



# Adsorption of Ethylbenzene from Aqueous Solution Using Recycled Rubber from Scrap Tyre

F. A. Aisien<sup>1</sup>, N. A. Amenaghawon<sup>1\*</sup> and S. A. Akhidenor<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, University of Benin, PMB 1154, Benin City, Edo State, Nigeria.

## Authors' contributions

*This work was carried out in collaboration between all authors. Author FAA, in collaboration with author NAA, designed the study. Author SAA performed the experiments, and wrote the first draft of the manuscript. Authors NAA and SAA managed the literature searches. Authors FAA, provided analytical advice and manuscript correction. All authors read and approved the final manuscript.*

Research Article

Received 17<sup>th</sup> May 2013  
Accepted 19<sup>th</sup> July 2013  
Published 25<sup>th</sup> July 2013

## ABSTRACT

The adsorption of ethylbenzene from aqueous solution using waste tyre rubber granules (WTRG) was investigated in a batch system. The effect of various factors such as contact time, initial concentration of ethylbenzene, amount of adsorbent, size of adsorbent particles, and temperature of solution on the adsorption capacity of WTRG was determined. The equilibrium contact time was obtained to be 70 minutes indicating fast adsorption. The adsorption of ethylbenzene on WTRG was observed to increase from 8.4 to 57.85 mg/g with increase in initial ethylbenzene concentration from 250 to 850 mg/L. The adsorption capacity of WTRG increased from 55.35 to 71.6 mg/g with decrease in particle size from 2.36 to 0.212mm. Increasing the temperature of the aqueous solution from 5 to 40°C resulted in a decrease in the adsorption capacity of WTRG from 59.83 to 45.15mg/g. Kinetic and isotherm studies indicate that the adsorption of ethylbenzene was best described by the Lagergren pseudo-first order kinetic equation and Langmuir isotherm equations respectively. Results obtained indicate that recycled rubber from scrap tyres can be used as an efficient adsorbent for the removal of ethylbenzene from aqueous solution.

\*Corresponding author: E-mail: [andrew.amenaghawon@uniben.edu](mailto:andrew.amenaghawon@uniben.edu);

*Keywords: Adsorption; ethylbenzene; WTRG; adsorption capacity.*

## 1. INTRODUCTION

Increased vehicle ownership and traffic volume has led to an increase in the quantity of waste tyres in Nigeria. As the country's population and economy grow, so does the amount and type of scrap tyres generated. With an annual generation rate of 15%, between 700,000 and 850,000 scrap tyres are added to the waste stream each year. Recently, Aisien et al. [1] estimated that about 15 million scrap tyres are now in existence in Nigeria. These waste tyres represent a major environmental problem as a result of their volume, non-biodegradability and indiscriminate disposal [2,3].

In developed nations of the world, scrap tyres have been recycled to obtain value added products. They are currently employed for such uses as tyre derived fuels, incorporation into asphalt for road pavement, floor mats, liquid waste treatment etc. Even with these uses, a huge amount of waste tyres are discarded improperly annually [4,5]. It is therefore imperative to explore other possible applications such as use as adsorbents.

The improper discharge of industrial organic effluents contaminates the environment. Ethylbenzene is a predominant aromatic compound usually contained in industrial wastewater. It is the basic structural unit of a variety of synthetic organic compounds found in wastewater originating from industrial operations such as plastics, resin, rubber, textile, pharmaceuticals manufacture as well as tanning [6-8]. Ethylbenzene is usually found only infrequently at level less than 1 µg/L in drinking water from ground or surface sources. For surface water, the levels of ethylbenzene are generally less than 0.1 µg/L in non-industrial areas while levels as high as 15 µg/L have been reported in industrial and urban areas [9]. It is important to remove ethylbenzene from wastewater before discharge into any naturally occurring water body because it is highly hazardous, and resistant to degradation [6,10].

Conventional methods for removing aromatic compounds such as ethylbenzene from industrial wastewater include solvent extraction, steam distillation, irradiation as well as chemical techniques such as electrochemical oxidation, reverse osmosis photocatalytic degradation and adsorption on activated carbon, ion exchange resins and silicates [8,11,12]. The major drawback with these methods is the cost associated with start-up and subsequent sustainability. Adsorption remains the best option for ethylbenzene removal as it can generally remove all types of aromatic compounds in a simple and easy operation. However, conventional adsorption using activated carbon is costly and its use is sometimes restricted on economic considerations. In comparison with conventional adsorbent, waste tyre rubber granules offers an excellent alternative in that it is cheap and readily available. Recently, interest has been shown in the use of waste tyre rubber granules in the treatment of industrial wastewater [3,13-15].

Hence the objective of the present study is to investigate the potential use of recycled waste tyre rubber as adsorbent in the removal of ethylbenzene from industrial wastewater. The study was focused on the sorption capability of waste tyre rubber for ethylbenzene from aqueous solution by testing the effect of various operational variables such as contact time, initial ethylbenzene concentration, adsorbent dosage, adsorbent particle size, and temperature of the aqueous solution.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of Adsorbent

Scrap tyres were collected from Akhidenor scrap tyre dump site in Benin City, Nigeria. The tyres were washed with water to remove dirt and were subsequently air dried. The cleaned sides of the tyre free from steel breeds were cut into sections with the aid of a hacksaw and later into small pieces using very sharp knives. The size of the tyre chips were further reduced using an electric grinding machine. The resulting tyre particles were mechanically sieved to obtain particles in the size range 2.36 to 0.212 mm using different sieve trays as shown in Tables 1 and 2. The tyre granules were then washed with distilled water to remove any foreign materials by agitating it with a mechanical shaker operating at 150 rpm for 3 hours. It was subsequently oven dried at 60°C for 5 hours and stored in airtight containers for subsequent use [16].

