Journal of Hazardous Materials 185 (2011) 107–111

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Sorption study of toluene and xylene in aqueous solutions by recycled tires crumb rubber

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ARTICLE INFO

Article history:
Received 3 March 2010
Received in revised form 9 July 2010
Accepted 1 September 2010
Available online 15 September 2010

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

ABSTRACT

Sorption of toluene and xylene by tire crumb rubber (TCR) and its main components: carbon black (CB) and styrene-butadiene polymer (SBP) were evaluated. The 12 starting concentrations of adsorbates in aqueous solutions ranged from 0.05 mg/L to 100.0 mg/L. 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 parameter was estimated at 0.65 for CB and 1.0 for both TCR and SBP. A removal of 60% of toluene and 81% of xylene from starting 50 ppm solutions was attained in the first 30 minutes of contact using 5 g/L of TCR.

1. Introduction

Despite existing environmental protection policies, severe water pollution events are still frequent worldwide. One of the sources of water pollution is petroleum derivatives. For example, high concentrations of aromatic compounds such as ethylbenzene, toluene and xylene have been detected in oil and gasoline spills [1]. These compounds can be mobilized into the aqueous phase, making the contamination problem even worse. It is known that exposure to toluene and xylene can cause disturbances in the central nervous system and damage to the kidneys and liver [2]. Accordingly, the maximum contaminant levels (MCL) established by the US-EPA for drinking water are 1.0 and 10 mg/L for toluene and xylene, respectively [1].

Several approaches to remove toluene and xylene from aqueous solutions have been reported; the use of granular activated charcoal (GAC) is the most common alternative. Other options include the use of zeolites, surfactant-modified zeolites and polymeric sorbents [3]. The prohibitive costs involved with the synthesis of the above mentioned sorbents limit their applicability to treat large volumes of polluted effluents. Evidently, the ideal sorbent should exhibit uptake capacities comparable to commercial products while being cost-effective.

It has been estimated that over 10 billion tires are discarded worldwide every year; in 2005, approximately 259 million tires were fabricated in the US. Although the market for the scrap tires utilizes around 80% of used tires, the remaining 20% is stockpiled or put in land fills [4,5]. Tire crumb rubber (TCR) consists of a complex mixture of elastomers including polyisoprene, polybutadiene and styrene-butadiene. Stearic acid (1.2%), zinc oxide (1.9%), extender oil (1.9%) and carbon black (31.0%), are also important components of tires [6]. Carbon black (CB) is used to strengthen the rubber, improve its abrasion resistance and reduce its degradation by UV rays [7]. This nanosize component should exhibit adsorption properties similar to those of activated charcoal, a well known agent used to remove organic and inorganic compounds from aqueous and gaseous effluents [8,9]. Therefore, the levels of CB in waste tires should promote the removal of the targeted dissolved species through adsorption mechanisms [10–14]. Stearic acid could also behave as an ionic exchanger because the carboxylic group can promote ion exchange with metal ions. Moreover, non-polar organic pollutants are expected to interact with the rubber matrix via van der Waals interactions [15].

The present study addresses the evaluation of TCR (as a composite material) and its main components as sorbents from organic pollutants in water. CB and SBP have been evaluated separately and their sorption capability has been compared with those from actual TCR in order to understand their role in the overall sorption process. To our knowledge no prior studies about the effect of TCR components on its sorption capability have been reported. Adsorption data

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doi:10.1016/j.jhazmat.2010.09.003

at equilibrium were fitted to the Freundlich's equation. Linearity of the isotherms was evaluated using factor P (probability) and regression analysis. Also, proposed herein is the use of Scatchard-type plots to evaluate the interactions between adsorbate and sorbent. Scatchard's relationship is derived from the Langmuir's equation and is very useful to interpret sorption mechanisms based on the availability of binding sites onto the sorbent.

2. Materials and methods

Tires crumb rubber (TCR) was provided by REMA Inc., a tire rubber recycling company located in Caguas, Puerto Rico. TCR mesh 14–20 (average diameter 2.45 mm) was washed with deionized water for 24 hours and dried at room temperature. Toluene and o-xylene were ACS certified grade and were used without further purification. Amorphous carbon black N330 was produced by 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. Concentrations below the solubility in water of the organic solvents were selected to assure their stability during sorption tests.

