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ADSORPTION OF TOLUENE USING LOW COST ADSORBENT

BASSIM H. HAMEED[1], ABDUL RAHMAN MOHAMED[2] &
CHONG HUI YING[3]

Abstract. This paper discusses the effectiveness of a less expensive adsorbent, a discarded rubber tyre (DRT) in removing toluene from aqueous phase. Adsorption of toluene on a DRT has been studied by using batch system at 25 and 30°C. It was found that up to 70% of toluene was removed for the range of toluene initial concentrations studied between 50-300 mg/l. Using linearized forms of equilibrium models, namely Langmuir and Freundlich models, the maximum adsorptive capacities were determined. It was evident from the experimental data that, although both Langmuir and Freundlich isotherm models could describe the isotherm data, the adsorption of toluene on a DRT was described well by the Freundlich isotherm. For Freundlich K values, sorption capacities were 6.6374 and 7.7535 mg/l at 25 and 30°C, respectively. The values of Freundlich exponent *n* were greater than one for both temperatures.

Keywords: Toluene, adsorption, isotherms, discarded rubber tyre, Langmuir isotherm model, Freundlich isotherm model

Abstrak. Kertas kerja ini membincangkan tentang kecekapan penjerap yang lebih murah, iaitu tayar getah terbuang (DRT), dalam menyingkirkan toluena daripada fasa akuas. Penjerapan toluena pada tayar getah terbuang dikaji menggunakan sistem berkelompok pada suhu 25°C dan 30°C. Daripada kajian ini, didapati toluena dapat disingkirkan sehingga 70% dengan menggunakan julat kepekatan awalan antara 50 mg/l hingga 300 mg/l. Dengan menggunakan model keseimbangan terlelurus, iaitu model Langmuir dan Freundlich, keupayaan penjerapan maksimum dapat ditentukan. Daripada data eksperimen, terbukti bahawa walaupun kedua-dua model isoterma Langmuir dan Freundlich boleh menjelaskan data isoterma, tetapi penjerapan toluena pada DRT dapat ditunjukkan dengan lebih baik oleh isoterma Freudlich. Bagi nilai K Freundlich, keupayaan penjerapan ialah 6.6374 mg/l dan 7.7535 mg/l, pada suhu 25°C dan 30°C. Nilai eksponen *n* Freudlich adalah lebih daripada satu untuk kedua-dua suhu.

Kata kunci: Toluena, penjerapan, isoterma, tayar getah terbuang, model isoterma Langmuir, model isoterma Freundlich

1.0 INTRODUCTION

Problems of environmental pollution have arisen from the discharge of all types of hazardous substances including organic compounds. Many organic compounds are often present in the wastewater from the chemical and petrochemical industries. Due

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[1,2&3] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia.
[1] Corresponding author: E-mail: chbassim@eng.usm.my

to their toxicity to human and marine life, stringent regulations have been imposed on the concentrations of these compounds in such wastewaters for safe discharge. Benzene, toluene, Ethylbenzene, and xylene (BTEX) are typical toxic organic compounds that appear very often in chemical and petrochemical wastewaters. Petroleum refineries do not like salts in their feedstock since these substances corrode and foul process equipment. The first refining step is desalting where a hot water extracts the salts. If feedstock contains aromatics then some will be in the desalter effluent and this is a major source of refinery wastewater containing BTEX. Thus treatment of BTEX-containing wastewater becomes an integral part of wastewater treatment for the chemical and petrochemical industries.

Traditionally, activated sludge treatment has been the most widely used method. The microorganism in an activated sludge system can only deal with chemical wastewater containing relatively low BTEX concentration, usually much less than 100 mg/l, due to low biodegradability and/or inhibitory effects of these compounds [1,2]. Unfortunately, there are various kinds of chemical and petrochemical wastewaters that contain BTEX far exceeding this concentration level. For such cases, chemical or physical treatment methods may offer acceptable alternatives.

Incineration is such a chemical alternative. It is practical for dealing with waste solvents, but is considered too costly for other practical applications. Wet air oxidation (WAO) is another alternative [3-5]. The WAO method is capable of oxidizing high concentrations of organic compounds in aqueous solution under elevated temperatures and pressures. However, maintaining the reaction conditions at high temperatures and pressures is not an easy task and can be rather expensive due to high capital investments and operating costs. Hence, a better alternative is to remove BTEX from the aqueous solution by adsorption which permits recovery of these compounds for possible recycling to the manufacturing process.

