentrations of phenanthrene and at low concentrations of acenaphthene. The corresponding "*n*" values for the sorption of acenaphthene and

Table 1
Freundlich parameters for acenaphthene and phenanthrene sorption by TCR, CB, and SBP

		Crumb Rubber	Carbon Black	SBP (polymer)
Acenaphthene	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	3.32 ± 0.02	30 ± 1	8.6 ± 0.2
	P	22 ± 1	7.8 ± 0.4	9 ± 3
Phenanthrene	r^2	0.94 ± 0.01	0.97 ± 0.02	0.987 ± 0.001
	n	0.655 ± 0.004	1.6 ± 0.2	1.08 ± 0.03
	K_f	55 ± 5	80 ± 38	10 ± 2
	P	7.8 ± 0.5	5 ± 1	4.2 ± 0.7

K_f: Freundlich parameter (Uptake capacity mg/g).
r^2: R square.
n: Freundlich parameter (Sorption behavior).
P: Probability of the model.

phenanthrene using CB were 1.58 ± 0.02 and 1.6 ± 0.2. The similarity between these values suggests analogous sorption behavior of these adsorbates onto this sorbent. Also, the data are in agreement with other carbonaceous sorbents that used to remove PAHs [51].

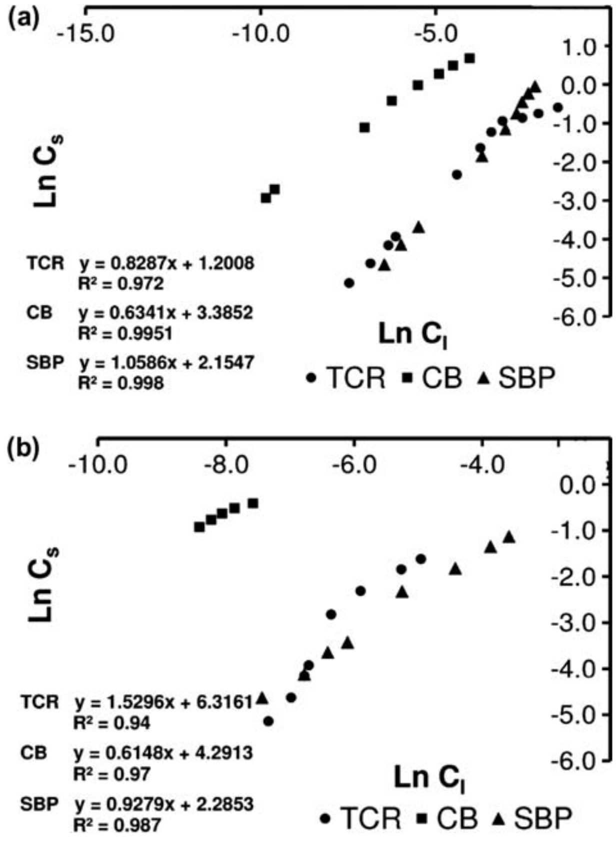

Fig. 4. Freundlich isotherms for (a) acenaphthene and (b) phenanthrene using TCR, CB, and SBP.

As Table 1 also shows, 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.

The uptake capacity (K_f) for phenanthrene (55 mg/g) was far larger than acenaphthene (3.32 mg/g) when TCR was used as sorbent (Table 1). The low solubility in water of phenanthrene (1.18 mg/L) [52] compared to acenaphthene (3.4 mg/L) [53] could explain the obtained differences in K_f values for those two adsorbates. Alamo et al. [15] have proposed that the low affinity of the adsorbate species for the solvent molecules (low solubility) should favor the displacement of the adsorbate from the aqueous into the solid phase (the sorbent). The uptake capacity (K_f) for acenaphthene and phenanthrene using CB was 30 ± 1 and 80 ± 38 mg/g, respectively. The corresponding K_f values when SBP was used as sorbent were 8.6 ± 0.2 and 10 ± 2 mg/g, respectively.

