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[1.] F.A. AISIEN, [2.] N.A. AMENAGHAWON, [3.] R. ADEBOYEJO

POTENTIAL APPLICATION OF RECYCLED RUBBER FROM SCRAP TIRE IN THE REMOVAL OF PHENOL FROM AQUEOUS SOLUTION

[1-3.] DEPARTMENT OF CHEMICAL ENGINEERING, FACULTY OF ENGINEERING, UNIVERSITY OF BENIN, PMB 1154, BENIN CITY, NIGERIA

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 initial concentration of phenol, amount of adsorbent, size of adsorbent particles, pH and temperature of solution on the adsorption capacity of WTRG and percentage removal of phenol was studied. The equilibrium time for a phenol concentration of 700mg/l was obtained to be 60 minutes indicating fast adsorption. The percentage removal of phenol and adsorption capacity of WTRG increased from 20.5 to 40% and 5 to 10.6 mg/g respectively with decrease in particle size from 2.36 to 0.30mm. The adsorption capacity of WTRG was observed to decrease from 13.4 to 9.9 mg/g with increase in solution temperature from 5 to 45°C indicating that low temperatures favoured the adsorption of phenol. Maximum adsorption was recorded at a pH of 8.5 and an adsorbent dosage of 4g. Isotherm data were analysed using Langmuir and Freundlich isotherm models. The equilibrium data for phenol adsorption on WTRG was observed to fit Langmuir isotherm best with an R^2 value of 0.995.
KEYWORDS: Adsorption, Phenol, waste tire, adsorption capacity, isotherm

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, 2010). 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, 2002; Aisien et al, 2006). It is therefore imperative to explore other possible applications such as use as adsorbents.

The improper discharge of industrial organic effluents contaminates 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 as well as chemical techniques such as 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 adsorbent, 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 (Aisien et al, 2002; Mousavi et al, 2010)

Hence 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 initial phenol concentration, adsorbent dosage, adsorbent particle size, pH and temperature of the aqueous solution.

MATERIALS & METHODS - Preparation of Adsorbent

Scrap tires were collected from Uwelu scrap tire dump site in 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 Tables 1 and 2. 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°C for 5 hours and stored in airtight containers for subsequent use.

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

Solution Preparation

All chemicals used in this study were of analytical reagent grade and were used without further purification. Phenol solutions were prepared by diluting stock solution of phenol to the desired concentrations. A stock solution containing 1000mg/l of phenol was prepared by dissolving 1g of phenol (British Drug Houses Ltd, England) in 1000ml of distilled water.

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. The instrument response was periodically checked by using standard phenol solutions.

Batch Adsorption Study

Adsorption of phenol on dried waste tire rubber granules was studied in batch experiments. The experiments were carried out in mechanically agitated 250ml Erlenmeyer flasks containing 2g of WTRG in 100ml of an aqueous solution of phenol of the desired concentration. The effects of pH, adsorbent dosage, contact time, initial phenol concentration and temperature on the adsorption capacity and percentage phenol removal 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 phenol was determined spectrophotometrically.

The percentage removal of phenol from solution was calculated as follows:

$$\%\ \text{Removal} = \frac{Co - Ce}{Co} \times 100 \quad (1)$$

where Co and Ce are the initial and equilibrium concentration of adsorbate respectively.

The adsorption capacity of the WTRG for phenol was expressed in terms of the ratio of the mass of phenol retained by the WTRG to that of the recycled rubber i.e.

$$\text{Adsorption capacity} = \frac{\text{Mass of phenol retained (mg)}}{\text{Mass of WTRG (g)}} \quad (2)$$

RESULTS AND DISCUSSION - 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 experiments, 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.

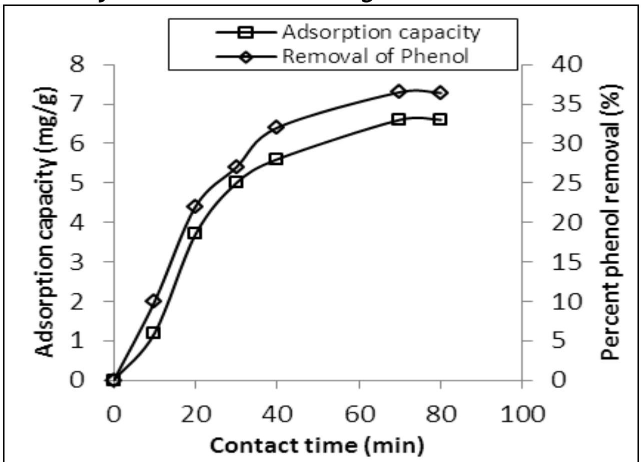

Figure 1: Effect of contact time on the removal of phenol from solution (pH 7; initial phenol concentration, 700 mg/l; WTRG dose, 2g; temperature, 31°C).

