Removal of parachlorophenol from the aquatic environment by recycled used tires as an adsorbent: Characterization, adsorption, and equilibrium studies

Akbar Eslami[1], Ehsan Aghayani[1], Gholamhosein Joshani[1], Nadereh Hezarkhani[1], Mohammad Hassan Momayyezi[1], Babak Djahed[2], Atiye Haddadnejad[1]

1 Department of Environmental Health Engineering, School of Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran
2 Department of Environmental Health Engineering, School of Public Health, Shiraz University of Medical Sciences, Shiraz, Iran

Original Article

Abstract

Parachlorophenol has an extended usage in refineries, petrochemical industries, insecticide, and herbicide manufacturing industries. Tire a solid waste, which is disposed in large amounts each year, a large number of them in landfills can cause irreparable environmental impacts. Consequently lots of efforts were done to produce activated carbon from used tires. Activated carbon was made in laboratory conditions by using pyrolysis furnace. Scanning electron microscopy was used for determining structural characteristics of the activated carbon produced from recycled used tires and Brunauer, Emmett, and Teller isotherm was used to find out its special surface. The structure of produced activated carbon in this study has a special surface of 111.702 m²/g. The internal diameter of holes was 1.54 nm, and the total volume of them was 0.124 ml/g. The removal efficiency was reduced from 88.59% to 69.25% by changing the pH from 3 to 9. In addition, the efficiency was reduced from 88.59% to 75.95% when the primary concentration of parachlorophenol increased from 10 to 60 mg/L. On the other hand, changing the temperature from 10°C to 30°C increased it from 65.86% to 74.53%. Moreover, contact time had direct impacts on the removal efficiency. The results conform Freundlich isotherm (R^2 = 0.9958). The efficiency of parachlorophenol removal would be decreased by increasing pH and concentration of the pollutant, and would be increased by adding temperature and contact time. As a conclusion, since the recycled tires are cheap, the produced activated carbon from them can be used as an effective and low-cost method for parachlorophenol removal from aqueous solutions.

KEYWORDS: Activated Carbon, Isotherm, Parachlorophenol, Recycling, Used Tires

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Introduction

Chlorophenols are made by replacing one or more chlorine on the benzene loop. Solubility of chlorophenols in water is low, and its insolubility would be increased by raising the number of chlorine atoms.[1] The main sources of chlorophenol are: paper pulping factories, coal factories, chemical materials factories, petroleum refinery, plastic productions, and the leachate of urban solid wastes.[2] Parachlorophenol (C_6H_5ClO) is one form of chlorophenol in which

Corresponding Author:
Gholamhosein Joshani
Email: hoseinjoshani@yahoo.com

the hydrogen in the benzene loop are replaced with a chlorine atom. Parachlorophenol has an extended usage in refineries and petrochemical industries, insecticide and herbicide manufacturing, and environmental antimicrobial agents producing.[3,4] Parachlorophenol with a molecular weight of 128.6 is yellow solid, and soluble in water and in the normal conditions it is almost acidic.[5,6] It enters to the body through skin, breathing and digesting system, and as a toxic and corrosive chemical cause's irritation for eyes, skin, nose, increasing cough, wheezing, and breathing problems. Long time exposure can cause headache, tiredness, impatience, adverse effects on the liver and kidney, muscle weakness, nausea and in the end, coma and death.[7-9] Some of the other health hazards related to these compounds are high toxicity, being carcinogen, destroying water quality and making it unsuitable for routine consumption and drinking.[10-12] Various methods have been used for removing parachlorophenol from aqueous solutions, such as: electrochemical oxidation, using photocatalysts, chemical oxidation, wet oxidation, and biological treatment.[13] Applications and expansions of the mentioned methods have been limited by the problems such as high cost, producing hazardous by-products, and low efficiency.[14,15]