3.1.2. Sorption of gasoline

The TIC mode in a GC-MS system can be used to quantify the compounds present in a complex mixture such as gasoline. The TIC-chromatogram in Fig. 5 gives an idea of the complexity of the aqueous dilution of gasoline. Each peak in the chromatogram represents at least one compound present in gasoline. The expanded part in Fig. 5 shows the chromatogram after 11 min of retention time that represents compounds with a high boiling point, low volatility, and high molecular weight (including poly aromatic hydrocarbons).

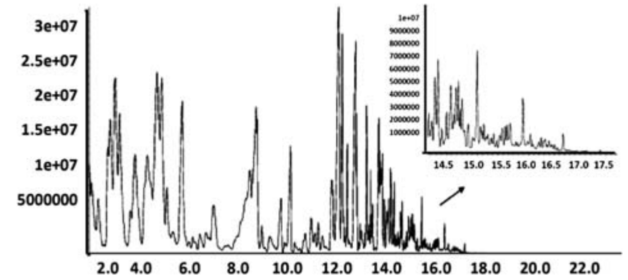

Fig. 5. TIC-chromatogram for gasoline (regular Texaco) aqueous solution (30 mg/L).

Fig. 6 shows the TIC-chromatogram of the aqueous dilution of gasoline after six hours of contact with 5 g/L of TCR. It can be observed that the intensity of all of the peaks decreased significantly when compared with the chromatogram of Fig. 5, which suggests that all the gasoline components were partially removed. The removal of gasoline components was 95.6 ± 0.4% from an initial concentration of 30 mg/L of gasoline water solution and using 5 g/L of TCR (Table 2).

The almost complete elimination of gasoline components after 11 min of retention time (expanded areas in Figs. 5 and 6) using 5 g/L of TCR suggests 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 sorbent [15]. Low solubility of those gasoline compounds should increase their removal through the increase in contact between adsorbates and sorbent that enhances the sorption through van der Waals forces [49].

3.1.3. *Sorption of toluene and o-xylene in gasoline*

The 65, 91, and 92 *m*/*z* ions for toluene and the 72, 91, and 106 *m*/*z* ions for o-xylene were 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, the ions for toluene were monitored for the first 5.5 min and then the ions for o-xylene.

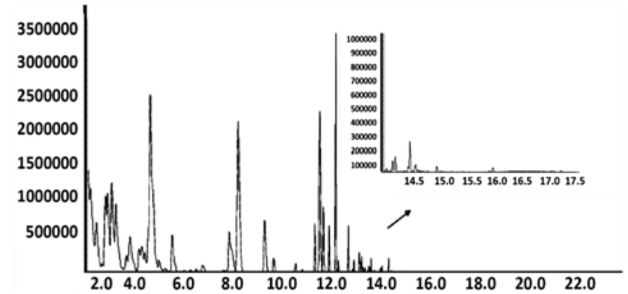

Fig. 6. TIC-chromatogram for gasoline aqueous solution (30 mg/L) after six hours of contact with 5 g/L of TCR.

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

Fig. 7 shows the chromatogram of gasoline water sample (40 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.

After six hours of contact with 5 g/L of TCR, the removal for toluene and o-xylene in a gasoline aqueous sample (30 mg/L) was 73 ± 2 and 86.4 ± 0.6%, respectively (Table 2). These results confirm that compounds with low solubility or high hydrophobicity (o-xylene) are more efficiently removed than compounds with low hydrophobicity (toluene) using TCR as sorbent [15].

The removal of gasoline components by TCR due to its components like CB and SBP has been reported [15]. CB as activated carbon has the capacity to remove inorganic and organic contaminants through adsorption mechanisms [7,53]. SBP is an organic polymer that can absorb or incorporate organic contaminants between its polymeric chains as an absorption mechanism [54]. The removal of total gasoline components by TCR is almost the same as the removal by its components (Table 2) which could suggest that the removal by TCR (95.6%) is due to the removal by 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 o-xylene by TCR (86.4%) should be due to the removal by CB (86.8%) and SBP (88.6%) at the same proportion.

