Application of Recycled Rubber from Scrap Tire in the Removal of Phenol from Aqueous Solution.

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ABSTRACT

The adsorption of phenol from aqueous solution using waste tire rubber granules (WTRG) was investigated in a batch system. The effect of various factors such as contact time, initial concentration of phenol, amount of adsorbent, size of adsorbent particles, pH, and temperature of solution on the adsorption capacity of WTRG was determined. Equilibrium data were analysed using Langmuir and Freundlich isotherm models while the kinetics of the process was elucidated using the Lagergren pseudo-first order, pseudo second-order, and intra-particle diffusion models. The equilibrium time was obtained to be 60 minutes indicating fast adsorption. The adsorption capacity of WTRG increased with decrease in both the size of adsorbent particles and the temperature of the solution. Maximum adsorption was recorded at a pH of 8.5. The results obtained from isotherm studies indicated that the equilibrium data for phenol adsorption on WTRG fit the Langmuir isotherm best with an R^2 value of 0.993. All the tested kinetic models exhibited good fit with the experimental data while the best fit was obtained for the Lagergren pseudo-first order model.

(Keywords: adsorption, phenol, waste tire rubber granules, WTRG, adsorption capacity, kinetics, isotherm models)

INTRODUCTION

One of the most important types of municipal solid wastes (MSW) is waste tires resulting from the increase in vehicle ownership and traffic volume around the world. These waste tires represent a major environmental problem as a result of their volume, non-biodegradability and indiscriminate disposal (Mousavi et al., 2010a). An estimated 5 million tires from trucks, cars and motorcycles existed in Nigeria the early 1980s (Ebewele et al., 1990). As the country's population and economy grow, so does the amount and type of scrap tires generated. With an annual generation rate of 15%, between 700,000 and 850,000 scrap tires are added to the waste stream each year. Recently, Aisien et al. (2006) estimated that about 15 million scrap tires are now in existence in Nigeria.

Although some recycling methods for waste tire are currently employed such as uses in road pavement, rubber roofs, floor mats, liquid waste treatment, playground surfaces and as solid fuels for cement kiln and paper mill, still a huge amount of tires are discarded improperly (Aisien et al., 2003; Aisien et al., 2006; Grayson, 2010; Mousavi et al., 2010b). It is therefore imperative to explore other possible applications such as use as adsorbents.

The improper discharge of industrial waste water contaminated with organics poses a problem to the environment. Phenol 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 oil refineries, pesticide and dye manufacture, phenolic resin manufacture, textile, plastic, tanning, rubber, pharmaceuticals etc. (Mahvi et al., 2004; Manojlovic et al., 2007; Nagda et al., 2007). It is important to remove phenol from wastewater before discharge into any naturally occurring water body because it is highly hazardous, carcinogenic and resistant to degradation (Dabhade et al., 2007; Mahvi et al., 2004).

Conventional methods for removing phenolic compounds from industrial wastewater include solvent extraction, steam distillation, irradiation, electrochemical oxidation, reverse osmosis photocatalytic degradation and adsorption on activated carbon, ion exchange resins and silicates (Carmona et al., 2006; Goncharuk et al., 2002; Mokrini et al., 1997; Nagda et al., 2007; Polcaro et al., 1997). The major drawback with these methods is the cost associated with start-up and subsequent sustainability. Adsorption remains the best option for phenol removal as it can generally remove all types of phenolic 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 adsorbents, waste tire rubber granules offers an excellent alternative in that it is cheap and readily available. Recently, interests has been shown in the use of waste tire rubber granules in the treatment of industrial wastewater (Alam et al., 2006; Alamo-Nole et al., 2006; Mousavi et al., 2010a)

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

MATERIALS AND METHODS

Preparation of Adsorbent

Scrap tires were collected from the Rubber Research Institute of Nigeria, Iyanomo, Benin City, Nigeria. The tires were washed with water to remove dirt and were subsequently air dried. The cleaned sides of the tire 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 tire chips were further reduced using an electric grinding machine. The resulting tire particles were mechanically sieved to obtain particles in the size range 2.36 to 0.075 mm using different sieve trays as shown in Table 1. The tire 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^{o}C for 5 hours and stored in airtight containers for subsequent use (Adebayo et al., 2012).