The surface structure and other properties of the WTRG were evaluated by nitrogen adsorption method at -196°C. Nitrogen adsorption isotherms were determined using an adsorption equipment (BET 624, Micro-meritics, Germany). The surface area of the WTRG was determined using the standard BET equation. Micropore volume was determined using the 3-D pore size distribution model developed at ISGS/UIUC while the total pore volume was determined at a relative pressure ( $P/P_0$ ) value of approximately 0.98. The WTRG was also analyzed for carbon, nitrogen, oxygen, hydrogen, sulphur, moisture and ash contents using standard ASTM methods.

**Table 1. Modified design gradations and Federal Ministry of Works (FMW) specification**

Sieve size	FMW specification limit (% passing)	Gradation used (% passing)
19mm (3/4 in.)	100	100
12.5mm (1/2 in.)	85-100	85
9.5mm (3/8 in.)	75-92	77
4.75mm (#4)	65-82	65
2.36mm (#8)	50-65	50
1.18mm (#16)	36-61	41
0.6mm (#30)	26-40	26
0.3mm (#50)	18-30	21.5
0.15mm (#100)	13-24	13
0.075mm (#200)	7-14	8

**Table 2. Rubber gradation**

Sieve size	(% passing)
2.36mm (#8)	100
1.18mm (#16)	90
0.60mm (#30)	75
0.425mm (#40)	50
0.212mm (#75)	20

## 2.2 Preparation of Standard Solution

All chemicals used in this study were of analytical reagent grade and were used without further purification. Ethylbenzene (British Drug Houses Ltd, England) solution was prepared in a 1 liter amber glass bottle with a Teflon-lined septum screw-on lid to minimize vaporisation. The appropriate amount of reagent grade ethylbenzene was extracted from its original container with a micro syringe and injected into the 1 liter bottle containing deionised water. A co-solvent (ethanol) was added to enhance the solubility of ethylbenzene in water. The cap was then placed on the bottle and the solution was mechanically agitated for one minute. Standards solutions of volume 100 mL were prepared by adding a quantity of ethylbenzene in 250 mL amber bottles. Each bottle had a magnetic stirrer and was capped with a septum and sealed with paraffin. The desired concentrations were prepared from a 1000mg/l ethylbenzene solution using the dilution formula:

$$C_1V_1=C_2V_2 \quad (1)$$

Where:  $C_1$ =concentration of standard solution mg/l  
 $V_1$ =volume from standard solution in ml  
 $C_2$ =required concentration in mg/l  
 $V_2$ =volume of required solution (100ml)

## 2.3 Analysis of Ethylbenzene

The concentration of unadsorbed ethylbenzene in the sorption medium was measured using a UV-Vis spectrophotometer (PG Instruments model T70). A set of standard solutions of ethylbenzene were prepared and the absorbance of each standard solution was measured at a wavelength of 290nm. This value was obtained by scanning the UV-Vis spectrum of ethylbenzene and the wavelength that resulted in the maximum absorbance was selected. The instrument response was periodically checked by using standard ethylbenzene solutions.

## 2.4 Batch Adsorption Study

Adsorption of ethylbenzene on dried waste tyre rubber granules was studied in batch experiments. The experiments were carried out in mechanically agitated stoppered 250ml Erlenmeyer flasks. The batch study consisted of mixing a solute of a known concentration of ethylbenzene with water and crumb rubber. The solution was mechanically agitated until both the liquid and the solid medium reached chemical equilibrium at which point the ethylbenzene concentration on both solid and liquid medium remained constant. The effects of initial ethylbenzene concentration, size of adsorbent particles, adsorbent dosage, contact time, and temperature of solution on the adsorption capacity were investigated. At the end of each experiment the agitated solution mixture was filtered using Whatmann No.1 filter paper and the residual concentration of ethylbenzene was determined spectrophotometrically.

The adsorption capacity of the WTRG for ethylbenzene  $q$  was expressed in terms of the amount of ethylbenzene retained by the WTRG. This is written as:

$$q = \frac{V_s(C_i - C_e)}{W} \quad (2)$$

Where:  $q$  = Equilibrium concentration of contaminant in the rubber (mg/g)  
 $C_i$  = Initial concentration of contaminant in the solution (mg/L)  
 $C_e$  = Equilibrium concentration of contaminant in the solution (mg/L)  
 $V_s$  = Volume of solution (L)  
 $W$  = Mass of crumb rubber (g)

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterisation of WTRG

In terms of chemical composition, WTRG is a very complex material. It is generally made of vulcanized rubber and different kinds of materials such as textile cords, fabric belts, fillers and vulcanizing agents which serve to reinforce the tyre. The most commonly used polymer in tyre manufacture is styrene butadiene rubber. In addition, WTRG consists of carbon black, zinc oxide, natural rubber, sulfur etc. The properties of waste tyre rubber granules as obtained from proximate analysis as determined by above tests methods are presented in Table 3.