Table 3 shows the parameters of linear, Langmuir, and Freundlich isotherms for gasoline aqueous samples and toluene and xylene in gasoline aqueous samples. The r^2 and the P values (probability of the model) indicate that the results fit quite well to linear isotherm, 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 (Fig. 8) were better than the

Table 2
Removal (%) of gasoline, toluene, and o-xylene in aqueous solution using TCR, CB, and SBP

	Gasoline	Toluene	o-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

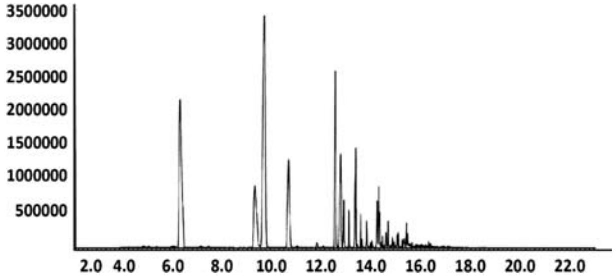

Fig. 7. SIM-chromatogram of gasoline aqueous solution (30 mg/L).

values for the 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 that the sorption process is more favorable at higher starting adsorbate concentrations. In addition, the small differences among "*n*" values would suggest similar sorption mechanisms for gasoline and its components (toluene and xylene) in aqueous solutions.

The K_f (mg adsorbate/g sorbent) in Freundlich's relationship represents the loading factor or uptake capacity of the sorbent. The K_f value for gasoline in water samples using TCR as sorbents was 4.0 ± 0.1 mg/g. The K_f values for toluene and xylene contained in the gasoline aqueous samples were 0.55 ± 0.05 and 1.87 ± 0.08 mg/g (Table 3 and Fig. 8). The uptake capacity for gasoline is higher than the values for toluene and xylene, because it includes the sorption of all the components present in the gasoline. The K_f values for toluene and xylene in gasoline water samples are close to the reported values [14,15,43]. The organic molecules can be adsorbed onto the CB and they also have the ability to migrate between polymeric chains, in adsorption and absorption processes, respectively [54–56].

The very low cost of TCR ($0.15/lb in Puerto Rico) compared to CB ($64/lb) and SBP ($40/lb) is an additional asset in using waste TCR material as sorbent to clean water streams and simultaneously expanding its recycling options. Although, some authors stated that

Table 3
Linear, Langmuir, and Freundlich parameters for gasoline, toluene, and o-xylene sorption by TCR

		Gasoline	Toluene	o-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).
K_b: Lagmuir parameter (Uptake capacity mg/g).
K_f: Freundlich parameter (Uptake capacity mg/g).
n: Freundlich parameter (Sorption behavior).
r^2: Leariy of the model.
q_m: Lagmuir model parameter.
P: Probability of the model.

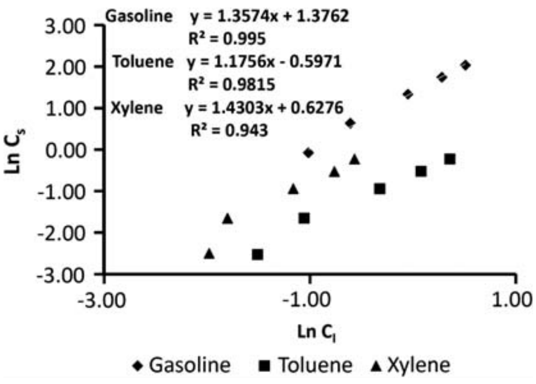

Fig. 8. Freundlich isotherms for gasoline, toluene, and xylene sorption by TCR.

TCR can release toxic components as inorganic (heavy metals) or organic compounds. Alamo et al. found that TCR contacted with aqueous solutions at pH 6.0 does not release As, Cr, Cu, or lead [15]. As expected, some zinc ions were released to the solution due to the zinc is a constituent of the TCR [38]. Also, our analysis during the sorption of PAHs did not show the release of organic compounds, because the chromatograms did not show other peaks (data not showed).