Adsorption may potentially avoid producing minor materials while it brings about high efficiency. Activated carbon is the most common substance for adsorption. The high price of commercial types is a big obstruction for using them in processes.[16,17] Therefore, lots of efforts have been made for producing activated carbon from low cost materials in the recent years, which the main parts of these materials are commercial and industrial waste products. As an example, Stavropoulos and Zabaniotou produced activated carbon from olive-seed and removed methylene blue dye from aqueous solutions in 2005.[18] Rahman et al. produced activated carbon from rice hunks and removed

green malachite from aqueous solutions in 2005.[19] Valix et al. derived activated carbon from sugarcane dregs and removed blue acid 80 from water in 2004.[20] Bansode et al. could produce activated carbon from almond shell and removed volatile organic carbon in 2003.[21] Kadirvelu et al. could make activated carbon from coir and removed heavy metals from industrial wastewater.[11]

Tire is a solid waste, which is disposed in large amounts each year. As an example, about 299 million tires were manufactured in United States in 2005; large number of them in landfills can cause irreparable environmental impacts.[12] Consequently lots of efforts were made to produce activated carbon from used tires, because they are almost free raw materials. For instance, Amri et al.,[22] Troca-Torrado et al.,[7] Tanthapanichakoon et al.,[6] Ariyadejwanich et al.,[23] Ko et al.,[24] Alexandre-Franco et al.,[25] produced activated carbon from tires and reported high quality of their products in removal of different substances.

Also in Iran, thousands of used tires are being disposed to the environment uselessly; these tires can be free raw materials to produce activated carbon. The produced activated carbon is beneficial for the removal of various contaminants from aqueous solutions, including parachlorophenol, thereby it decreases polluted water treatments' cost and somehow it causes recycling of used tires. Thus, it preserves the environment from being polluted by such extremely hazardous materials. The purpose of this study to investigate the removal of parachlorophenol from water by adsorbing it on the used tires derived activated carbon. The effect of contact time, temperature, pH, and the concentration of contaminant were evaluated in this study. Determining the adsorption isotherms in designing the pollutant treatment systems, which are working by adsorption method has a great importance.[26] Langmuir, Freundlich, Redlich-Peterson, and Temkin models were used for analyzing the result of

adsorption and its isotherm.

Materials and Methods

Tests were done in a batch reactor by changing pH, temperature, contact time, and parachlorophenol concentration. Adsorption process was surveyed in each step by adding 20 mg activated carbon derived from used tires in a reactor with the volume of 50 ml (0.4 g/l), which was put in the incubator (for temperature adjusting). It is worth noting that to avoid the probability of evaporation of parachlorophenol and causing errors in the test results, all the reactors were completely closed during the test.

The used parachlorophenol in this research was purchased from Merck Company and 4-aminoantipyrine was bought from Fisher Company. During the different steps of the test, pH of the samples was measured by WTW unit, Inolab pH 720 pH meter. After testing and sampling at the determined time, parachlorophenol concentration was measured by colorimeter 4-aminoantipyrine method according to the standard methods for examination of water and wastewater (5530A) with a set of UV-Visible HACH DR 5000 spectrophotometer.

Chemical activation and carbonation methods were used for producing activated carbon from waste tires. Therefore, first waste tires were shredded to 3-4 mm pieces. Then in order to activate them, the rubbery pieces were put in contact with thick potassium hydroxide in a glass container for 3 h; the temperature was adjusted on 85° C. During the reaction process, a magnetic stirrer was mixing the mentioned mixture at the rate of 150 rpm for a better reaction between potassium hydroxide and pieces of tire. Mass ratio was considered as 4:1 potassium hydroxide to tire. After a 3-h contact time with potassium hydroxide, tire pieces were taken out of mentioned solution and were put in the oven with 110° C for 24 h. After drying, tire pieces were heated in an Argon furnace with 85 cm³/min gas stream up to 750° C for carbonation. The rate of temperature increase in the furnace was 5° C/min. The intended samples were put in the furnace (25-750° C) for approximately 2.5 h. After reaching this temperature, the furnace was turned off immediately, and it was allowed to become cool slowly. Then the produced activated carbon was rinsed with distilled water, until pH comes to 7; then the derived activated carbon was put in 110° C oven for 24 h to become completely dry, and after passing from a standard 100 mesh sieve, it was maintained in desiccators.[27,28] The effective factors in performing the intended processes were: detention time (5, 20, 60, and 90 min), pH (3, 5, 7, 8, and 9), the amount of used activated carbon (0.4 g/l), parachlorophenol concentration in water (10, 20, 40, and 60 mg/l), and test temperature (10° C, 20° C, and 30° C).