Many researchers have shown that activated carbon is an effective adsorbent for organic compounds [6-9]. However, its high initial cost and the need for a costly regeneration system makes it less economically viable as an adsorbent. Cost effectiveness, availability, and adsorptive properties are the main criterias taken into consideration. Many researchers have investigated the adsorptive properties of unconventional adsorbents such as olive shells, montmorillonite, peat, fly ash, and others.

The disposal of used tyres is becoming a serious environmental issue. An estimated 1.5×10^6, 2.5×10^6, and 0.5×10^6 tonnes of used tyres are generated each year in European Community, North America, and Japan, respectively [10]. The majority of this tyre waste is dumped in open dumping or landfill sites. However, tyres that do not degrade in landfills and open dumping may result in accidental fires with high pollution emissions.

Discarded tyres have caused many public health and aesthetic problems. This makes waste tyre disposal and management a prime issue for environmental discussion.

Legislation is important in managing the waste tyre problem but alternatives to disposal are the best long-term solutions. The objective of this paper is to discuss the alternative to waste tyre disposal: the potential of ground discarded rubber tyres to remove organic contaminants from wastewater.

2.0 EXPERIMENTAL

2.1 Materials

A discarded rubber tyre was cut into fine particles by using a driller. Then, it was sieved to 1.0 mm size. The sieved particles were then washed using distilled water and filtered using vacuum filtration techniques. Toluene (AR grade min. 99.6% Merck) was supplied by Quicklab Sdn. Bhd., Ipoh, Perak.

2.2 Adsorption Procedure

In the adsorption experiment (Figure 1), the adsorbate solution was prepared by mixing a known amount of adsorbate with deionized water to yield various desired concentrations. The adsorption experiment was carried out isothermally in static mode

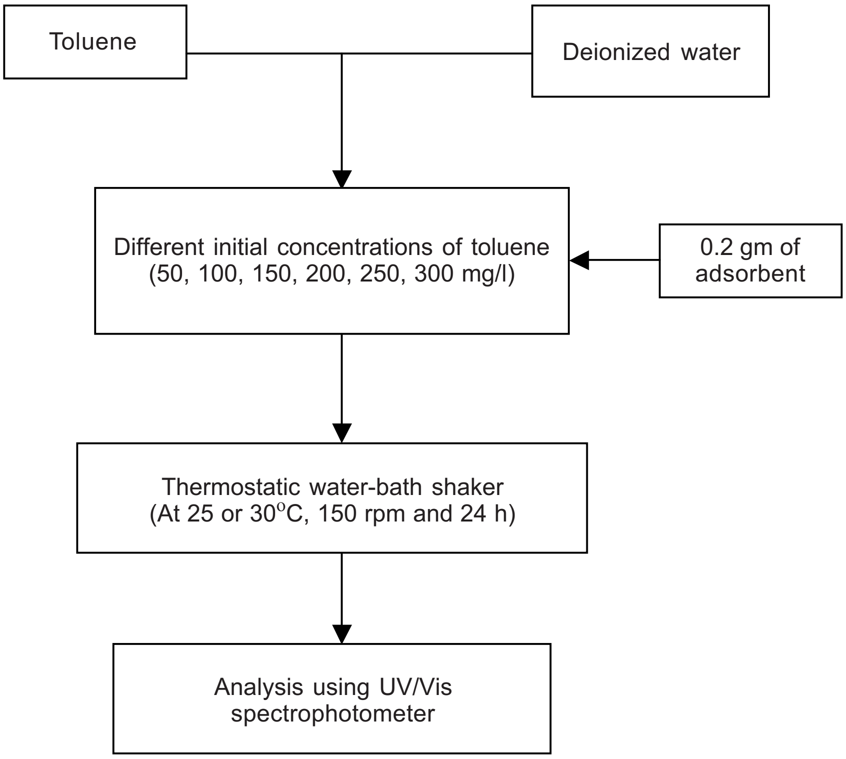

Figure 1 Block diagram for the experimental procedure

at two different temperatures, 25 and 30°C. Toluene with initial concentration of 50, 100, 150, 200, 250, and 300 mg/l were prepared. The experiments were conducted by adding a fixed amount of ground DRT, 0.2 g to a series of 250 ml glass-stoppered flasks filled with 200 ml diluted solutions. The glass-stoppered flasks were then placed in a thermostatic shaker bath and shaken at 150 rpm for 24 hours to achieve an equilibrium condition.