3.2. Sorption experiments in gaseous phase

3.2.1. Sorption of gaseous toluene

The total percentage removal of toluene ranged between 60 and 81% based on the system pressure. The highest percentage removal was achieved at high system pressures. The highest percentage removal for gaseous toluene (81%) is higher than the removal of toluene in aqueous phase in this study (73%) and the values reported for some authors using TCR (68%) [15]. Fig. 9 shows the Freundlich isotherm for gaseous toluene using TCR as the sorbent. Table 4 shows 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 the Freundlich isotherm were lower than the *P* values obtained for the Langmuir isotherm, which means the results fitted the Freundlich relation quite well. There are two Freundlich parameters related to sorption process. The "*n*" parameter is related to the sorption behavior at different adsorbate concentrations. The "*n*" values higher than 1 suggest that the sorption process is promoted at low adsorbate concentrations. 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.

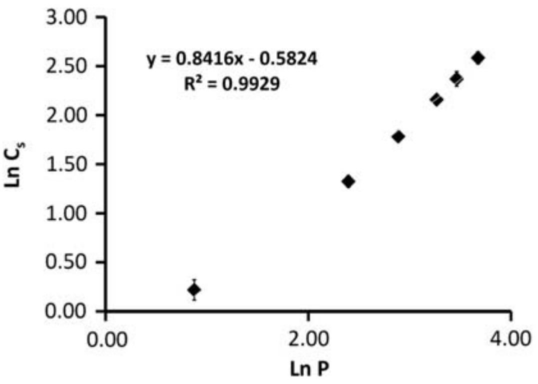

Fig. 9. Freundlich isotherm for toluene sorption in gas phase by TCR.

The "*n*" value for the sorption of toluene in the gas phase by TCR was 1.19 ± 0.08. This value is slightly higher than 1. This "*n*" value close to 1 should indicate that absorption process could be the most dominant as it was discussed above. An "*n*" value of 1 indicates that the process does not depend on adsorbate concentration but rather 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

Table 4
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.

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 onto TCR and toluene molecules. In gas phase, there are no water molecules and therefore the sorption process only depends on the partition coefficient of toluene between the solid and the gas phases [49]. The CB nanoparticles in the TCR are confined inside the polymeric matrix and only a fraction of them would be accessible, therefore the organic molecules would have to migrate between polymeric chains, (swelling) in an absorption process [54–56].

4. Conclusions

TCR mesh 14–20 can be used as sorbent to remove organic contaminant from aqueous and gaseous phases. The removal of acenaphthene and phenanthrene from a 1.0 mg/L aqueous solution was 97.6 and 99.3%, respectively, using 5 g/L of TCR. The corresponding uptake capacities for acenaphthene and phenanthrene using TCR were 3.32 and 54.6 mg/g, respectively. The TCR sorption capacity for compounds with low solubility or high hydrophobicity is higher than compounds with high solubility or hydrophilic. The SIM mode in GC-MS systems is a powerful tool to quantify PAHs at low concentrations. The removal of total gasoline components was 95.6% and the removal of toluene and o-xylene present in the gasoline was 73 and 86.4% using 30 mg/L of initial concentration of gasoline and 5 g/L of TCR. The chromatogram analysis suggests that all kind of compounds in the gasoline can be removed by TCR. The SIM mode allowed a direct quantification of toluene and xylene present in gasoline samples. The removal of toluene by TCR in gas phase was higher than aqueous phase. The sorption of gaseous toluene was dependent of system pressure. (High pressures have higher toluene removal). The uptake capacity for toluene in gas phases using TCR was 0.54 ± 0.04 mg/g. Analyses of data suggested that the sorption by TCR is a combination of adsorption process by CB and absorption process by SBP.

Acknowledgments

The authors acknowledge the support of Rubber Recycling and Manufacturing Company (REMA), the Puerto Rico Water Resources and Environmental Research Institute (PRWRERI), the TOYOTA Foundation, Solid Waste Management Authority of Puerto Rico (ADS), and the United States Department of Agriculture (2008-02146 USDA-HSI Program).

References

[1] D.R. Reyes, O. Rosario, J.F. Rodriguez, B.D. Jimenez, Toxic evaluation of organic extracts from airborne particulate matter in Puerto Rico, Environ. Health Perspect. 108 (2000) 635–640.