Ultimate elemental analysis of the WTRG indicate that the principal constituent was carbon accounting for about 87% of the weight of the granules followed by hydrogen which accounts for about 7% as shown in Table 4. The inorganic ash content of the WTRG used in this study obtained from ultimate analysis was about 3% as indicated in Table 4. The ash content is important because concentrations of trace species, especially metals, can likely affect the adsorptive properties of the WTRG. The values indicated in the Tables 3 and 4 are similar to those reported in the literature. The surface area, bulk density and pore volumes (micro and total) are indicated in Table 5.

**Table 3. properties of WTRG obtained from proximate analysis**

Property	Value (wt%)				
	This work	Lee et al. [17]	Chang [18]	Orr et al. [19]	Gonzales et al. [20]
Fixed carbon	28.35	28.50	26.26	23.30	29.20
Moisture	0.51	0.50	1.31	0.40	0.70
Ash	7.60	3.7	10.29	7.60	8.0
Volatile	63.54	67.30	62.32	68.70	61.90

**Table 4. ultimate elemental analysis of WTRG**

Property	Value (wt%)				
	This work	Roy et al. [21]	Cunliffe and Williams [22]	Senneca et al. [23]	Gonzales et al. [20]
Carbon	86.50	86.6	86.4	86.7	86.7
Hydrogen	6.64	8.1	8.0	6.9	8.1
Oxygen	1.10	2.2	3.4	1.0	1.3
Nitrogen	0.40	0.5	0.5	0.3	0.4
Sulphur	2.0	0.8	1.7	1.9	1.4
Inorganic Ash	2.85	-	2.4	3.3	2.9

**Table 5. physical properties of waste tire rubber granule**

<b>Property</b>	<b>Value</b>
Surface area (m <sup>2</sup> /g)	0.203
Bulk density (g/cm <sup>3</sup> )	0.230
Total pore volume (cm <sup>3</sup> /g)	0.660
Micro pore volume (cm <sup>3</sup> /g)	0.230

### 3.2 Time Dependent Studies of the Adsorption of Ethylbenzene by WTRG

The rate of adsorption is one of the influential factors that must be taken into consideration before planning batch adsorption experiments, hence the need to carry out time dependent studies. The profile of time dependent study of adsorption of ethylbenzene by WTRG is shown in Fig. 1.

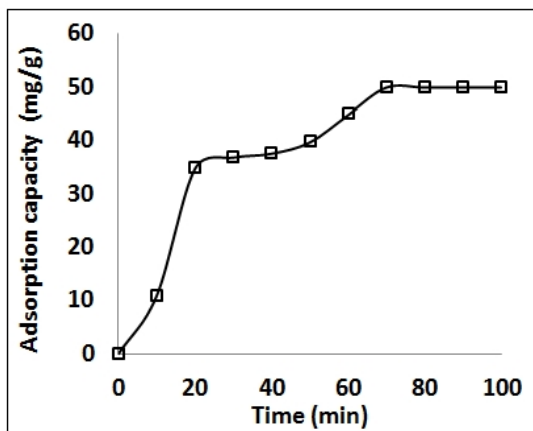
It can be observed from the Figure that adsorption was rapid within the first 20 minutes as indicated by the steep increase in the adsorption capacity. The rate of adsorption continues to increase but less rapidly for the next 50 minutes and the profile levels off after 70 minutes of contact indicating that the adsorbent has been saturated and equilibrium reached. At equilibrium, all available active binding sites are occupied by the ethyl benzene molecules which causes some desorption to take place simultaneously with the adsorption process. As a result of this, no noticeable increase in adsorption of ethylbenzene is observed.

The equilibrium contact time of 70minutes indicates fast adsorption of ethylbenzene by the WTRG. The fast kinetic process observed at the initial stage can be attributed to the abundant availability of active binding sites on the adsorbent, which are later occupied as the adsorption process progresses, thereby resulting in the inability of the WTRG to remove ethylbenzene at later stages of the adsorption process [6]. Gunasekara et al. [24] reported fast uptake of naphthalene, toluene and mercury on granulated waste tyres. Alam et al. [14] reported an equilibrium contact time of 100 minutes for the sorption of 2,4-D and phenol on WTRG. Alamo-Nole, [15] reported an equilibrium contact time of 30 minutes for the sorption of ethylbenzene, toluene and xylene on granulated crumb tyre rubber. In yet another work on the use of WTRG for organic pollutants abatement, Aisien et al. [13] reported fast adsorption of crude oil on WTRG as is mostly observed in adsorption of organic solvents on WTRG.