A Shimadzu UV/Vis spectrophotometer UV-160 was used to measure the toluene concentrations. The wavelength was set at 261.4 nm. A calibration curve was drawn between the concentration ranges from 50 to 300 mg/l. The amount of toluene adsorbed by the adsorbent was determined from its concentration at initial condition (C_o) and equilibrium (C_e).

The amount of adsorbates adsorbed on ground DRT was calculated by using the following equation:

$$q_e = \frac{V(C_o - C_e)}{W} \tag{1}$$

2.3 Adsorption Isotherm

Two important physisorption aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between adsorbents and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and the remainings in solution at a fixed temperature, at equilibrium. There are two types of adsorption isotherms: Langmuir adsorption isotherms and Freundlich adsorption isotherms.

2.3.1 Langmuir Isotherm

The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as:

$$q_e = \frac{X_m K C_e}{(1 + K C_e)} \tag{2}$$

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{X_m K} + \frac{C_e}{X_m} \tag{3}$$

The linear form can be used for linearization of experimental data by plotting C_e/q_e

against C_e. The Langmuir constant X_m and K can be evaluated from the slope and intercept of a linear equation, respectively.

2.3.2 Freundlich Isotherm

The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$q_e = K_f C_e^{1/n} \tag{4}$$

This equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

A plot of (log q_e) against (log C_e) yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and intercept.

3.0 RESULTS AND DISCUSSION

The toluene adsorption capacities of DRT at two different temperatures were presented as a function of equilibrium concentration of toluene within the aqueous phase (Figure 2). It can be seen that the adsorption capacities increased with increasing equilibrium concentration of toluene.

Rubber tyres are composites primarily composed of rubber vulcanized with sulfur, steel, and carbon black. The carbon black used to strengthen the rubber, is similar to activated carbon, a good sorbent to remove dissolved organic substances from wastewater [11]. Likewise, Park and Bontoux [12] investigated the permeation of organic compounds through rubber gaskets commonly found in portable water containers. They concluded that rubber is a good sorbent for organic compounds.

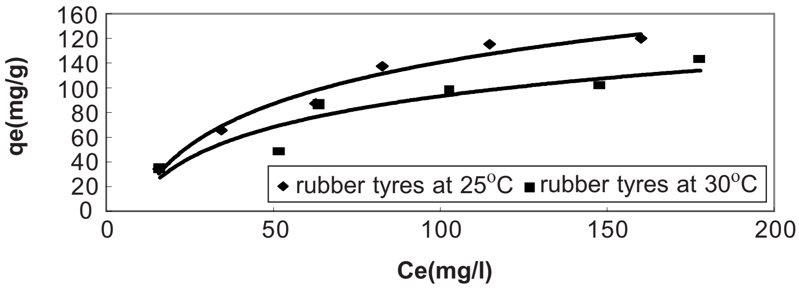

Figure 2 Adsorption isotherm of toluene using rubber tyres at different temperatures

It is clear that at a higher temperature, the maximum capacity of toluene adsorbed will be reduced. The amount of toluene adsorbed on the adsorbent is highest at 25°C and decreases as the temperature increases over the whole range of the concentrations studied. This is due to the fact that surface tension decreases monotomically with increasing temperature, and as a consequence, the strength of binding to non-polar surfaces decreases with increasing temperature, due to the decrease in the surface tension of the aqueous medium, as long as the "cavity effect" serves as the main driving force for binding.

3.1 Effect of Toluene Initial Concentration

Figure 3 shows plots between the equilibrium concentration and percentage of toluene removal at 25 and 30°C. At the lowest toluene initial concentration of 50 mg/l, around 70% of toluene was removed and the equilibrium concentration was 15 mg/l at both temperatures. However, at the highest initial concentration of 300 mg/l, the percentages of removal were 50 and 40 mg/l and the equilibrium concentrations were 160 and 180 mg/l at 25 and 30°C, respectively. It is clear that the adsorption conditions favour lower concentration of adsorbate. Hence, for lower initial concentration of toluene, the percentage of toluene removal is higher compared to high initial concentration of toluene.