[2] NIOSH, Manual of Analytical Methods, fourth ed., National Institute for Occupational Safety and Health and Human Services, Cincinnati, OH, 1994.

[3] A. Khodadoust, L. Li, J. Antia, R. Bagchi, M. Suidan, H. Tabak, Adsorption of PAHs in aged harbor sediments, J. Environ. Eng. 131 (2005) 403–409.

[4] B. Mahler, P. Van Metre, T. Bashara, J. Wilson, D. Johns, Parking Lot Sealcoat: An unrecognized source of urban polycyclic aromatic hydrocarbons, Environ. Sci. Technol. 39 (2005) 5560–5566.

[5] S. Sanches, A. Penetra, C. Granado, V.V. Cardoso, E. Ferreira, M.J. Benoliel, M.T. Barreto Crespo, V.J. Pereira, J.G. Crespo, Removal of pesticides and polycyclic aromatic hydrocarbons from different drinking water sources by nanofiltration, Desalin. Water Treat. 27 (2011) 141–149.

[6] A. Imran, V.K. Gupta, Advances in water treatment by adsorption technology, Nature Protocols 1 (2007) 2661–2667.

[7] J. Carratala-Abril, M.A. Lillo-Rodenas, A. Linares-Solano, D. Cazorla-Amoros, Activated carbons for the removal of low-concentration gaseous toluene at the semipilot scale, Ind. Eng. Chem. 48 (2009) 2066–2075.

[8] J.M. Abdul, S. Vigneswaran, W.G. Shim, J. Kandasamy, Removal of metsulfuron methyl by granular activated carbon adsorption, Desalin. Water Treat. 21 (2010) 247–254.

[9] M. Landi, V. Naddeo, V. Belgiorno, Influence of ultrasound on phenol removal by adsorption on granular activated carbon, Desalin. Water Treat. 23 (2010) 181–186.

[10] J.M. Ranck, R.S. Bowman, J.L. Weeber, L.E. Katz, E.J. Sullivan, BTEX removal from produced water using surfactant-modified zeolite, J. Environ. Eng. 131 (2005) 434–442.

[11] V.K. Gupta, R. Jain, S. Varshney, Electrochemical removal of the hazardous dye Reactofix Red 3 BFN from industrial effluents, J. Colloid Interf. Sci. 312 (2007) 292–296.

[12] V.K. Gupta, R. Jain, A. Mittal, M. Mathur, S. Sikarwar, Photochemical degradation of the hazardous dye Safranin-T using TiO_2 catalyst, J. Colloid Interf. Sci. 309 (2007) 464–469.

[13] D.S. Kershaw, B. Crouthamel Kulik, S. Pamukcu, Ground rubber: Sorption media for ground water containing benzene and o-xylene, J. Geotech. Geoenviron. Eng. 123 (1997) 324–334.

[14] A.S. Guanasekara, J.A. Donovan, B. Xing, Ground discarded tire remove naphthalene, toluene, and mercury from water, Chemosphere 41 (2000) 1155–1160.

[15] L. Alamo-Nole, O. Perales-Perez, F. Roman-Velazquez, Sorption study of toluene and xylene in aqueous solutions by recycled tires crumb rubber, J. Hazard. Mater. 185 (2011) 107–111.

[16] F. Calisir, F.R. Roman, L. Alamo, O. Perales, M.A. Arocha, S. Akman, Removal of Cu(II) from aqueous solutions by recycled tire rubber, Desalination 249 (2009) 515–518.

[17] V.K. Gupta, A. Imran, V.K. Saini, Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA13 from aqueous solutions using carbon slurry developed from a waste material, J. Colloid Interf. Sci. 315 (2007) 87–93.

[18] V.K. Gupta, I. Ali, Removal of endosulfan and methoxychlor from water on carbon slurry, Environ. Sci. Technol. 42 (2008) 766–770.

[19] V.K. Gupta, I. Ali, V.K. Saini, Defluoridation of wastewaters using waste carbon slurry, Water Res. 41 (2007) 3307–3316.