2.1. Crumb rubber chemical stability test

In order to evaluate the possibility of metal ion release from TCR, one gram of the sorbent was placed in contact with 100 mL of distilled water at room temperature and pHs of 1.5, 3.0, 6.0 and 9.0 for 24 hours. Nitric acid (HNO_3) or NaOH (10% w/w) solutions were used to adjust the pH. Solution samples were withdrawn at the end of the contact period and analyzed for copper, cadmium, arsenic, zinc, lead and chromium using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Direct Reading Echelle from LEEMAN INC) according to EPA 200.7 rev 5.0. All analyses were run in triplicate. A Hewlett Packard 5890 gas chromatography coupled to a HP 5970 mass spectrometry (GC-MS) with electron impact ionization of 70 eV was used to determine the presence of volatile compounds generated during contact of TCR with the pH 6 water solutions.

2.2. Single component sorption experiments

Toluene and xylene solutions at pH 6.0 were contacted with 5.0 g/L of TCR, 1.5 g/L of CB or 3.0 g/L of SBP. The concentrations of CB and SBP were calculated considering their concentration in tire crumb rubber matrix (30% and 60% w/w, respectively). The initial concentrations of aqueous solutions of toluene and xylene ranged between 0.05 mg/L and 100 mg/L.

2.3. Adsorption isotherms

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

$$q = K_f C^{1/n} \quad (1)$$

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

The Scatchard relationship (Eq. (3)) is derived from Langmuir's equation (Eq. (2)). The analysis of the Langmuir isotherms provides quantitative information related to the sorption capacity in sorbent materials whereas the Scatchard relationship, derived from Langmuir's equation, is used to asses the types of binding sites involved in a sorption process. In a more qualitative way, the interactions between adsorbate and sorbent can also be evaluated from the shape of the Scatchard plot; e.g. a single sorption process would be suggested by a linear trend [16].

$$q = q_m \frac{K_b C}{1 + K_b C} \quad (2)$$

$$\frac{q}{C} = q_m K_b - q K_b \quad (3)$$

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)). This factor indicates the probability that the experimental results fit the considered model; the lowest P values are representative of the best fit to the model [16].

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

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

2.4. Quantitative analyses of toluene and xylene in aqueous solutions

Toluene and xylene solutions were prepared in 120-mL amber bottles leaving an optimum 10-mL head space. The solution headspace was sampled at defined contact time intervals following a Solid Phase Micro Extraction Method (SPME) [17] and submitted for quantitative analyses of residual toluene and xylene by GC-MS. SPME fiber, made of polydimethylsiloxane, was placed in the headspace for 10 seconds and then introduced into the GC-MS injector and heated for 2 minutes to desorb the analyte. Quality control (QC) samples were prepared at the same concentrations of middle calibration standard (80 and 40 ppm) and used to evaluate both the integrity of the SPME fiber and the calibration status. These QC standards were run in all experiments, and the corresponding calibration curves were redone when the fitting error was higher than 15%. The Q-test was used to evaluate outlier values.

3. Results and discussion

3.1. TCR and chemical stability test

TCR mesh 14–20 reported an average diameter of 2.45 mm (Figure 1a). Scanning Electron Microscopy (SEM) analysis evidenced the surface roughness exhibited by crumb rubber (Figure 1b).

As evidenced by the data in Table 1, the release of metals from TCR into aqueous systems was below EPA regulations at all evaluated pH values. At pH 6, concentrations of 1 ppb Cd and 0.41 ppm Zn were detected at the end of 24-hour contact time, while no levels of As, Cr, Cu or Pb were detected. Although at pH 1.5 trace concentrations of Zn, Cu, Cr and As were found, all levels were below the EPA MCL for drinking water. The presence of Zn in the samples can be attributed to the leaching of ZnO, which is a constituent of tire rubber [18]. No release of volatile compounds was found for TCR aqueous solutions at 5 g/L and pH of 6.0 at room temperature.