It can be observed from Figure 1 that adsorption was rapid within the first 40 minutes as indicated by the steep increase in both the adsorption capacity and percentage phenol removal. The profile flattens out after 60 minutes of contact indicating that equilibrium has been reached. Therefore, for further studies, the contact time was set at 60 minutes. 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). Aisien et al, (2002) reported fast adsorption of crude oil on WTRG as is mostly observed in adsorption of organic solvent 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 are presented in Figure 2.

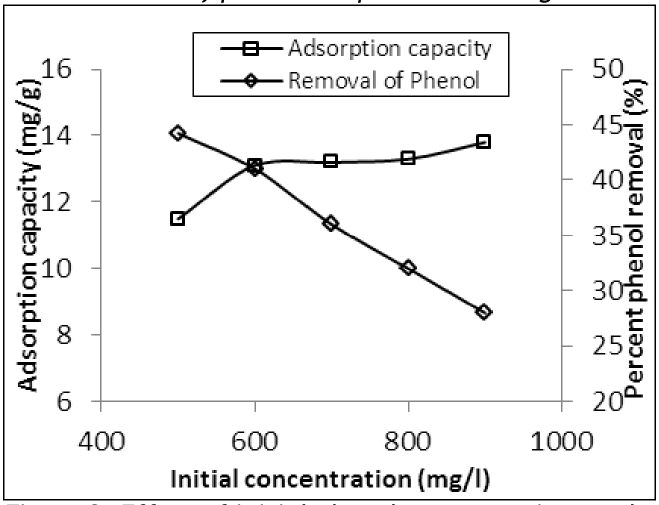

Figure 2: Effect of initial phenol concentration on the removal of phenol from solution (pH 7; WTRG dose, 2g; temperature, 31°C).

It can be observed from Figure 2 that the adsorption capacity increased with increase in initial phenol concentration. 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). A different trend was however observed for the percentage removal of phenol from solution in relation to the initial phenol concentration as shown in Figure 2. The percentage removal decreased from 44.2 to 27.3% when the initial phenol concentration was increased from 500 to 1000mg/l because at high concentrations of phenol, the ratio of phenol present in solution to the available surface area for adsorption is high (Dabhade et al, 2007).

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 and the percentage removal of phenol. It is evident from the Figure that for an initial phenol concentration of 1000 mg/l, increasing the adsorbent dose led to the enhancement of phenol uptake as a result of the greater surface area provided and availability of more active sites (Ho et al., 1995; Nagdah et al, 2007). Maximum removal of phenol was observed with an adsorbent dose of 4g.

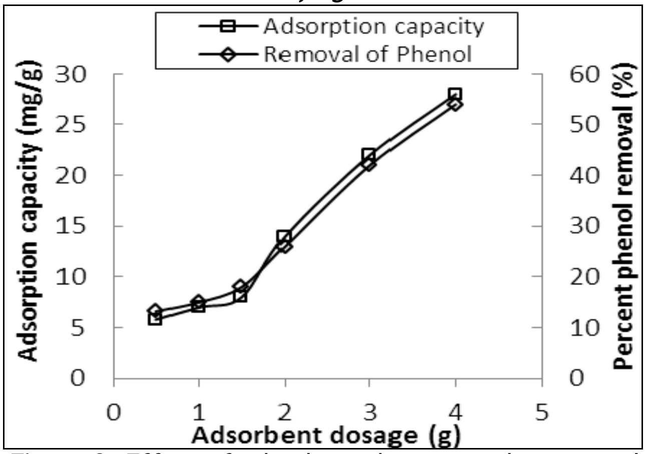

Figure 3: Effect of adsorbent dosage on the removal of phenol from solution (pH 7; initial phenol concentration, 1000 mg/l; temperature, 31°C).

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.

