

# Sorption of Ethylbenzene, Toluene and Xylene onto Crumb Rubber from Aqueous Solutions

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## ABSTRACT

Samples of waste tires crumb rubber mesh 14-20, produced by REMA Inc., were contacted with 30ppm aqueous solutions of ethylbenzene (E), toluene (T) and xylene (X) to evaluate the corresponding sorption capability. The concentration of the sorbent varied from 0.1 to 10 g crumb rubber/L. Solution aliquots were withdrawn at different times and analyzed by GC-MS to monitor the progress of the sorption process. Obtained results confirmed the capability of crumb rubber to remove ETX compounds from aqueous solutions. This removal efficiency was dependent on solution pH and crumb rubber concentration. The ethylbenzene concentration dropped from 30 ppm down to 1.4 ppm in the first 30 minutes of contact when 10 g/L of crumb rubber were used. The maximum removal of xylene, ethylbenzene and toluene were 99, 95 and 77%, respectively, at pH 6. The corresponding uptake capacities were 55, 48 and 24 mg/g crumb rubber. The sorption efficiency of crumb rubber was xylene > ethylbenzene > toluene.

**Keywords:** waste tire, crumb rubber, sorption, recycling, water treatment

## 1 INTRODUCTION

To assure the quality of life and health of living beings is of vital importance. Despite of existent environmental protection policies, pollution events are still frequent not only in Puerto Rico but also in the rest of the world. One of the most common pollution sources is represented by oil derivatives generated by refining, transport, uses and residues treatment activities. Among oil derivatives, high concentrations of aromatic compounds such as toluene (T), ethylbenzene (E) and xylene (X) have been detected in oil and gasoline [1]. These compounds can also get mobilized into the aqueous phase, which would make the contamination problem even worse. The maximum contaminant levels (MCL) established by US-EPA in drinking water for ethylbenzene, toluene and xylene are 0.7, 1.0 and 10 mg/L, respectively [1]. Exposure to ETX solvents can cause disturbances in the central nervous system, and damage to kidney and liver [2].

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 [3]; but the prohibitive costs involved with the sorbent fabrication limit their applicability to treat large volumes of polluted effluents. Evidently, the ideal sorbent should exhibit removal capacities comparable to commercial products under cost-effective conditions. Moreover, the sorption of organic pollutants will require a polymeric matrix with non polar components.

On the other hand, there are at least 275 million waste tires in stockpiles in the U.S. It has been estimated that the amount of discarded tires reaches 10 billion every year worldwide. Although, markets now exist for 76% of these waste tires, up from 17% in 1990, the remaining is still stockpiled, or land filled [4]. Crumb rubber is composed of a complex mixture of elastomers like polyisoprene, polybutadiene and styrene-butadiene. On a rubber-composition point of view the major components of tires are rubber vulcanized with sulfur (1.1%), stearic acid (1.2%), ZnO (1.9%), extender oil (1.9%) and carbon black (31.0%) [5]. Carbon black is used to strengthen the rubber and improve its abrasion resistance. This component should exhibit similar adsorbing characteristics as activated charcoal, a well known agent used to remove organic and inorganic compounds from aqueous and gaseous effluents, a fact that makes viable the removal of target species through sorption/adsorption mechanisms [6-10]. Stearic acid would also behave as an ionic exchanger. Moreover, non-polar organic pollutants are expected to interact with the rubber matrix via van der Waals interactions [11].

Under these premises, the present work addresses the evaluation of waste tires crumb rubber as potential sorbent for ETX pollutants from aqueous solutions.

## 2 MATERIALS AND METHODS

### 2.1 Materials

Waste tires crumb rubber was provided by REMA Inc., a tire rubber recycling company located in Caguas, Puerto Rico. The crumb rubber mesh 14 -20, (Figures 1 and 2), was washed with deionized water for 24 hours and dried at

room temperature. The average rubber particle size was estimated at 2.45 mm. Ethylbenzene, toluene and o-xylene were ACS certified grade and were used without further purification. Low concentrations of these compounds assure complete solubility in water. Accordingly, the adsorbates concentration was kept constant at 30 ppm in all tests.



Figure 1: Crumb rubber mesh 14–20, as provided by REMA, Inc.

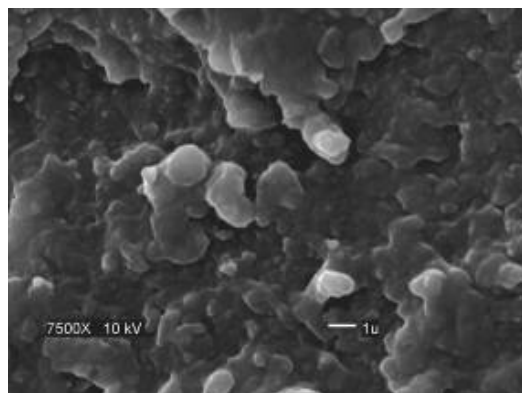


Figure 2: Typical SEM image of crumb rubber. Although the surface exhibits significant roughness, no mesopores were observed.