The percentage of produced activated carbon was estimated by using Eq. 1:

$$\text{Carbon yield \%} = \left[\frac{W_{ac}}{W_{ti}} \right] \times 100 \tag{1}$$

In this equation, W_{ac} is the weight of produced activated carbon and W_{ti} is the weight of used tire. Scanning electron microscopy (SEM) was used for surveying the surface of activated carbon. The special surface of the activated carbon was measured by Brunauer, Emmett, and Teller method.

Results and Discussion

Specifications of adsorbent

The percentage of produced activated carbon was estimated to be 36.46%. The SEM image is shown in figure 1. The structure of the produced activated carbon in this study has a special surface of 111.702 m²/g. The internal diameter of the hole was 1.54 nm, and the total volume of them was 0.124 ml/g.

The effect of temperature

One of the effective factors in adsorption process is the temperature of the reaction. For surveying the effect of this factor on the removal efficiency,

adsorption was evaluated at temperatures of 10° C, 20° C, and 30° C. In order to adjust temperature, all the experiments were performed in a chamber incubator with adjustable temperature. Figure 2 shows the result of temperature effect on the removal efficiency. As it shows removal efficiency is increased by temperature rising. In this way, changing temperature from 10 to 30 increased the removal efficiency from 65.86% to 74.53%.
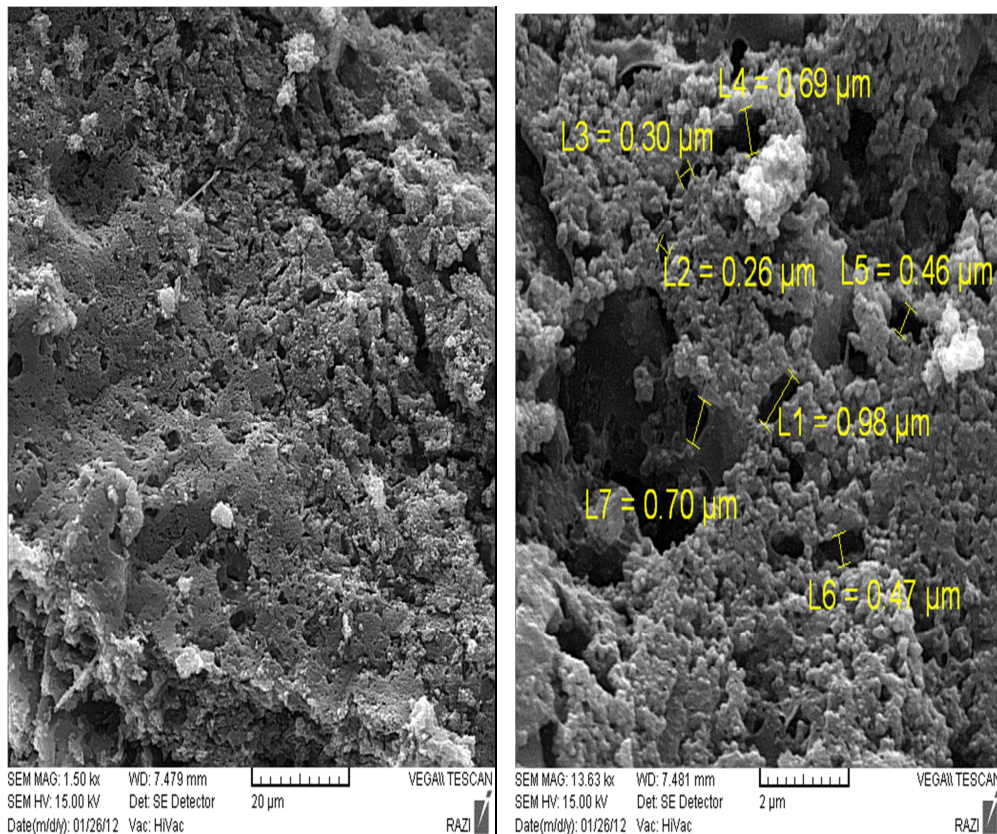