The effect of different initial concentrations of toluene can be explained as follows. It is known that the adsorbent capacity is determined by the total active sites on the surface of the adsorbent. If high toluene concentration is present in the solution, it means that the amount of toluene molecules in the solution is also increased. Generally, the ability of the toluene molecules to adsorb to the adsorbents is proportional to the amount of adsorbents' active sites. As the active sites of the adsorbents are insufficient for the adsorption of extra toluene molecules present in the solution, therefore, longer

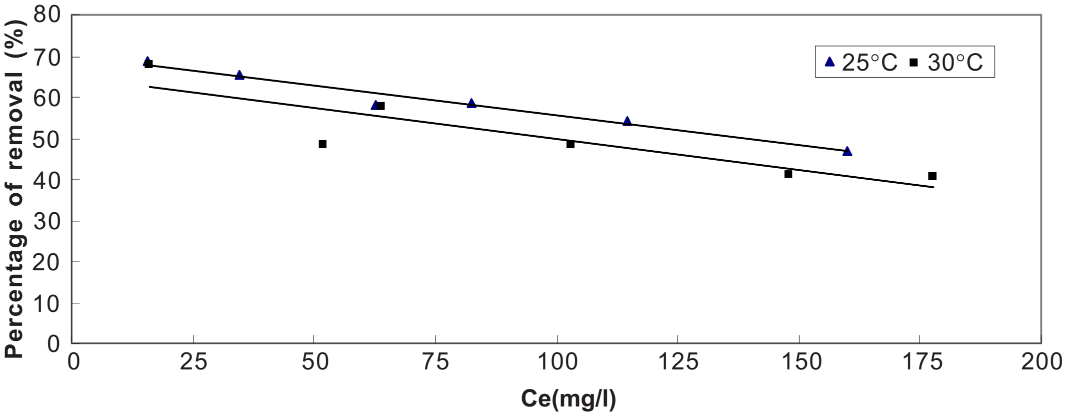

Figure 3 Percentage of toluene removal using DRT at 25 and 30°C

time is needed to approach adsorption equilibrium and effluent quality deteriorates to an unacceptable level. The adsorbent is then considered spent.

3.2 Adsorption Models

Based on the equilibrium data gathered, plots for two models of Langmuir and Freundlich isotherms at different temperatures are shown in Figures 4 and 5, respectively.

These figures show comparisons of the two computed isotherms by using the measured data. It can be noticed that both isotherm equations describe the equilibrium adsorption data fairly well.

For the calculated isotherms, the constants in both adsorption isotherms were obtained by plotting the figures of the empirical isotherm equations to the experimental isotherms. The calculations were done for both temperatures. The optimal parameters from the fitting of Freundlich and Langmuir equations with the experimental data are summarized in Table 1.

It is evident from this table that, although both empirical isotherm equations could describe the isotherm data, the adsorption of toluene on rubber tyre was described well by the Freundlich isotherm (Table 1 and Figure 5). Freundlich K's values were 6.6374 and 7.7535 mg/g at 25 and 30°C, respectively. The values of Freundlich exponent *n* were greater than one for both temperatures (Table 2).

4.0 CONCLUSIONS

In conclusion, ground discarded tyre rubber is an attractive and inexpensive medium for the sorption of organic compounds contaminants in water. The results show that up to 70% of toluene can be removed at the lowest value of toluene initial concentration. Although the adsorption behavior of adsorbents studied followed both Freundlich