The surface structure and other properties of the WTRG were evaluated by nitrogen adsorption method at -196^{o}C. Nitrogen adsorption isotherms were determined using 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/Po) value of approximately 0.98. The WTRG was also analyzed for carbon, nitrogen, oxygen, hydrogen, sulfur, moisture and ash contents using standard ASTM methods.

Table 1: 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
0.075 (#120)	10

Preparation of Standard Solution

All chemicals used in this study were of analytical reagent grade and were used without further purification. Phenol (British Drug Houses Ltd., England) solution was prepared in a 1 liter glass bottle with a screw-on lid to minimize vaporization. The appropriate amount of reagent grade phenol was extracted from its original container with a micro syringe and injected into the 1 liter bottle containing de-ionized 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 phenol in 250 mL amber bottles. Each bottle had a magnetic stirrer and was capped with a septum and sealed with paraffin.

Quantitative Analysis of Phenol

The concentration of un-adsorbed phenol in the sorption medium was measured using a UV-Vis spectrophotometer (PG Instruments model T70) at a wavelength of 248nm. A standard phenol calibration curve was used to evaluate the concentration of phenol.

Batch Adsorption Studies

Adsorption of phenol on waste tire rubber granules was studied in a batch process. The process was carried out in mechanically agitated stoppered 250mL Erlenmeyer flasks. The batch study consisted of mixing 100mL of an aqueous solution of phenol of known concentration with an appropriate amount of WTRG. The solution was mechanically agitated until both the liquid and the solid medium reached chemical equilibrium at which point the phenol concentration on both solid and liquid medium remained constant.

The effects of pH, adsorbent dosage, contact time, initial phenol concentration and temperature on the adsorption capacity were investigated. At the end of each study, the agitated solution mixture was filtered using Whatmann No.1 filter paper and the residual concentration of phenol was determined spectrophotometrically.

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

$$q = \frac{V_s(C_i - C_e)}{W} \quad \textbf{(1)}$$

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

RESULTS AND DISCUSSION

Characterisation of WTRG

The properties of waste tire rubber granules as obtained from proximate analysis are presented in Table 2. 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 accounted for about 7% as shown in Table 3. The inorganic ash content of the WTRG used in this study obtained from ultimate analysis was about 3% as indicated in Table 3. The ash content is important because concentrations of trace species, especially metals, can affect the adsorptive properties of the WTRG. The values indicated in the Tables 2 and 3 are similar to those reported in the literature. The surface area, bulk density and pore volumes (micro and total) are presented in Table 4.

Table 2: Properties of WTRG obtained from Proximate Analysis.

Property	Value (wt%)		
	This work.	Lee et al., (1995)	Gonzales et al., (2001)
Fixed carbon	28.35	28.50	29.20
Moisture	0.51	0.50	0.70
Ash	7.60	3.7	8.0
Volatile	63.54	67.30	61.90

Table 3: Ultimate Elemental Analysis of WTRG.

Property	Value (wt%)		
	This work.	Senneca et al., (1999)	Gonzales et al., (2001)
Carbon	86.50	86.7	86.7
Hydrogen	6.64	6.9	8.1
Oxygen	1.10	1.0	1.3
Nitrogen	0.40	0.3	0.4
Sulphur	2.0	1.9	1.4
Inorganic Ash	2.85	3.3	2.9

Table 4: Physical Properties of Waste Tire Rubber Granule.

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

Effect of Contact Time on the Adsorption of Phenol on WTRG

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

It can be observed from Figure 1 that adsorption was rapid within the first 30 minutes as indicated by the steep increase in the adsorption capacity. The rate of adsorption continues to increase but less rapidly for the next 30 minutes and the profile levels off after 60 minutes of contact indicating that the adsorbent has been saturated and equilibrium reached. Therefore, for further studies, the contact time was set at 60 minutes. At equilibrium, all available active binding sites are occupied by the phenol molecules which causes some desorption to take place simultaneously with the adsorption process. As a result of this, no noticeable increase in adsorption of phenol is observed.