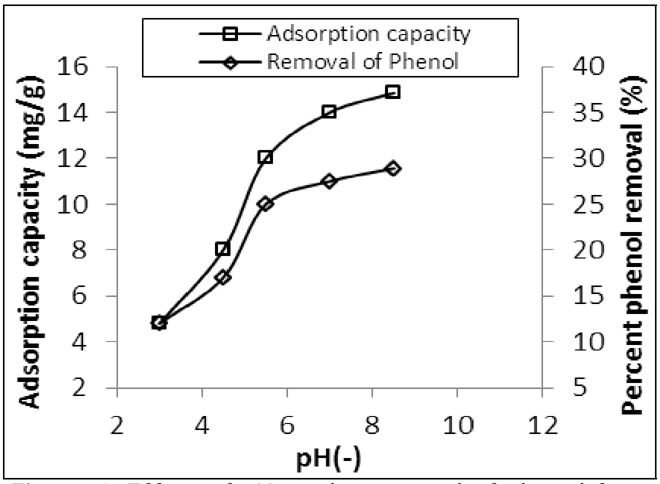

Figure 4: Effect of pH on the removal of phenol from solution (initial phenol concentration, 1000 mg/l; WTRG dose, 2g; temperature, 31°C).

The same trend was observed for both the adsorption capacity and percentage phenol removal. 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).

Effect of adsorbent particle size the adsorption of phenol on WTRG

Figure 5 shows the percentage removal of phenol and adsorption capacity of WTRG at various sizes of adsorbent particles. The trend observed indicate that as the particle size increases, percentage phenol removal and adsorption capacity decreases. The percentage removal of phenol and adsorption capacity of WTRG decreased from 40 to 20.5% and 10.6 to 5mg/g respectively with increase in particle size from 0.30 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). Aisien et al, (2002) reported similar trends for the uptake of crude oil by WTRG.

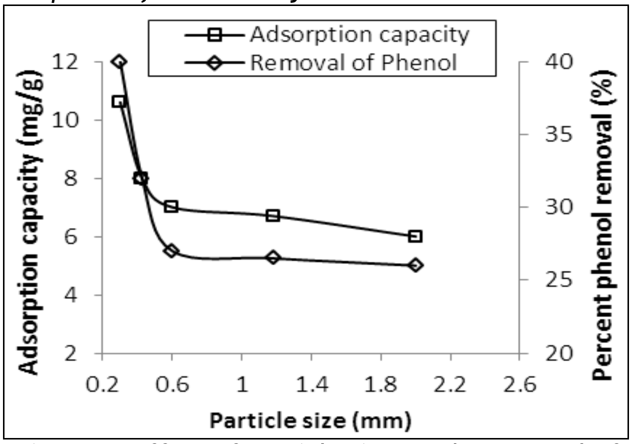

Figure 5: Effect of particle size on the removal of phenol from solution (initial phenol concentration, 1000 mg/l; pH 7; WTRG dose, 2g; temperature, 31°C).

Effect of solution temperature the adsorption of phenol on WTRG

The effect of temperature on the WTRG/phenol system is shown in Figure 6. Percentage removal of phenol and 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 and the percentage removal of phenol from solution from 49.6 to 37.4 % with increase in temperature from 5 to 45°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 similar trend for the adsorption of Nickel, Chromium and Cobalt ions from Aqueous Solutions using Cocoyam (Colocasia esculenta) Leaf. Aisien et al (2003) also reported similar results for the use of WTRG in the treatment of crude oil contaminated water.

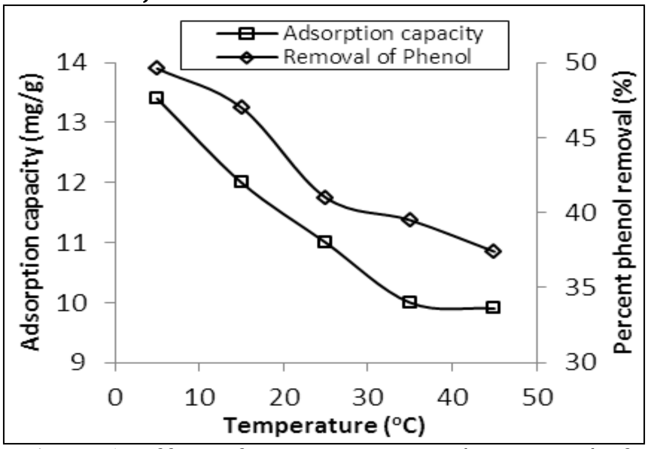

Figure 6: Effect of temperature on the removal of phenol from solution (initial phenol concentration, 1000 mg/l; WTRG dose, 2g; pH 8.5; temperature, 31°C).