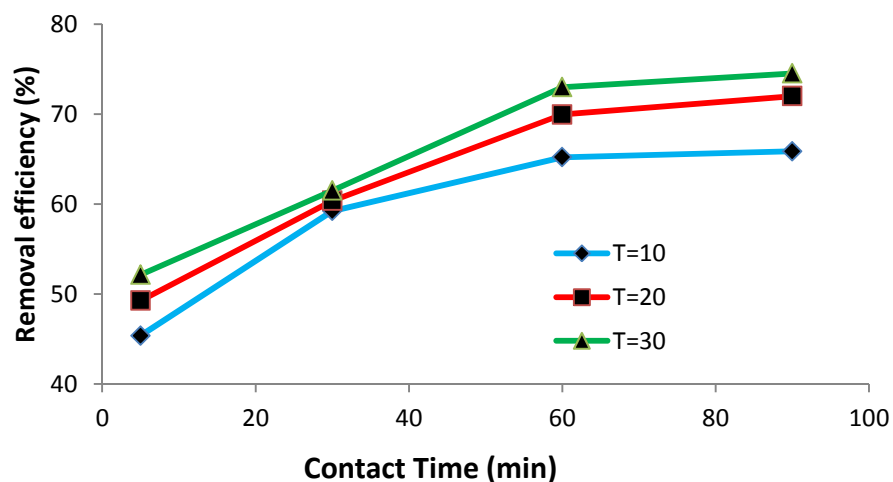**Figure 1. Scanning electron microscopy images of activated carbon produced from used tire**

Figure 2. Effect of temperature on parachlorophenol removal (the amount of adsorbent 0.4 g/l, pH = 7)

Hence, it can be said that temperature can have a great effect on adsorption capacity of the adsorbent. In general, adsorption process is an exothermic process, and adsorption should be decreased by increasing the temperature. But in some cases, that the amount of adsorption is under control by emission process, temperature increase will cause an increase in the amount of adsorption. Therefore, according to found data, temperature process is controlling adsorption of phenol on the produced adsorbent. This study which is done by Srivastava et al. approves this result.[29]

The effect of pH

Figure 3 shows the effect of pH on the removal efficiency of parachlorophenol. It shows that the removal efficiency decreases by increasing pH, in a way that by changing pH from 3 to 9, removal efficiency decreases from 88.59% to 69.25%, in contact time of 90 min. In adsorption systems, pH of the intended solution is very important, because it affects chemical characteristics of the adsorbent attribute of self-absorption.[30] This study which was done by Wan Ngah and Hanafiah shows that the produced adsorbent from tires and the optimum pH for the highest adsorption was 5.[31] In other study by Fan et al., it was found that the most

chlorophenol adsorption amount was achieved in the pH of 2 and the removal percentage was decreased by increasing pH.[32]

As it is observed in figure 3, the percentage of parachlorophenol removal is higher in lower pHs, which is because of the protonation of existing phenol in solution. This point is approved by the result of the studies, which were done by Blanco-Martinez et al.[33] and Srivastava et al.[29]