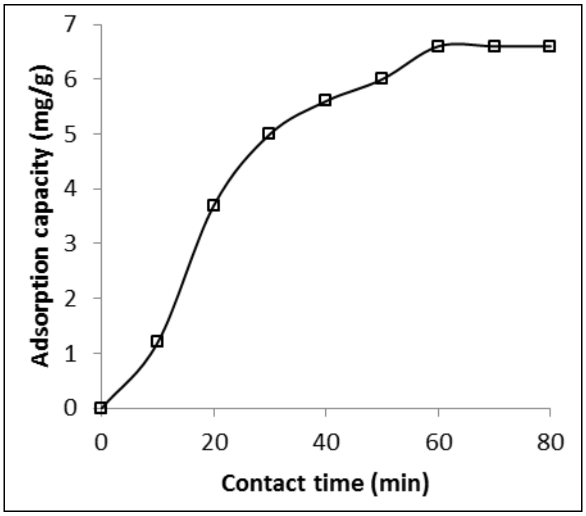

Figure 1: Effect of Contact Time on the Removal of Phenol from Solution (pH 8.5; initial phenol concentration, 900 mg/L; WTRG dose, 2g; temperature, 31°C).

The equilibrium contact time of 60 minutes indicates fast adsorption of phenol 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 phenol at later stages of the adsorption process (Mahvi et al., 2004). Gunasekara et al. (2000) reported fast uptake of naphthalene, toluene and mercury on granulated waste tires. Alam et al. (2006) reported an equilibrium contact time of 100 minutes for the sorption of 2,4-D and phenol on WTRG. Alamo-Nole, (2006) reported an equilibrium contact time of 30 minutes for the sorption of ethylbenzene, toluene and xylene on granulated crumb tire rubber. In yet another work on the use of WTRG for organic pollutants abatement, Aisien et al., (2002) reported fast adsorption of crude oil on WTRG as is mostly observed in adsorption of organic solvents on WTRG.

Effect of Initial Phenol Concentration on the Adsorption of Phenol on WTRG

The efficiency of WTRG in removing phenol from aqueous solution at different initial phenol concentrations was determined. The equilibrium sorption capacities of WTRG for different concentrations of phenol is presented in Figure 2. It can be observed from Figure 2 that the adsorption capacity increased from 11.5 to 13.8 mg/g with increase in initial phenol concentration from 500 to 900 mg/L. This indicates that there is a direct relationship between the uptake of phenol and the concentration of phenol in solution. The trend observed can be explained by the fact that increasing the concentration of phenol in solution increases the mass transfer driving force and therefore the rate at which phenol molecules pass from the bulk solution to the adsorbent surface.

Mahvi et al. (2004) reported similar observations for the uptake of phenol from aqueous solution using rice husk and rice husk ash. Adebayo et al., (2012) also reported an upward trend for the uptake of lead ions using the leaves of the sand paper plant in a batch system.

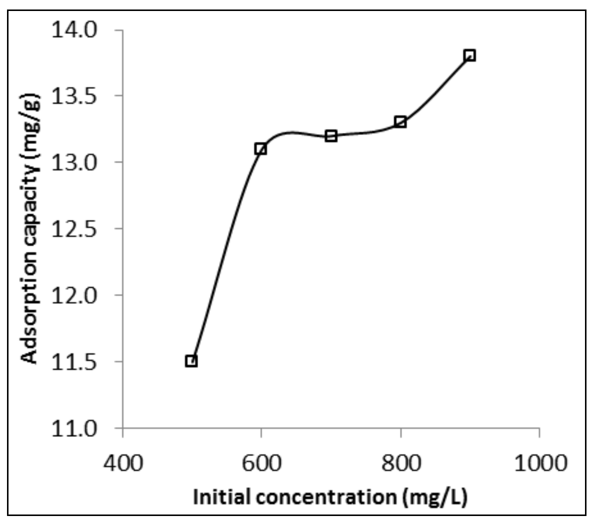

Figure 2: Effect of Initial Phenol Concentration on the Removal of Phenol from Solution (pH 7; WTRG dose, 2g; temperature, 31°C).