## 2.2 Crumb Rubber Chemical Stability Test

In order to evaluate the possibility to release metals from crumb rubber, 1 gram of the sorbent was contacted with 100 mL of distilled water at pH 1.5, 3.0, 6.0 and 9.0 for 24 hours.  $\text{HNO}_3$  or  $\text{NaOH}$  10% w/w solutions were used to adjust the pH values. Solution samples were withdrawn at the end of the contact period and submitted for copper, cadmium, arsenic, zinc, lead and chromium analyses by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). EPA 200.7 rev 5.0 protocol was followed. All analyses were run by triplicate.

## 2.3 Sorption Experiments

Crumb rubber, at concentrations varying from 0.10 g/L to 10 g/L, were contacted with 30ppm ETX aqueous solutions. ETX solutions were directly prepared in 250-mL amber bottles leaving an optimum 10-mL head space. The solution head-space was sampled at 0.5, 1, 2 and 6 hours intervals using a Solid Phase Micro Extraction Method (SPME) and submitted for quantitative analyses by GC-MS.

## 2.4 Solution Analyses

After selecting the most suitable sampling technique, the SPME fiber made of polydimethylsiloxane was placed in the crumb rubber-ETX solution head-space for 15 seconds and then into the GC-MS injector. There, it was treated thermally for 2 minutes to desorb the analytes. The concentrations of ETX were determined using GC-MS Q Plus with ion trap, electron impact ionization of 70 eV and an ion trap mass spectrometer in the Single Ion Monitoring mode at 65, 91 and 92 m/z. Quality controls (QC) samples of 30 ppm for each solvent were run in all experiments and new calibration curves were conducted when the lack of fitting error was higher than 15%.

# 3 RESULTS AND DISCUSSION

## 3.1 Crumb Rubber Chemical Stability Test

As evidenced by the data in table 1, the release of metals from crumb rubber is below EPA regulations even for pH values as low as 1.5. In all cases, the terminal concentrations were below EPA regulations for drinking water. The zinc detected in solutions can be attributed to the dissolution of  $\text{ZnO}$ , which is a constituent of tire rubber. Since the sorption of ETX compounds in our work took place at extremely short contact times (30 minutes, or so) and at pH 6, there are no concerns about the potential release of toxic metal ions during the sorption process.

	pH values in solutions				EPA regulation mg/L
	1.5	3.0	6.0	9.0	
<b>Cu</b>	0.0828	0.043	ND	0.0001	1.3
<b>Cd</b>	0.0023	ND	0.001	ND	0.005
<b>As</b>	0.04	ND	ND	ND	0.050
<b>Zn</b>	2.38	1.11	0.41	0.29	5.0
<b>Pb</b>	ND	ND	ND	ND	0
<b>Cr</b>	0.05	0.09	ND	ND	0.1

Table 1. Metals release, in mg/L, from crumb rubber at different pH values. ND: no detected by ICP-OES

### 3.2 Sorption of ETX

The removal of ethylbenzene, toluene and xylene by mesh 14-20 crumb rubber at pH 6.0 was highly efficient and rapid. Above 80% of the pollutants was removed in the first 30 minutes of contact, which is in good agreement with previous works [12, 13]. Terminal ETX concentrations exhibited a rising trend when the concentration of crumb rubber was less than 10 g/l. This behavior was attributed to the expected decrease in the amount of sorption sites for fewer amounts of the sorbent. Figure 3 shows the variation in the sorption of ethylbenzene with time and concentrations of crumb rubber. Almost 95% of ethylbenzene was removed by using 10 g/L of crumb rubber at pH 6. The removal percentage went down to 17% for a crumb rubber concentration as low as 0.1 g/L, i. e. one-hundred times less crumb rubber than at 10 g/L. The sorption efficiency of crumb rubber was pretty high for xylene followed by ethylbenzene and, lastly, toluene (Figure 4-a). In turn, a 5% decrease in the removal efficiency of ethylbenzene and xylene was observed for pH 1.5 (Figure 4-b). The sorption of organic compounds should not be dependent on the solution pH value; however, the release of zinc ions during the contact time could be conducive to some structural modification of the polymeric structure. The composition of crumb rubber is the key for its sorption capability. Isoprene and butadiene are hydrocarbon chains present in crumb rubber that can interact with the alkyl groups in the organic pollutants [14]. For instance, the presence of methyl groups in the structure of o-xylene can account for its rapid and efficient removal. In turn, the length of the ethyl group –that is larger than the methyl group– can be related to the comparatively less adsorption of ethylbenzene when compared to xylene. Toluene has the largest solubility in water (515 mg/L at 25°C), thus its partition between crumb rubber and water is expected to be significantly different from the observed for xylene and ethylbenzene (with solubility of 200 mg/L and 152 mg/L, respectively). Furthermore, the remarkable hydrophobicity of xylene and ethylbenzene can also explain their fast removal by crumb rubber.