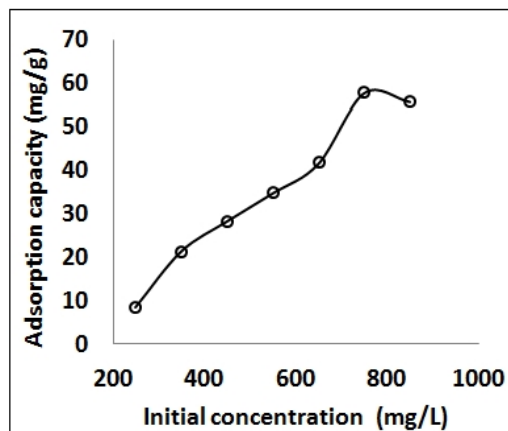
### 3.3 Effect of Initial Ethylbenzene Concentration on the Adsorption of Ethylbenzene on WTRG

The efficiency of WTRG in removing ethylbenzene from aqueous solution is dependent on the initial ethylbenzene concentration. The equilibrium sorption capacity of WTRG for different concentrations of ethylbenzene is presented in Fig. 2. In general, it can be observed from Fig. 2 the adsorption capacity increased with increase in initial ethylbenzene concentration. This indicates that there is a direct relationship between the uptake of ethylbenzene and the concentration of ethylbenzene in solution. The maximum adsorption capacity recorded was 57.85 mg/g. The trend observed can be explained by the fact that increasing the concentration of ethylbenzene in solution increases the mass transfer driving force and therefore the rate at which ethylbenzene molecules pass from the bulk solution to the adsorbent surface. Mahvi et al. [6] reported similar observations for the uptake of phenol from aqueous solution using rice husk and rice husk ash. Adebayo et al. [16] also reported

an upward trend for the uptake of lead ions using the leaves of the sand paper plant in a batch system.



**Fig. 1. Effect of contact time on the adsorption capacity of WTRG for ethylbenzene**



**Fig. 2. Effect of initial ethylbenzene concentration on the adsorption of ethylbenzene by WTRG**

### 3.4 Effect of Adsorbent Dosage on the Adsorption of Ethylbenzene by WTRG

Fig. 3 shows the effect of adsorbent dosage on the adsorption of ethylbenzene by WTRG. In general, it can be observed that the adsorption capacity increased with increase in adsorbent dosage indicating that adsorbent dose has a great influence on the adsorption process. It is evident from Fig. 3 that increasing the adsorbent dose led to the enhancement of ethylbenzene uptake as a result of the increase in population (number) of active sites [8,25]. This indicates that the adsorption tends to increase with adsorbent dosage. The amount of adsorbent added into the solution determines the number of binding sites available for adsorption [26]. Mousavi et al. [3] reported the adsorption of lead ions from aqueous solution using waste tyre rubber ash as adsorbent. They observed that increasing the adsorbent dose resulted in an increase in the adsorption capacity of the waste tyre rubber ash. Agarry and Owabor, [27] reported enhanced iron (III) uptake by activated rubber seed shells when the dosage of the adsorbent was increased. Similar results were obtained by Annadurai et al. [28] and Annadurai and Krishnan [29] owing to increase in the number of sites.

### 3.5 Effect of Adsorbent Particle Size the Adsorption of Ethylbenzene on WTRG

Fig. 4 shows the adsorption capacity of WTRG for ethylbenzene at various sizes of adsorbent particles. The trend observed indicate that as the particle size is increased, adsorption capacity decreases. The maximum adsorption capacity of WTRG for ethylbenzene recorded was 71.60 mg/g, obtained for a particle size of 0.212mm. The trend observed is explained by the fact that the smaller the size of the adsorbent particles, the greater the interior surface area and micro pore volume and consequently more active sites are available for adsorption [28]. However, for larger particles, the pore diffusion resistance to mass transfer is higher and most of the internal surfaces of the particle may not be utilized

for adsorption and consequently the amount of ethylbenzene adsorbed is small [28]. Similar results were obtained by Rao et al. [30] and Ajay et al. [31].

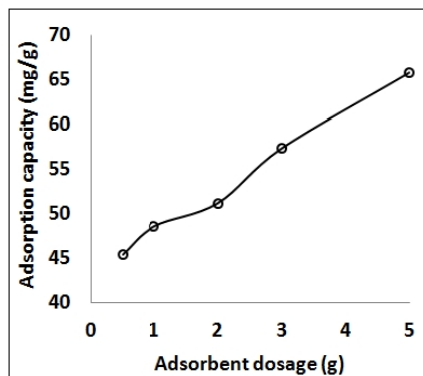


Fig. 3. Effect of adsorbent dosage on the adsorption of ethylbenzene by WTRG

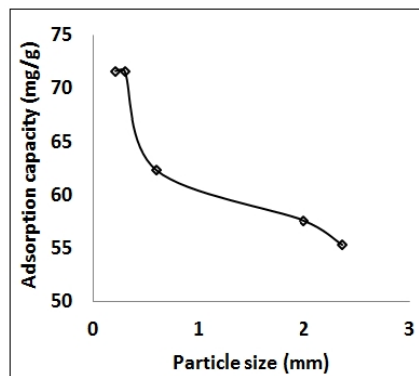


Fig. 4. Effect of adsorbent particle size on the adsorption of ethylbenzene by WTRG