Effect of Adsorbent Dosage on the Adsorption of Phenol on WTRG

Adsorbent dose has a great influence on the adsorption process. Dosage of adsorbent added into the solution determines the number of binding sites available for adsorption (Zafar et al., 2007). Figure 3 shows the effect of adsorbent dosage on the adsorption capacity of WTRG for phenol. It is evident from the Figure that increasing the adsorbent dose led to the enhancement of phenol uptake as a result of the increase in the population of active sites (Ho et al., 1995; Nagdah et al., 2007). Maximum removal of phenol was observed with an adsorbent dose of 4g. Mousavi et al. (2010a) reported the adsorption of lead ions from aqueous solution using waste tire rubber ash as adsorbent. They observed that increasing the adsorbent dose resulted in an increase in the adsorption capacity of the waste tire rubber ash. Agarry and Owabor, (2012) 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. (2000) and Annadurai and Krishnan (1998) owing to increase in the number of active sites.

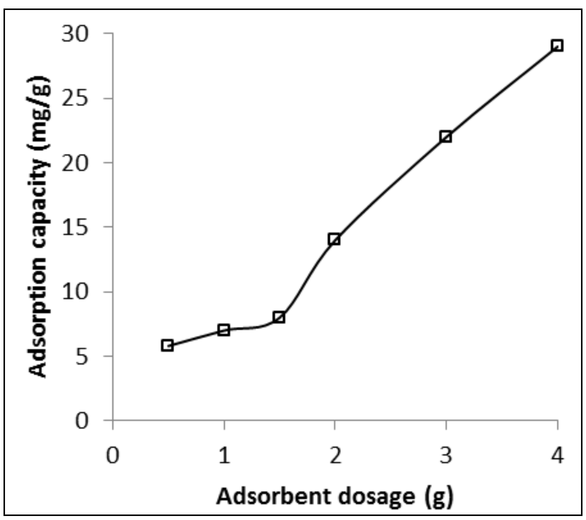

Figure 3: Effect of Adsorbent Dosage on the Removal of Phenol from Solution (pH 7; initial phenol concentration, 900 mg/L; temperature, 31°C).

Effect of pH on the Adsorption of Phenol on WTRG

Adsorption of phenol by WTRG is pH dependent as shown in Figure 4. The Figure shows that adsorption of phenol increases as the pH of the solution increases up to a maximum value of 8.5 after which it decreased. Atef et al. (2009) reported similar trends for the effect of pH on the adsorption of phenol on activated phosphate rock. Banat et al. (2010) also reported a similar trend for the effect of pH on the adsorption of phenol on bentonite. Phenol which is a weak acid (PKa=9.89) will be adsorbed to a lesser extent at pH values higher than its PKa value due to repulsive forces between negative surface charge on the adsorbent and the phenolate ion prevailing at such high pH values. This observation is explained by the fact that at pH values higher than its PKa value, phenol forms salts which readily ionize leaving a negative charge on the phenolic group. At the same time, the presence of the hydroxyl ions (OH^-) on the adsorbent limits the uptake of phenol (Atef et al., 2009). On the other hand, at low pH values, the surface of the adsorbent will also be surrounded by the hydroxyl ions but is less negative compared to surface charge on the adsorbent at higher pH, which reduces the attraction of the phenolic group towards it (Tiemann et al., 2002).