3.2. Single-component sorption experiments

The removal of toluene and xylene using 5 g/L of TCR and pH 6.0 was a very fast process. Above 90% of xylene and 68% of toluene were removed in the first 30 minutes. The results are in agreement with previous studies [19,20]. The sorption data fits Freundlich's relationship quite well. According to the corresponding isotherm (Figure 2a), at least two kind of interactions may have taken place between each adsorbate and TCR; i.e. each type of interaction could

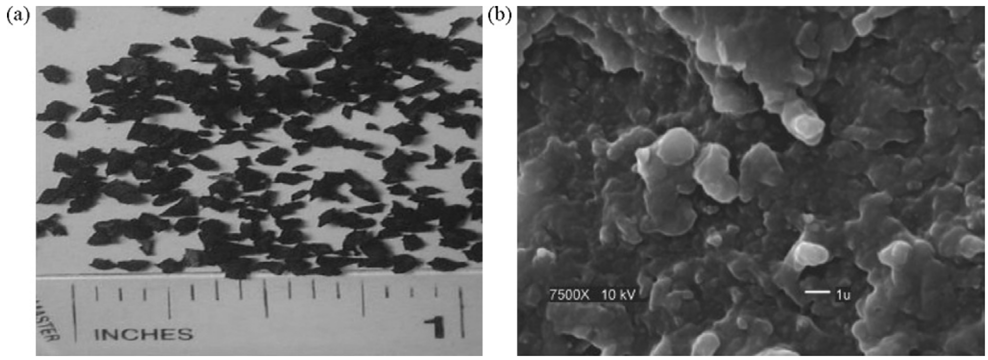

Fig. 1. (a) Crumb rubber mesh 14–20 as provided by REMA, Inc; (b) Typical SEM image of crumb rubber. Although the surface exhibits significant roughness, no mesopores were observed.

Table 1
Metals released in mg/L from crumb rubber at different pH values.

Average of metal concentration	pH values in solutions				EPA Regulation (MCL) mg/L
	1.5	3.0	6.0	9.0	
Cu	0.083 ± 0.008	0.043 ± 0.04	ND	ND	1.3
Cd	0.002 ± 0.001	ND	0.001 ± 0.001	ND	0.005
As	0.04 ± 0.02	ND	ND	ND	0.010
Zn	2.38 ± 0.06	1.11 ± 0.02	0.41 ± 0.05	0.29 ± 0.02	5.0
Pb	ND	ND	ND	ND	0
Cr	0.05 ± 0.04	0.09 ± 0.02	ND	ND	0.1

ND: not detected by ICP-OES.
MCL: Maximum contaminant level for drinking water.

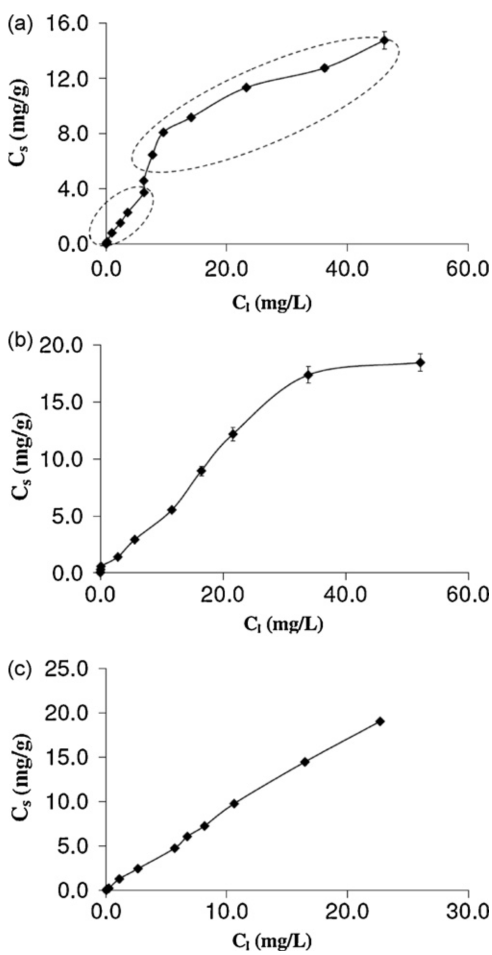

Fig. 2. Linear isotherms for xylene using a. Crumb rubber, b Carbon black and c Styrene-butadiene polymer.

be due to two different sorption mechanisms in crumb rubber. In order to investigate this possibility, sorption tests for xylene and toluene were carried out by evaluating the sorption behavior of two main components of crumb rubber: CB and SBP. The results for CB at a concentration of 1.5 g/L, (Figure 2b) were well fitted to the Freundlich relationship (Table 2), which is common for carbonaceous sorbents [21]. On the other hand, the sorption behavior of SBP, 3.0 g/L, (Figure 2c) 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 polymer-water 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.