Isotherm Study

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

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:

$$\frac{Ce}{Qe}=\frac{1}{bQo}+\frac{Ce}{Qo} \quad (3)$$

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. 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 (4).

$$R_L=\frac{1}{(1+bCo)} \quad (4)$$

Co is the initial concentration of phenol. The dependence of the nature of adsorption on the value of R_L is presented in Table 3. For the highest initial phenol concentration of 1000mg/l, R_L was calculated to be 0.0000115. Since this value is between zero and one, it implies that the adsorption is favourable.

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 4.

Table 3: 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

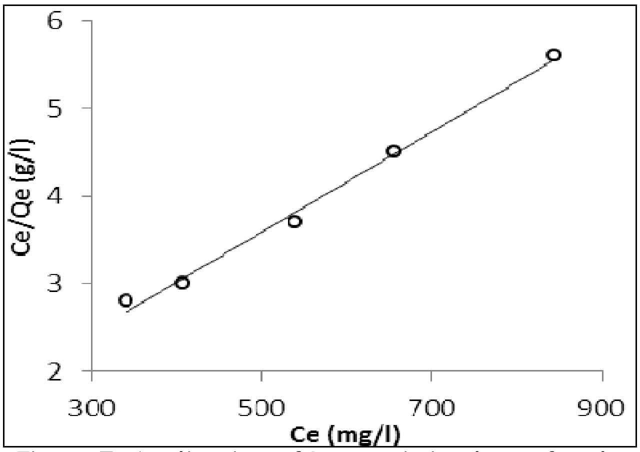

Figure 7: Application of Langmuir isotherm for the adsorption of phenol on WTRG

Table 4: Values of Langmuir isotherm constants for WTRG/phenol system

Qo (mg/g)	b (l/mg)	R^2
15.6	87.09	0.995

Freundlich Isotherm

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

$$Qe = K_f (Ce)^{1/n} \tag{5}$$

This equation can be expressed in linear form as follows:

$$\ln Qe = \ln K_f + 1/n \ln Ce \tag{6}$$

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 log Qe against log 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 5.

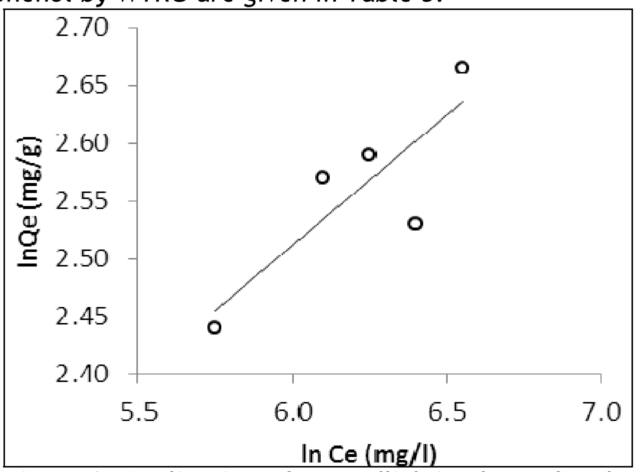

Figure 8: Application of Freundlich isotherm for the adsorption of phenol on WTRG

Table 5: Values of Freundlich isotherm constants for WTRG/phenol system

K_f (mg/g)	n	R^2
2.710	6.369	0.721

Comparison of the results presented in Tables 4 and 5 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 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.

CONCLUSIONS

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

- Adsorption of phenol by WTRG is affected by operational parameters such as contact time, initial phenol concentration, adsorbent dosage and solution temperature.
- The excellent capability of WTRG as adsorbent for organic pollutants like phenol in aqueous solutions has been verified.
- The equilibrium contact time was obtained as 60 minutes indicating that the adsorption process was a fast kinetic process.
- Maximum removal efficiency was achieved at a pH of 8.5 and an adsorbent dosage of 4g.
- A low temperature (5°C) and small adsorbent particle size (0.212mm) favored 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 0.995.
- This study has revealed that the low cost WTRG can be widely used for removal of phenol from aqueous solution.

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