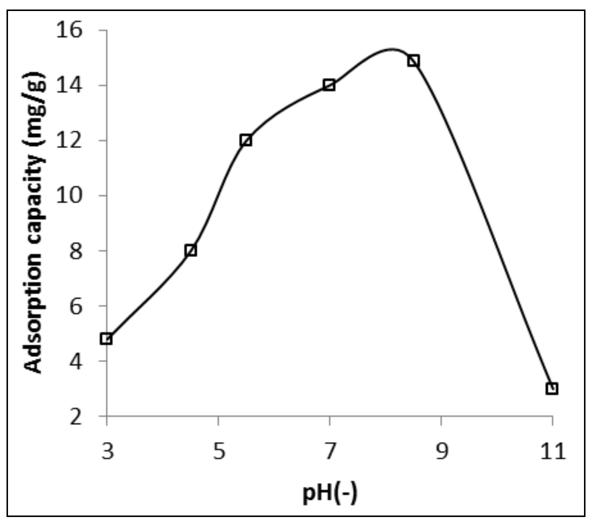

Figure 4: Effect of pH on the Removal of Phenol from Solution (initial phenol concentration, 900 mg/L; WTRG dose, 2g; temperature, 31°C).

Effect of Adsorbent Particle Size the Adsorption of Phenol on WTRG

Figure 5 shows the adsorption capacity of WTRG at various sizes of adsorbent particles. The trend observed indicate that as the particle size increases, the adsorption capacity decreases. The adsorption capacity of WTRG decreased from 10.6 to 5mg/g with increase in particle size from 0.212 to 2.36mm. 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 (Annadurai et al., 2000). 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 phenol adsorbed is small (Annadurai et al., 2000). Similar results were obtained by Rao et al. (2000) and Ajay et al. (2004).

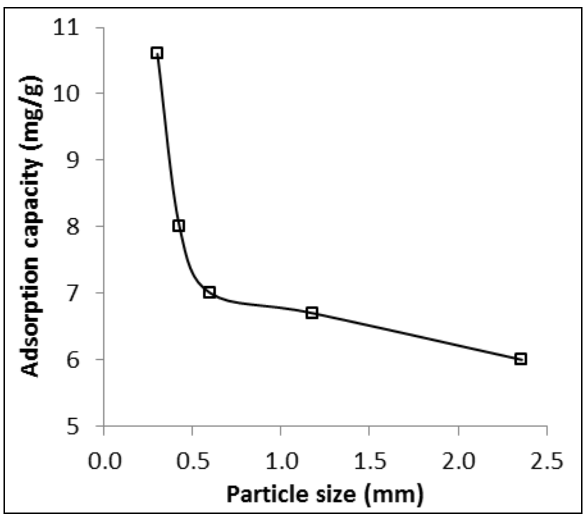

Figure 5: Effect of Particle Size on the Removal of Phenol from Solution (initial phenol concentration, 900 mg/L; pH 8.5; WTRG dose, 2g; temperature, 31°C).

Effect of Solution Temperature the Adsorption of Phenol on WTRG

The effect of temperature on the WTRG/phenol system is shown in Figure 6. The adsorption capacity of WTRG decreased with increase in temperature. The adsorption capacity of WTRG was observed to decrease from 13.4 to 9.9 mg/g with increase in temperature from 5 to 45^{o}C. This indicates that a lower temperature is more favorable for the adsorption of phenol on WTRG. The trend observed is due to the weakening of the attractive force between phenol 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 (phenol) and adsorbent insufficient to retain the adsorbed molecules at the binding sites (Jadhav et al., 2003). Babarinde et al, (2012) reported a similar trend for the adsorption of Nickel, Chromium and Cobalt ions from aqueous solution using cocoyam (*Colocasia esculenta*) leaves. Mousavi et al. (2010a) reported that the adsorption rate could decrease with increasing temperature a trend which may be indicative of physical adsorption. The increase of the rate of adsorption by decreasing the temperature indicates that the adsorption process is exothermic and vice versa (Dogan and Alkan, 2003; Jain et al., 2003). An increase in uptake of organic molecules is expected when the adsorption temperature decreases because adsorption is a spontaneous process.