As discussed previously, the presence of various linear plots with different slopes in the Scatchard plot corresponding to the sorption test with TCR (Figure 3a), confirms that more than one sorption process could have taken place. Exposed CB particles on the TCR surface would have favoured the rapid adsorption of most of the adsorbates at early contact times. And, the migration of the adsorbate molecules within the chains of the crumb rubber polymeric matrix

Table 2
Freundlich parameters for toluene and xylene sorption by crumb rubber, carbon black and styrene-butadiene polymer.

		Crumb Rubber	Carbon Black	Polymer
Toluene	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	239 ± 4	621 ± 14	355 ± 3
	P value	19 ± 1	6 ± 1	10.6 ± 0.5
Xylene	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	723 ± 14	1327 ± 40	991 ± 2
	P value	13 ± 1	34 ± 6	3.1 ± 0.6

n: Freundlich parameter (ug/g).
K_f : Freundlich Parameter.

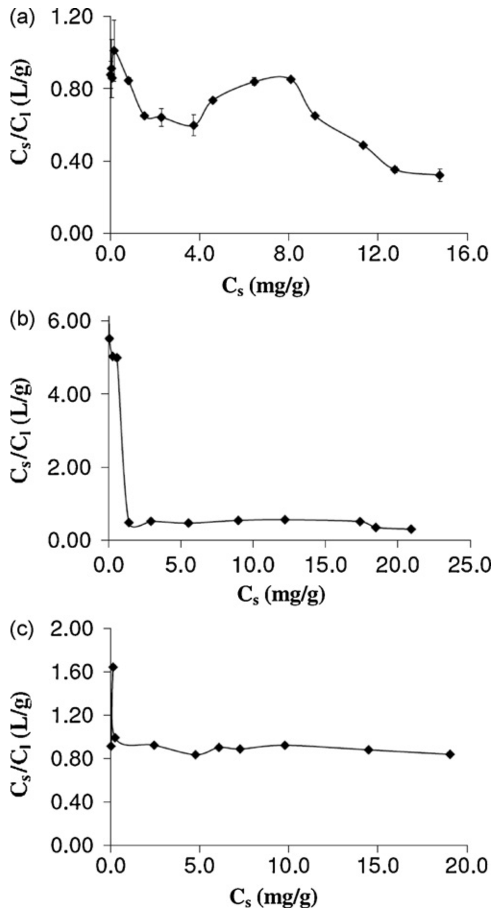

Fig. 3. Scatchard plots for xylene using a. Crumb rubber, b Carbon black and c Styrene-butadiene polymer.

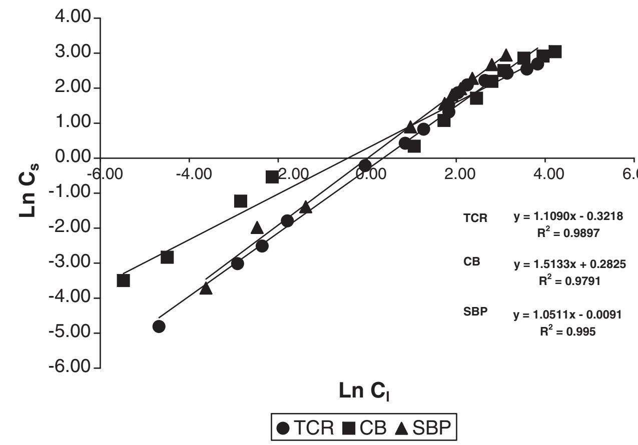

Fig. 4. Freundlich isotherms for xylene using a. Crumb rubber, b Carbon black and c Styrene-butadiene polymer.

could account for the observed second sorption step. On the other hand, the presence of the linear relation in the Scatchard plot for the sorption of xylene and toluene by CB (Figure 3b) could evidence that the sorption process takes place through a single mechanism. In this case xylene should have been adsorbed onto active sites on CB surface. The Scatchard plot for the sorption of xylene and toluene by SBP (Figure 3c) exhibited two linear profiles with different slopes. This is indicative of a two-stage sorption process. These two stages would involve the diffusion of xylene species through the polymeric matrix and their final incorporation between polymer chains, as expected in absorption–based processes.