### 3.6 Effect of Solution Temperature the Adsorption of Ethylbenzene on WTRG

The effect of temperature on the WTRG/ethylbenzene system is shown in Fig. 5. The adsorption capacity of WTRG decreased from 59.83 to 45.15 mg/g with increase in temperature from 5 to 45°C. This indicates that a lower temperature is more favourable than higher temperature for the adsorption of ethylbenzene on WTRG. The trend observed is due to the weakening of the attractive force between the ethylbenzene molecules and the adsorbent on the one hand and due to enhancement of thermal energies of the adsorbate on the other hand thus making the attractive force between the adsorbate (ethylbenzene) and adsorbent insufficient to retain the adsorbed molecules at the binding sites [32]. Mousavi et al. [4] reported that the adsorption rate could decrease with increasing temperature a trend which may be indicative of physical adsorption. The maximum value recorded for adsorption capacity was 59.83 mg/g. The increase of the rate of adsorption by decreasing the temperature indicates that the adsorption process is exothermic and vice versa [33,34]. An increase in uptake of organic molecules is expected when the adsorption temperature decreases because adsorption is a spontaneous process.

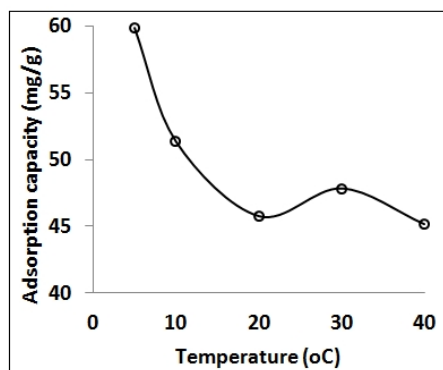


Fig. 5. Effect of temperature on the adsorption of ethylbenzene by WTRG



### 3.7 Kinetics of Adsorption

The kinetics of adsorption is important from the point of view that it controls the efficiency of the adsorption process. The Lagergren pseudo first-order, pseudo second-order and intra particle diffusion kinetic models were used to elucidate the mechanism of the adsorption process.

#### 3.7.1 Lagergren pseudo first-order kinetic model

The Lagergren rate equation [35] is one of the most widely used kinetic equations for the adsorption of a solute from a liquid solution. The model assumes a first order adsorption kinetics and can be represented by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Where:  $q_e$  and  $q_t$  are adsorption capacity at equilibrium and at time  $t$ , respectively (mg/g),  $k_1$  is the rate constant of pseudo first order adsorption ( $\text{min}^{-1}$ ). After integration and applying boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_e$ , the integrated form becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Note that the natural logarithm (ln) has been used.

The values of  $\ln(q_e - q_t)$  were linearly correlated with  $t$ . The plot of  $\ln(q_e - q_t)$  versus  $t$  should give a linear relationship from which  $k_1$  and  $q_e$  can be determined from the slope and intercept of the plot, respectively. Fig. 6 depicts the pseudo-first order plot for the adsorption of ethylbenzene by WTRG. A linear relationship observed in the semi-log plot is indicative of the applicability of the above equation and the first order of the process. The first order rate constants calculated from the plots are given in Table 6.

#### 3.7.2 Pseudo second-order kinetic model

The pseudo-second order kinetic model which is based on the assumption that chemisorption is the rate-determining step and can be expressed as in Equation (5):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

Where:  $k_2$  is the rate constant of the pseudo second order adsorption ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ).

After integration and applying boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_e$ , the integrated form becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (6)$$

Equation (6) can be rearranged to the linear form as below (Equation 7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

If the initial adsorption rate,  $h$  ( $\text{mg.g}^{-1}.\text{min}^{-1}$ ) is:

$$h = k_2 q_e^2 \quad (8)$$

then equation (7) becomes:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (9)$$

The plot of  $(t/q_t)$  and  $t$  of equation (9) as presented in Fig. 7 resulted in a linear relationship from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively. The respective constant values are given in Table 6.

### 3.7.3 Intra particle diffusion model

The intra particle diffusion kinetic model [36] can be written as presented in Equation (10):

$$q_t = K_p t^{1/2} + C \quad (10)$$

Where  $K_p$  is the intra particle diffusion rate constant ( $\text{mg.g}^{-1} \text{min}^{-1/2}$ ) and  $C$  is the boundary layer thickness.

The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater is the contribution of the surface sorption in the rate controlling step. The result presented in Fig. 8 indicates the existence of some boundary layer effect and further showed that intra particle diffusion was not the only rate limiting step. The calculated diffusion coefficient values are presented in Table 6.