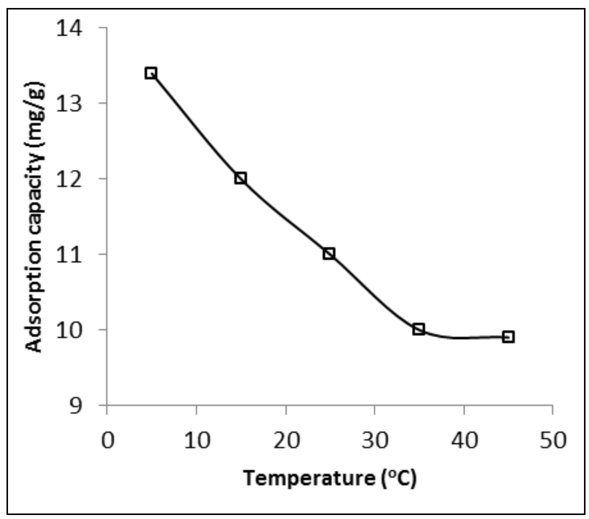

Figure 6: Effect of Temperature on the Removal of Phenol from Solution (initial phenol concentration, 900 mg/L; WTRG dose, 2g; pH 8.5; temperature, 31°C).

Isotherm Study

To examine the relationship between phenol uptake (Qe) and its equilibrium concentration in the solution (Ce), adsorption isotherm models are employed for fitting 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.

Langmuir Isotherm

The Langmuir model (Langmuir, 1918) has been used empirically because it contains the two useful parameters (Qo and *b*), which reflect the two important characteristics of the sorption system (Holan and Volesky,1994; Volesky and Holan, 1995). 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:

$$\frac{Ce}{Qe} = \frac{1}{bQo} + \frac{Ce}{Qo} \qquad \textbf{(2)}$$

Qo 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 *Ce/Qe* against *Ce* as shown in Figure 7 was employed to obtain the values of *Qo* and b from the slope and intercept of the plot respectively.

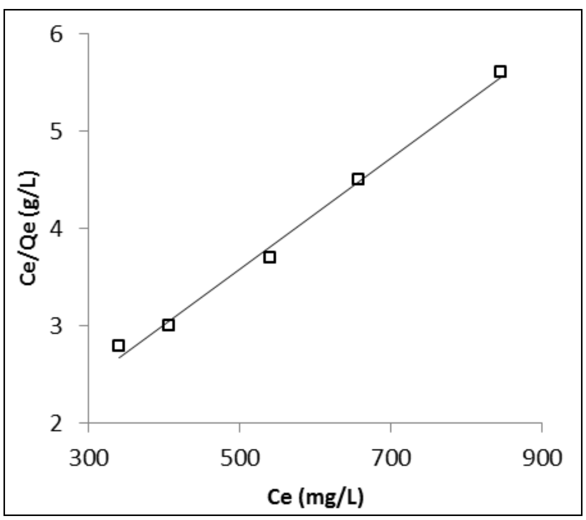

Figure 7: Application of Langmuir Isotherm for the Adsorption of Phenol on WTRG.

The values of the Langmuir isotherm parameters as well as the correlation coefficient (R^2) of the Langmuir equation for the adsorption of phenol by WTRG are given in Table 5.

Table 5: Values of Langmuir Isotherm Constants for WTRG/Phenol System.

Qo (mg/g)	b (L/mg)	R^2
200	0.0067	0.993

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 (3).

$$R_L = \frac{1}{(1+bCo)} \qquad \textbf{(3)}$$

Co is the initial concentration of phenol. The dependence of the nature of adsorption on the value of R_L is presented in Table 6.

Table 6: 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 study, the values of R_L are given in Table 7. Since these values are between zero and one, it implies that the adsorption was favorable.

Table 7: R_L Values and Type of Isotherm.

Initial concentration (mg/L)	R_L Value
500	0.230
600	0.199
700	0.176
800	0.157
900	0.142

Freundlich Isotherm

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

$$Qe = K_f (Ce)^{1/n} \quad \textbf{(4)}$$

This equation can be expressed in linear form as follows:

$$\ln Qe = \ln K_f + 1/n \ln Ce \quad \textbf{(5)}$$

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 Qe against ln Ce at given experimental conditions as shown in Figure 8 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 phenol by WTRG are given in Table 8.