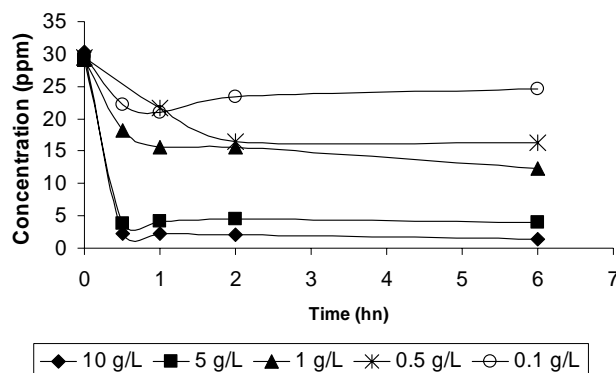


Figure 3: Removal of ethylbenzene as a function of contact time and concentrations of crumb rubber, in g/L, at pH 6. The ethylbenzene concentration was 30 ppm.

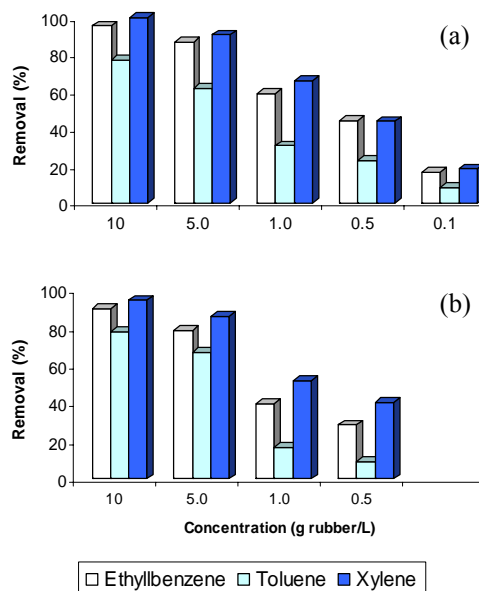


Figure 4: Comparative sorption behaviour of ETX by crumb rubber at pH 6.0 (a), and 1.5 (b). The Initial ETX and crumb rubber concentrations were 30ppm, and 10 g/L, respectively.

### 3.3 Freundlich Isotherms

Freundlich's equation permitted a very good fitting of the sorption data for ethylbenzene, toluene and xylene. Values of  $1/n \leq 1$  indicate a rapid removal of the adsorbate at high concentrations. The other isotherm parameter is the  $K_f$  constant that is related to the loading factor of the sorbent; a large  $K_f$  value will mean high removal capacity. These two parameters have been calculated from the experimental data and are shown in Table 2. This table includes the data from other groups that also worked with scrap tires, although with different particle sizes. As observed, our results are in good agreement with reported information and confirms the capability of waste tires crumb rubber as a cheap and efficient sorbent for ETX compounds

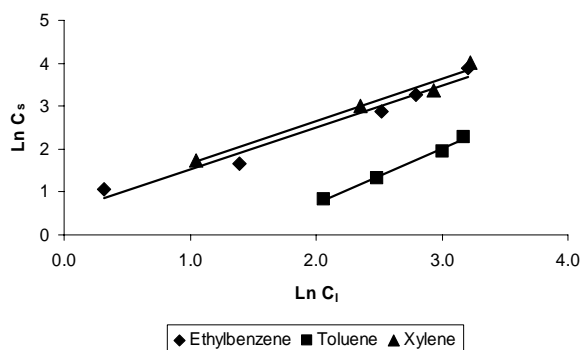


Figure 5: Freundlich isotherms for ethylbenzene, toluene and xylene at room temperature and pH 6.0.

Studied Analytes	Kim et al. [12]		Guanasekara et al.[13]		This study	
	1/n	K <sub>f</sub>	1/n	K <sub>f</sub>	1/n	K <sub>f</sub>
Ethylbenzene	0.998	1014	--	--	0.9728	1750
Toluene	0.991	297	0.999	264	1.2683	166
O-Xylene	0.990	1011	--	--	0.9913	1949

Table 2: Freundlich's parameters for ETX sorption by crumb rubber

## 4 CONCLUSIONS

The capability of waste tires crumb rubber mesh 14-20 to remove ETX pollutants from aqueous solutions has been verified. The best removal efficiency was observed for xylene followed by ethylbenzene and toluene. The corresponding removal efficiency was 99, 95 and 77% at pH 6.0. No significant variation was observed at other pH values.

## 5 ACKNOWLEDGEMENTS

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