3.3. Freundlich isotherm parameters

Figure 4 shows the Freundlich isotherm plot and Table 2 includes the Freundlich's parameters and the 'P' values (probability of the model) corresponding to toluene or xylene sorption by TCR, CB, SBP., In all cases, these 'P' values were the lower than those for Langmuir's (shown in Table 3) and linear isotherms (not shown here). Although the r^2 values for Langmuir's isotherm resulted close to Freundlich's ones (in two cases the r^2 values for Langmuir's fitting were higher than Freundlich's values), the data dispersion was higher in the Langmuir's isotherm than in the Freundlich's case. This lower data dispersion in the Freundlich's fitting was also suggested by the corresponding low P values.

The n value in Freundlich's relationship is related to the sorption behavior; a n value close to one indicates that the sorption process is independent of the adsorbate concentration, whereas a lower value suggests 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.

The n values for the sorption of toluene and xylene using TCR were 1.018 ± 0.003 and 0.90 ± 0.01, respectively. The small differences in the n values would suggest similar sorption behaviour of those two adsorbates when contacted with TCR. 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 [21–23]. 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 n values suggest the sorption process is independent of adsorbate concentration and dependent on the partition coefficient only.

The K_f (uptake capacity) estimated results for toluene using TCR, CB and SBP as sorbents were 239 ± 4 μg/g, 621 ± 14 μg/g and 355 ± 3 μg/g of sorbent, respectively. The corresponding uptake capacity for xylene were 723 ± 14 μg/g, 1,327 ± 40 μg/g and 991 ± 2 μg/g. These uptake capacities for TCR are in agreement with previously reported values [19,20]. The larger uptake capacity of pure carbon black can 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, (swelling) in an absorption process [24–26]. Although, nanosize CB ($64/lb) and SBP ($40/lb) 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.

Table 3
Langmuir parameters for toluene and xylene sorption by crumb rubber, carbon black and styrene-butadiene polymer.

		Crumb Rubber	Carbon Black	Polymer
Toluene	r^2	0.992 ± 0.008	0.80 ± 0.04	0.967 ± 0.009
	K_b	0.0002 ± 0.00002	0.0006 ± 0.00009	0.0001 ± 0.00002
	q_m	$2 \pm 2 \times 10^3$	$2.8 \pm 0.2 \times 10^3$	$4.6 \pm 0.7 \times 10^3$
	P value	255 ± 196	80 ± 8	77 ± 11
Xylene	r^2	0.9996 ± 0.0003	0.95 ± 0.07	0.9999 ± 0.0001
	K_b	0.00006 ± 0.00008	0.002 ± 0.001	0.00005 ± 0.00003
	q_m	$4 \pm 3 \times 10^4$	$4 \pm 2 \times 10^3$	$2 \pm 1 \times 10^4$
	P value	20 ± 7	161 ± 88	27 ± 14

K_b : Langmuir parameter.
q_m : Langmuir Parameter (ug/g).

The capability of TCR to remove other organic compounds of environmental importance such as poly aromatic hydrocarbons and polychlorinated biphenyls will be evaluated and presented in our forthcoming publications.

4. Conclusions

The capability of tire crumb rubber (TCR) mesh 14–20 to remove toluene and xylene from aqueous solutions was demonstrated. The removal of toluene and xylene from a 50 ppm aqueous solution were 60% and 81%, respectively, for a 30-minute contact time using 5 g/L of TCR. The corresponding uptake capacities using Freundlich's equation were 239 μg/g and 723 μg/g.

Acknowledgments

The authors acknowledge the support 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).

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