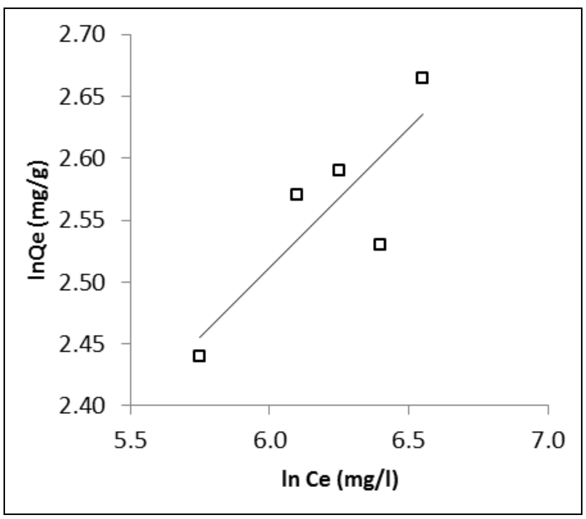

Figure 8: Application of Freundlich Isotherm for the Adsorption of Phenol on WTRG.

Table 8: Values of Freundlich Isotherm Constants for WTRG/Phenol System.

K_f (mg/g)	n	R^2
3.168	4.425	0.706

Comparison of the results presented in Tables 4 and 7 indicate that the adsorption 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 phenol by WTRG is of the mono-layer type and agrees with the observation that the phenol ions adsorbed from an aqueous solution usually forms a layer on the surface of the adsorbent.

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 describe the mechanism of the adsorption process.

Lagergren Pseudo First-Order Kinetic Model

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

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \textbf{(6)}$$

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 (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:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \textbf{(7)}$$

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 slop and intercept of the plot, respectively. Figure 9 depicts the pseudo-first order plot for the adsorption of phenol 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 plot are given in Table 8.

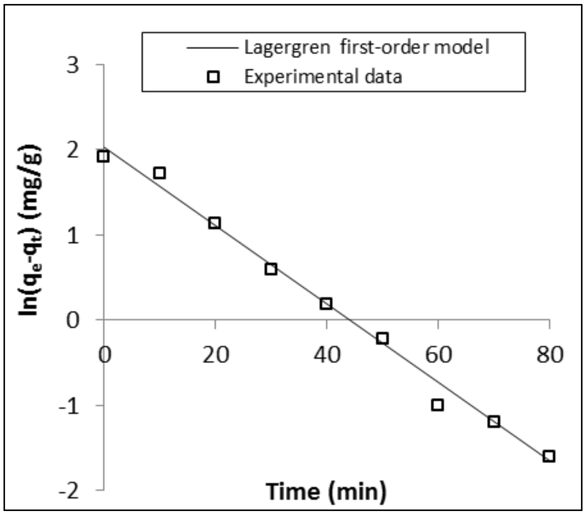

Figure 9: Lagergren First-Order Kinetic Model Fitted to the Batch Adsorption Data Obtained for Phenol Adsorption onto WTRG.

Pseudo Second-Order Kinetic Model

The pseudo-second order kinetic model which is based on the assumption that chemisorption is the rate-determining step can be expressed as in Equation (8):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \textbf{(8)}$$

Where: k_2 is the rate constant of the pseudo second order adsorption ($g.mg^{-1}.min^{-1}$).
After integration and applying boundary conditions t=0 to t=t and q_t=0 to q_t=q_e, the integrated form becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad \textbf{(9)}$$

Equation (9) can be rearranged to the linear form as below (Equation 10):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \textbf{(10)}$$

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

$$h = k_2 q_e^2 \quad \textbf{(11)}$$

then Equation (10) becomes:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad \textbf{(12)}$$

The plot of (t/q_t) and t of equation (12) as presented in Figure 10 resulted in a linear relationship from which q_e and k_2 was determined from the slope and intercept respectively. The respective constant values are given in Table 8.