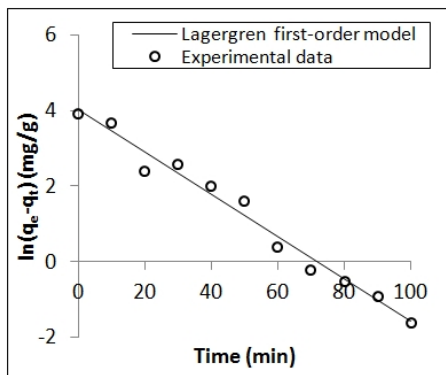


Fig. 6. Lagergren first-order kinetic model fitted to the batch adsorption data

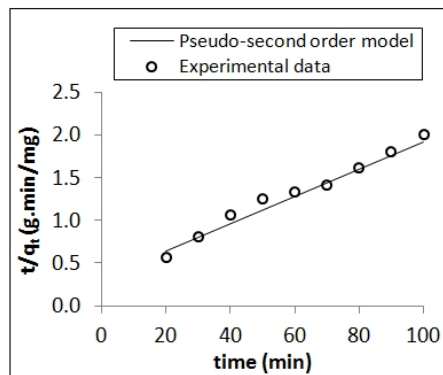
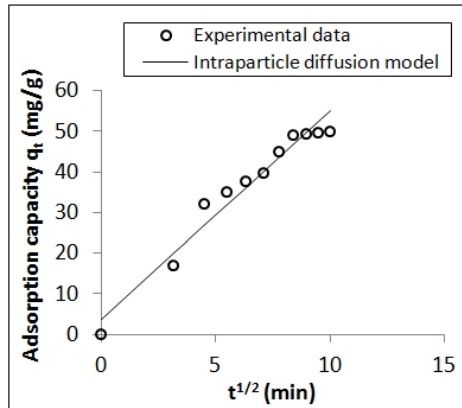


Fig. 7. Pseudo second order kinetic model fitted to the batch adsorption data



**Fig. 8. Intra particle diffusion model fitted to the batch adsorption data obtained for ethylbenzene adsorption onto WTRG**

**Table 6. Parameter values for pseudo first order, pseudo second order and intraparticle diffusion models**

Adsorption Kinetic Model	Parameters	Values
Lagergren Pseudo First-Order	$k_1$ ( $\text{min}^{-1}$ )	0.055
	$q_e$ (mg/g)	51.573
	$R^2$	0.991
Pseudo Second-Order	$k_2$ ( $\text{gmg}^{-1}\text{min}^{-1}$ )	6.329
	$q_e$ (mg/g)	3.145
	$R^2$	0.983
Intra particle diffusion	$K_p$	5.120
	$C$	3.705
	$R^2$	0.956

Generally, all the tested adsorption kinetic models fitted well to the adsorption kinetic data with high correlation coefficient at; however, the Lagergren first-order gave the best fit with highest correlation coefficient to describe the adsorption behaviour of ethylbenzene onto WTRG.

### 3.8 Isotherm Studies

To examine the relationship between ethylbenzene uptake ( $q_e$ ) and its equilibrium concentration in the solution ( $C_e$ ), adsorption isotherm models are widely employed for fitting experimental data, of which the Langmuir and Freundlich isotherm equations are the most widely used. The curves of the related adsorption isotherms are regressed and parameters of the equation are thus obtained.

#### 3.8.1 Langmuir isotherm

The Langmuir model [37] has been used empirically because it contains the two useful parameters ( $q_0$  and  $b$ ), which reflect the two important characteristics of the sorption system. It provides information on uptake capabilities and is capable of reflecting the usual

equilibrium adsorption process behavior. The linear form of the Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{bq_o} + \frac{C_e}{q_o} \quad (11)$$

$q_o$  is the maximum sorption capacity (mg/g) of the adsorbent while  $b$  is the sorption constant (L/mg) at a given temperature. A linear plot of  $C_e/q_e$  against  $C_e$  as shown in Fig. 9 was employed to obtain the values of  $q_o$  and  $b$  from the slope and intercept of the plot respectively. The essential characteristics of the Langmuir isotherm model can also be explained in terms of a dimensionless constant referred to as the separation factor ( $R_L$ ) defined in Equation (12).

$$R_L = \frac{1}{(1 + bC_o)} \quad (12)$$

$C_o$  is the initial concentration of ethylbenzene. The dependence of the nature of adsorption on the value of  $R_L$  is presented in Table 7.

**Table 7.  $R_L$  values and type of isotherm**

$R_L$	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

For this experiment, the values of  $R_L$  are given in Table 8. Since these values are between zero and one, it implies that the adsorption was favourable.

**Table 8.  $R_L$  values and type of isotherm**

Initial concentration (mg/L)	$R_L$ Value
250	0.374
350	0.299
450	0.249
550	0.213
650	0.187
750	0.166
850	0.149

The values of the Langmuir isotherm parameters as well as the correlation coefficient ( $R^2$ ) of the Langmuir equation for the adsorption of ethylbenzene by WTRG are given in Table 9.

**Table 9. Kinetic parameters for Langmuir and Freundlich isotherms**

Langmuir isotherm			Freundlich isotherm		
$q_o$ (mg/g)	$b$ (l/mg)	$R^2$	$K_f$ (mg/g)	$1/n$	$R^2$
200	0.0067	0.993	3.168	0.226	0.706

### 3.8.2 Freundlich isotherm

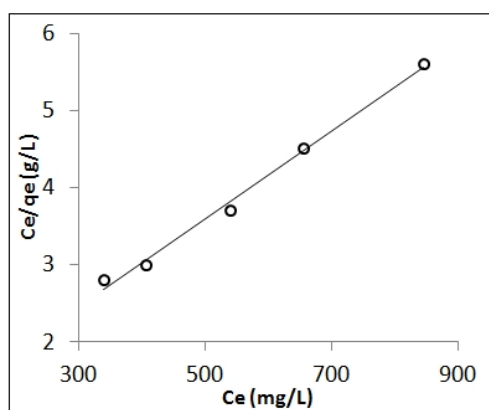
The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

$$q_e = K_f (C_e)^{1/n} \quad (13)$$

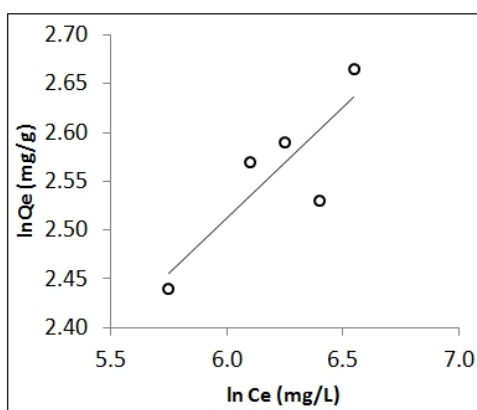
This equation can be expressed in linear form as follows:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (14)$$