[20] V.K. Gupta, A. Mittal, V. Gajbe, J. Mittal, Removal and recovery of the hazardous azo dye Acid Orange 7 through adsorption over waste materials: Bottom ash and de-oiled soya, Ind. Eng. Chem. Res. 45 (2006) 1446–1453.

[21] V.K. Gupta, R. Jain, S. Varshney, Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk—An agricultural waste, J. Hazard. Mater. 142 (2007) 443–448.

[22] V.K. Gupta, A. Mittal, R. Jain, M. Mathur, S. Sikarwar, Adsorption of Safranin-T from wastewater using waste materials—activated carbon and activated rice husks, J. Colloid Interf. Sci. 303 (2006) 80–86.

[23] V.K. Gupta, A. Mittal, A. Malviya, J. Mittal, Adsorption of carmoisine A from wastewater using waste materials—Bottom ash and deoiled soya, J. Colloid Interf. Sci. 335 (2009) 24–33.

[24] V.K. Gupta, A. Rastogi, A. Nayak, Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material, J. Colloid Interf. Sci. 342 (2010) 135–141.

[25] V.K. Gupta, A. Mittal, L. Kurup, J. Mittal, Adsorption of a hazardous dye, erythrosine, over hen feathers, J. Colloid Interf. Sci. 304 (2006) 52–57.

[26] H.A. AL-Aoh, M.J. Maah, A.A. Ahmad, M.R.B. Abas, Adsorption of 4-nitrophenol on palm oil fuel ash activated by amino silane coupling agent, Desalin. Water Treat. 40 (2012) 159–167.

[27] P. Chakravarty, D.C. Deka, N.S. Sarma, H.P. Sarma, Removal of copper (II) from wastewater by heartwood powder of Areca catechu—Kinetic and equilibrium studies, Desalin. Water Treat. 40 (2012) 194–203.

[28] P.D. Saha, A. Dey, P. Marik, Batch removal of chromium(VI) from aqueous solutions using wheat shell as adsorbent: Process optimization using response surface methodology, Desalin. Water Treat. 39 (2012) 95–102.

[29] Z.-j. Hu, N.-x. Wang, J. Tan, J.-q. Chen, W.-y. Zhong, Kinetic and equilibrium of cefradine adsorption onto peanut husk, Desalin. Water Treat. 37 (2012) 160–168.

[30] I. Ali, V.K. Gupta, Advances in water treatment by adsorption technology, Nature Protocols 1 (2007) 2661–2667.

[31] A. Mittal, V.K. Gupta, A. Malviya, A. Mittal, Process development for the batch and bulk removal and recovery of a hazardous, water-soluble azo dye (Metanil Yellow) by adsorption over waste materials (bottom ash and de-oiled soya), J. Hazard. Mater. 151 (2008) 821–832.

[32] V.K. Gupta, A. Nayak, S. Agarwal, R. Dobhal, D.P. Uniyal, P. Singh, B. Sharma, S. Tyagi, R. Singh, Arsenic speciation analysis and remediation techniques in drinking water, Desalin. Water Treat. 40 (2012) 231–243.

[33] V.K. Gupta, A. Rastogi, Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions, J. Hazard. Mater. 163 (2009) 396–402.

[34] V.K. Gupta, A. Rastogi, Equilibrium and kinetic modelling of cadmium(II) biosorption by nonliving algal biomass Oedogonium sp. from aqueous phase, J. Hazard. Mater. 153 (2008) 759–766.

[35] V.L. Shulman, Tyre Recycling After 2000: Status and Options, The European Tyre Recycling Association, Paris, 2000.

[36] RMA, U.S. Scarp Tire Markets 2005, (2006), Available from: https://www.rma.org/scrap_tires.

[37] CalRecycle, Rubberized Asphalt Concrete (RAC), Tire Managment, 2012, Available from: http://www.calrecycle.ca.gov/tires/rac/.

[38] T. Amari, N. Themelis, I. Wernick, Resource Recovery from Used Rubber Tires, Resources Policy 25 (1999) 170–188.