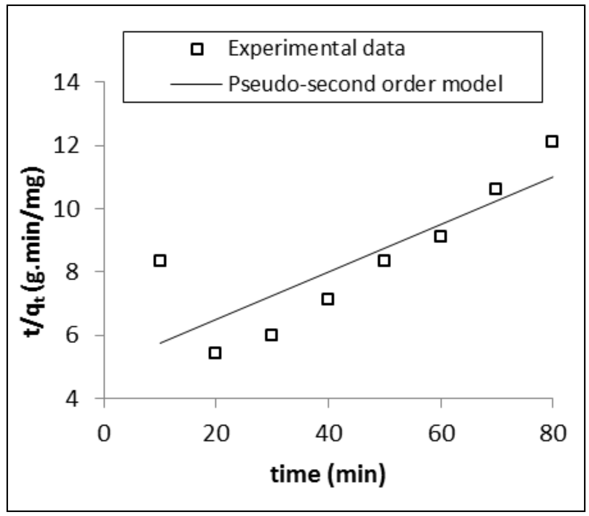

Figure 10: Pseudo second order kinetic model fitted to the batch adsorption data obtained for phenol adsorption onto WTRG

Intra Particle Diffusion Model

The intra particle diffusion kinetic model can be written as presented in Equation (13):

$$q_t = K_p t^{1/2} + C \quad \textbf{(13)}$$

Where Kp is the intra particle diffusion rate constant (mgg^{-1} $min^{-1/2}$) and C is a constant which is indicative of 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 Figure 11 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 9.

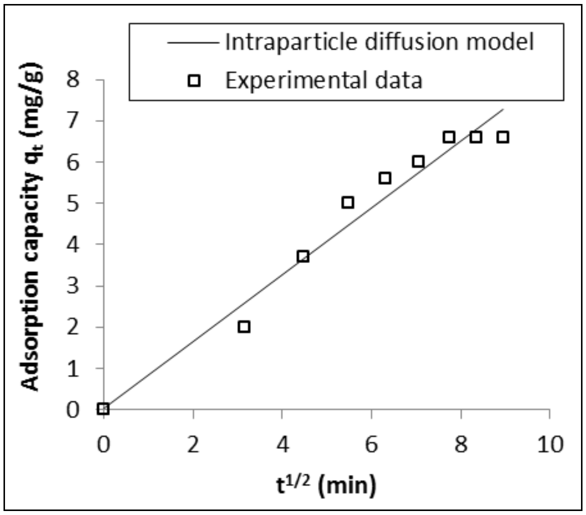

Figure 11: Intra Particle Diffusion Model Fitted to the Batch Adsorption Data Obtained for Phenol Adsorption onto WTRG.

Table 9: Parameter Values for Pseudo First Order, Pseudo Second Order and Intraparticle Diffusion Models.

Adsorption Kinetic Model	Parameters	Values
Lagergren Pseudo First-Order	k_1 (min^{-1})	0.046
	q_e (mg/g)	7.614
	R^2	0.991
Pseudo Second-Order	k_2 (gmg^{-1}min^{-1})	0.001
	q_e (mg/g)	13.33
	R^2	0.665
Intra particle diffusion	K_p	0.809
	C	0.039
	R^2	0.966

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

CONCLUSION

The present study investigated the adsorption of phenol from aqueous solution using waste tire rubber granules in a batch system. The optimum conditions of adsorption were determined by investigating the effects of contact time, initial phenol concentration, adsorbent dosage, solution temperature and pH. Adsorption of phenol by WTRG is a function of these operational parameters. The adsorption process was a fast kinetic process. Low temperature, medium pH, small size of adsorbent particles and a relatively high dosage of WTRG favoured the adsorption process. The adsorption of phenol by WTRG is of the mono-layer type and this was best described by the Langmuir isotherm with an R^2 value of 0.993. Kinetic studies indicate that the adsorption of phenol was best described by the Lagergren pseudo-first order kinetic equation with an R^2 value of 0.991. This study has revealed that the low cost WTRG can be used for removal of phenol from aqueous solution.

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SUGGESTED CITATION

Aisien, F.A., A.N. Amenaghawon, and A.R. Adeboyejo. 2013. "Application of Recycled Rubber from Scrap Tire in the Removal of Phenol from Aqueous Solution". *Pacific Journal of Science and Technology*. 14(2):330-341.

Pacific Journal of Science and Technology