$K_f$  and  $n$  are the Freundlich constants related to the adsorption capacity and adsorption intensity respectively. The intercept and slope of the linear plot of  $\ln q_e$  against  $\ln C_e$  at given experimental conditions as shown in Fig. 10 provides the values of  $K_f$  and  $n$ . Values of  $n$  between 1 and 10 represent beneficial adsorption. The values of these parameters as well as the correlation coefficient ( $R^2$ ) of the Freundlich equation for the adsorption of ethylbenzene by WTRG are given in Table 9.



**Fig. 9. Langmuir isotherm fitted to the batch adsorption data obtained for ethylbenzene adsorption onto WTRG**



**Fig. 10. Freundlich isotherm fitted to the batch adsorption data obtained for ethylbenzene adsorption onto WTRG**

Results presented in Table 9 indicate that the experimental data fitted the Langmuir isotherm better than the Freundlich isotherm as evident in the higher  $R^2$  value obtained for the Langmuir isotherm. This suggests that the adsorption of ethylbenzene by WTRG is of the mono-layer type.

## 4. CONCLUSIONS

The present study investigated the adsorption of ethylbenzene from aqueous solution using waste tyre rubber granules in a batch system. The following conclusions can be drawn.

- Adsorption of ethylbenzene by WTRG is affected by operational parameters such as contact time, initial ethylbenzene concentration, adsorbent dosage, and solution temperature.

- The capability of WTRG as adsorbent for organic pollutants like ethylbenzene in aqueous solutions has been verified.
- The equilibrium contact time was obtained as 70minutes indicating that the adsorption process was a fast kinetic process.
- A low temperature (5°C), small adsorbent particle size (0.212mm) and higher adsorbent dosage favoured the adsorption process with removal capacities of 59.83, 71.60 and 65.78mg/g respectively.
- Kinetic and isotherm studies indicate that the adsorption of ethylbenzene was best described by the Lagergren pseudo-first order kinetic equation and Langmuir isotherm equations respectively.
- This study has demonstrated that the low cost WTRG can be widely used for removal of ethylbenzene from aqueous solution.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

1. Aisien FA, Hymore FK, Ebewele RO. Application of Ground Scrap Tyre Rubbers in Asphalt Concrete Pavement. *Indian Journal of Engineering and Materials Science*. 2006;13:333-338.
2. Liu HS, Mead JL, Stacer RG. Environmental impact of recycled rubber in light fill applications: summary & evaluation of existing literature. Chelsea Center for Recycling and Economic Development, University of Massachusetts Lowell, Technical Report #2; 1998.
3. Mousavi HZ, Hosseynefar A, Jaheed V, Dehghani SA. Removal of Lead from Aqueous Solution using Waste Tyre Rubber Ash as Adsorbent. *Brazilian Journal of Chemical Engineering*. 2010a;27(1):79-87.
4. Mousavi HZ, Hosseynefar A, Jaheed V. Removal of Lead from Aqueous Solution using Waste Tyre Rubber Ash as Adsorbent. *Journal of the Serbian Chemical Society*. 2010b;75(6):845–853.
5. Grayson CA. Crumb Rubber as a Sorption Media for Ethylbenzene in Aqueous Solution. MSc Thesis. Department of Civil Engineering, Clemson University; 2010.
6. Mahvi AH, Maleki A, Eslami A. Potential of Rice Husk Ash for Phenol Removal in Aqueous Systems. *American Journal of Applied Sciences*. 2004;1(4):321-326.
7. Manojlovic D, Ostojic DR, Obradovic BM, Kuraica MM, Krsmanovic VD, Puric J. Removal of Phenol and Chlorophenols from Water by new Ozone Generator. *Desalination*. 2007;213:116-122.
8. Nagda GK, Diwan AM, Ghole VS. Potential of tendu leaf refuse for phenol removal in aqueous system. *Applied Ecology and Environmental Research*. 2007;5(2):1-9.
9. WHO. Ethylbenzene (Environmental Health Criteria 186), Geneva, International Programme on Chemical Safety; 1996.
10. Dabhade MA, Saidutta MB, Murthy DVR. Adsorption of Phenol on Granular Activated Carbon from Nutrient Medium: equilibrium and kinetic study. *International Journal of Environmental Research*. 2007;3(4):557-568.
11. Goncharuk VV, Kucheruk DD, Kochkodan VM, Badekha VP. Removal of organic compounds from aqueous solutions by reagent enhanced reverse osmosis. *Desalination*. 2002;143:45-51.