[39] G. Unnikrishnan, S. Thomas, S. Varghese, Sorption and diffusion of aromatic hydrocarbons through filled natural rubber, Polymer 37 (1996) 2687–2693.

[40] J. Xu, A. Ito, Removal of VOC from water by pervaporation with a hollow-fiber silicone rubber membrane module, Desalin. Water Treat. 17 (2010) 135–142.

[41] Y.J. Tham, P. Abdul Latif, A.M. Abdullah, A. Shamala-Devi, Y.H. Taufiq-Yap, Performances of toluene removal by activated carbon derived from durian shell, Bioresour. Technol. (2011) 724–728.

[42] K. Singh, R.S. Singh, B.N. Rai, S.N. Upadhyay, Biofiltration of toluene using wood charcoal as the biofilter media, Bioresour. Technol. (2010) 3947–3951.

[43] J.Y. Kim, J.K. Park, T.B. Edil, Sorption of organic compounds in the aqueous phase onto tire rubber, J. Environ. Eng. 123 (1997) 827–835.

[44] M. Belhachemi, F. Addoun, Adsorption of congo red onto activated carbons having different surface properties: Studies of kinetics and adsorption equilibrium, Desalin. Water Treat. 37 (2012) 122–129.

[45] J. Pawlizyn, Applications of Solid Phase Microextraction, The Royal Society of Chemistry, Cambridge, 1999.

[46] A. Ayar, S. Gürsal, A.A. Gürten, O. Gezici, On the removal of some phenolic compounds from aqueous solutions by using a sporopollenin-based ligand-exchange fixed bed—Isotherm analysis, Desalination 219 (2008) 160–170.

[47] A. Ozturk, T. Artan, A. Ayar, Biosorption of nickel(II) and copper(II) ions from aqueous solution by *Streptomyces coelicolor* A3(2), Colloids and Surfaces B: Biointerfaces 34 (2004) 105–111.

[48] A.A. Gurten, S. Ucan, M.A. Ozler, A. Ayar, Removal of aniline from aqueous solution by PVC-CDAE ligand-exchanger, J. Hazard. Mater. B 120 (2005) 81–87.

[49] W. Stumm, J. Morgan, Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters, Third ed., Wiley-Interscience, New York, NY, 1996.

[50] L.S. Clegg, W.E. Lindup, Scatchard plots with a positive slope: Dependence upon ligand concentration, J. Pharm. Pharmacol. 36 (1984) 776–779.

[51] M.-H. Lai, R. Quio Chu, H.-C. Huang, S.-H. Shu, T.-W. Chung, Equilibrium isotherms of volatile alkanes, alkenes, and ketones on activated carbon, J. Chem. Eng. Data 54 (2009) 2208–2215.

[52] T. Badr, K. Hanna, C. de Brauer, Enhanced solubilization and removal of naphthalene and phenanthrene by cyclodextrins from two contaminated soils, J. Hazard. Mater. B112 (2004) 215–223.

[53] C. Valderrama, J.L. Cortina, A. Farran, X. Gamisans, C. Lao, Kinetics of sorption of polyaromatic hydrocarbons onto granular activated carbon and Macronet hyper-cross-linked polymers, (MN200), J. Colloid Interf. Sci. 310 (2007) 35–46.

[54] C.G. Soney, T. Sabu, K.N. Ninan, Molecular transport of aromatic hydrocarbons through crosslinked styrene–butadiene rubber membranes, Polymer 37 (1996) 5839–5848.

[55] S. Ranimol, J. Kuruvilla, O. Zachariah, T. Sabu, Molecular transport of aromatic solvents through microcomposites of natural rubber (NR), carboxylated styrene butadiene rubber (XSBR) and their blends, Composites Sci. Technol. (2007) 1187–1194.

[56] Y. Iwai, T. Ishidao, S. Miyamoto, H. Ikeda, Y. Arai, Solubilities of nonane vapor in styrene–butadiene copolymers at 100 and 130°C, Fluid Phase Equilibria 68 (1991) 197–205.