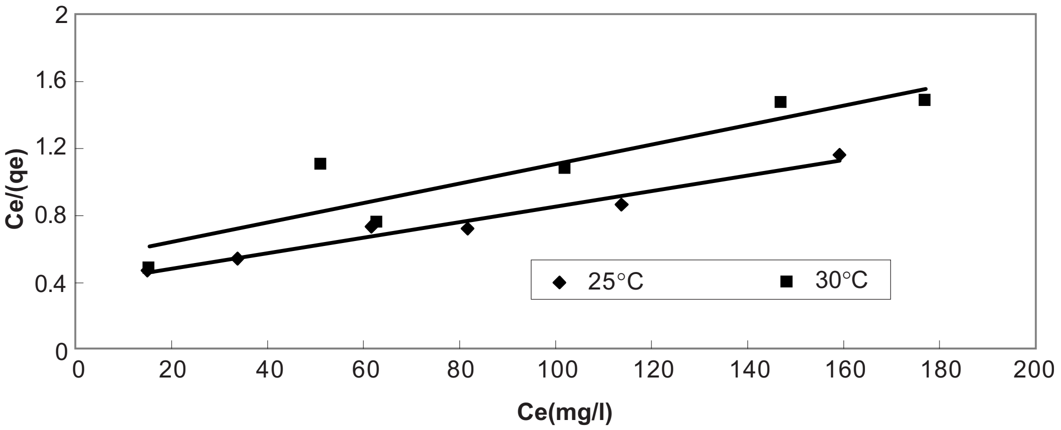

Figure 4 Langmuir isotherm for DRT at 25 and 30°C

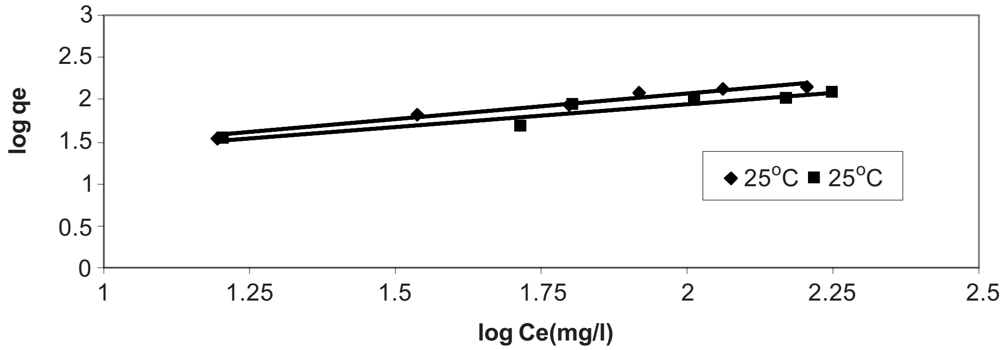

Figure 5 Freundlich isotherm for DRT at 25 and 30°C

Table 1 Equations and correlation coefficient for each adsorption isotherm at 25 and 30°C

Adsorption isotherm model	**Temperature (°C)**	**Equation**	**Correlation coefficient, R^2**
Langmuir	25	$\frac{C_e}{(q_e)} = 0.3759 + 0.0046C_e$	0.9675
	30	$\frac{C_e}{(q_e)} = 0.5011 + 0.0058C_e$	0.8365
Freundlich	25	$\log q_e = 0.822 + 0.6262 \log C_e$	0.9706
	30	$\log q_e = 0.8895 + 0.5257 \log C_e$	0.8945

Table 2 Fitted parameters of Langmuir and Freundlich isotherms

Temperature (°C)	**Langmuir**		**Freundlich**	
	X_m	K	K_f	n
25	217.391	0.0122	6.6374	1.5969
30	172.414	0.01157	7.7535	1.9022

and Langmuir isotherms, the adsorption of toluene on DRT was described well by the Freundlich isotherm.

The results of this study can be useful in designing a batch adsorption system for the removal of toluene. Such system will be applicable to small industries that generate Toluene-containing wastewater. The adsorbent can be added to the wastewater collected in a tank and the mixture agitated for equilibrium time. The amount of the adsorbent can be obtained from the isothermal data. The liquid can then be decanted and discharged.

NOMENCLATURE

C_o – Initial concentration of adsorbate (mg/l).
C_e – Concentration of adsorbate in solution (mg/l).
K – Langmuir constant related to energy of adsorption (l mg of adsorbent per mg of adsorbate).
K_f and n – Empirical constants and n is greater than one.
q_e – Adsorption density at the equilibrium solute concentration, C_e (mg of adsorbate per gm of adsorbent).
V – Volume of solution (l).
W – Weight of adsorbent (g).
X_m – Maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per gm of adsorbent).

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