12. Mokrini A, Ousse D, Esplugas S. Oxidation of aromatic compounds with UV radiation/ozone/hydrogen peroxide. *Water Science and Technology*. 1997;35:95-102.
13. Aisien FA, Hymore FK, Ebebele RO. Potential Application of Recycled Rubber in Oil Pollution Control. *Indian Journal of Engineering and Materials Science*. 2002;11:179-190.
14. Alam MJB, Chowdhury RK, Hasan MM, Huda A, Sobhan S. Study and simulation of competitive sorption of 2,4,-D and phenol on waste tire rubber granules. *ARNP Journal of Engineering and Applied Sciences*. 2006;1(3):45-51.
15. Alamo-Nole LA, Roman F, Perales-Perez O. Sorption of ethyl benzene, toluene and xylene onto crumb rubber from aqueous solutions. MSc Thesis. 2006:Puerto-Rico: University of Puerto-Rico.
16. Adebayo MA, Adebayo AA, Adediji JF, Adebayo TO. Isotherm, Kinetic, and Thermodynamic Studies of Lead (II) Biosorption by *Streblus asper*. *Pacific Journal of Science and Technology*. 2012;13(2):283-293.
17. Lee JM, Lee JS, Kim JR, Kim SD. Pyrolysis of waste tires with partial oxidation in a fluidized-bed reactor. *Energy*. 1995;20(10):969-976.
18. Chang Yu-Min. On pyrolysis of waste tire: degradation rate and product yields. *Resources, Conservation and Recycling*. 1996;17(2):125-139.
19. Orr EC, Burghard JA, Tuntawiroon W, Anderson LL, Eyring EM. Coprocessing waste rubber tire material and coal. *Fuel processing technology*. 1996;47(3):245-259.
20. González JF, Encinar JM, Canito JL, Rodríguez JJ. Pyrolysis of automobile tyre waste. Influence of operating variables and kinetics study. *Journal of Analytical and Applied Pyrolysis*. 2001;58:667-683.
21. Roy C, Darmstadt H, Benallal B, Amen-Chen C. Characterization of naphtha and carbon black obtained by vacuum pyrolysis of polyisoprene rubber. *Fuel Processing Technology*. 1997;50(1):87-103.
22. Cunliffe AM, Williams PT. Composition of oils derived from the batch pyrolysis of tyres. *Journal of Analytical and Applied Pyrolysis*. 1998;44(2):131-152.
23. Senneca O, Salatino P, Chirone, R. A fast heating-rate thermogravimetric study of the pyrolysis of scrap tyres. *Fuel*. 1999;78(13):1575-1581.
24. Gunasekara AS, Donovan JA, Xing B. Ground discarded tires remove naphthalene, toluene, and mercury from water. *Chemosphere*. 2000;41:1155-1160.
25. Ho YS, Wase DAJ, Forster CF. Batch Nickel Removal from Aqueous Solution by Sphagnum Moss Peat. *Water Resources*. 1995;29:1327-1332.
26. Zafar MN, Nadeem R, Hanif MA. Biosorption of Nickel from Protonated Rice Bran. *Journal of Hazardous Materials*. 2007;143:478-485.
27. Agarry SE, Owabor CN. Evaluation of the adsorption potential of rubber (*havea brasiliensis*) seed pericarp-activated carbon in abattoir wastewater treatment and in the removal of iron (III) ions from aqueous solution. *Nigeria Journal of Technology*. 2012;31(3):346-358.
28. Annadurai G, Rajesh BS, Mahesh KPO, Murugesan T. Adsorption and Biodegradation of Phenol by Chitosan-Immobilised *Pseudomonas Putida*. *Bioprocess Engineering*. 2000;22:493-501.
29. Annadurai G, Krishnan MRV. Adsorption of acid dye from aqueous solution by chitin: Batch Kinetic Studies. *Indian Journal of Chemical Technology*, 1997;4:169-172.
30. Rao M, Bhole AG. Removal of Chromium using low cost adsorbents. *Journal of American Environmental Microbiology*. 2000;27:291-296.
31. Ajay KJ, Vinod GK, Shubhi J, Suhas. Removal of Chlorophenol using industrial wastes. *Environmental Science and Technology*. 2004;38:1195–1200.
32. Jadhav DN, Vangara AK. Removal of Phenol from Wastewater using Sawdust and Sawdust Carbon. *Indian Journal of Chemical Technology*. 2004;11:35-45.

33. Doğan M, Alkan M. Removal of methyl violet from aqueous solution by perlite. *Journal of Colloid and Interface Science*. 2003;267(1):32-41.
34. Jain AK, Gupta VK, Bhatnagar A, Suhas. Utilization of industrial waste products as adsorbents for the removal of dyes. *Journal of Hazardous Materials*. 2002;101(1):31-42.
35. Lagergren S. Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska vetenskaps akademiens. Handlingar*. 1898;24:1-39.
36. Weber WJ, Morris JC. Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division of American Society of Civil Engineering*. 1963;89:31-60.
37. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*. 1914;40:361-368.

---

© 2013 Aisien et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*

*The peer review history for this paper can be accessed here:*  
<http://www.sciencedomain.org/review-history.php?iid=250&id=22&aid=1752>