The effect of contact time

The effect of contact time on the removal efficiency was studied by changing it from 5 to 90 min in pH = 3, with surveying the effect of concentration changes in the removal efficiency of adsorbent. As it is observed in figure 4, when the contact time is increased from 5 to 90 min, the removal efficiency by 10 mg/l primary parachlorophenol concentration increases from 60.28% to 88.59%. This contact time (90 min) is equilibrium time in tests. This point is also true in the concentration of 20, 40, and 60 mg/l parachlorophenol. In the study done by Chen and Chen, it was observed that increasing the contact time will increase the amount of Cu^{2+} removal.[34] In the other study, which was done by Fan et al., results showed that with an increase in the contact time, the removal
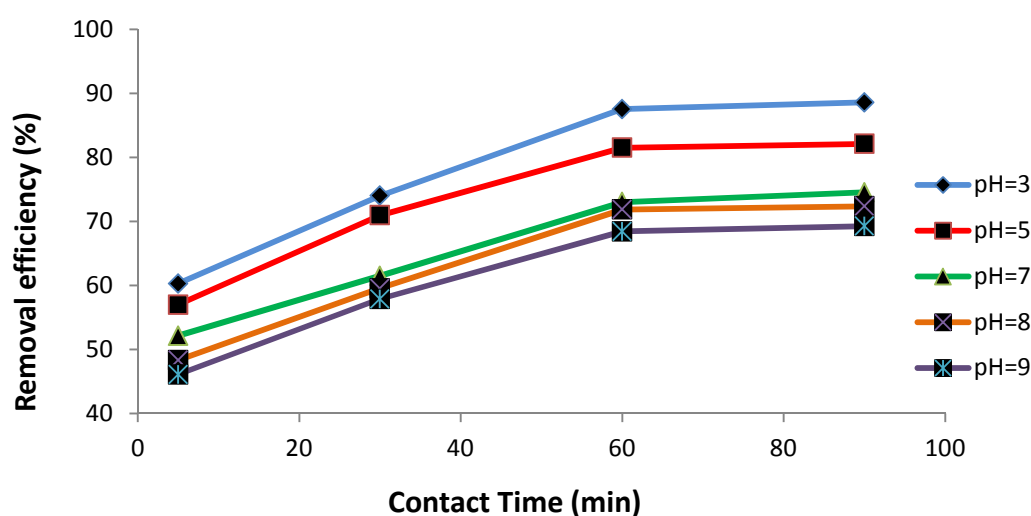

Figure 3. Effect of pH on parachlorophenol removal (amount of adsorbent = 0.4 g/l)
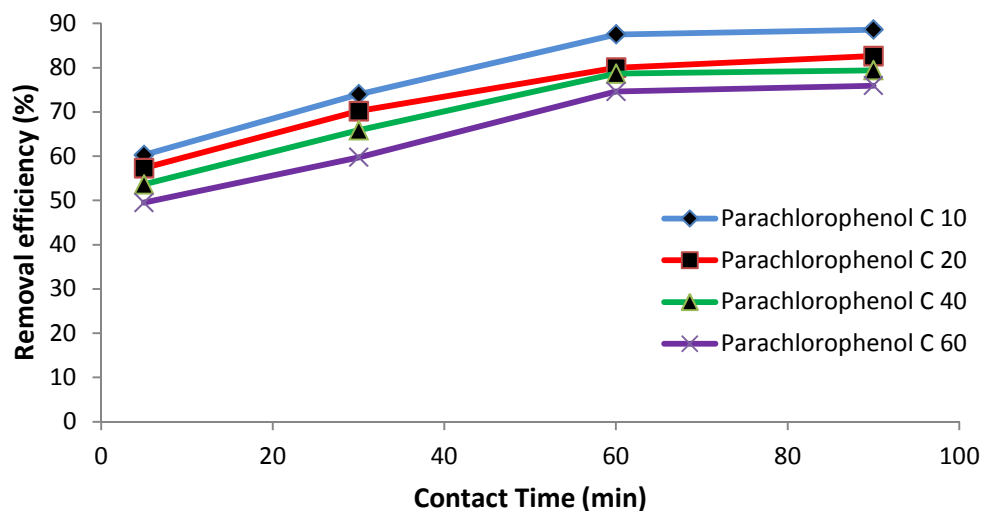
Figure 4. Effect of contact time on parachlorophenol removal (pH = 7 and 30° C)

efficiency of dielderin increased. Especially in the first 4 h when the adsorption rate is higher.[32]

The effect of different parachlorophenol concentration

The effect of primary phenol concentration in the intended study was surveyed by changing the phenol concentration (10, 20, 40, and 60 mg/l) in pH = 3 and 0.4 mg/l adsorbent and 90 min contact time. pH = 3 was chosen because in surveying the effect of pH changes on the amount of pollutant removal, it was determined that the adsorbent has the best removal of pollutant in pH = 3. So that, in surveying the effect of concentration changes on adsorption efficiency, the temperature of 30° C was chosen as the best temperature. As shown in figure 5, the effect of primary parachlorophenol concentration on the removal efficiency. It can be observed that removal efficiency is decreasing by increasing primary parachlorophenol concentration. So when the primary parachlorophenol concentration is increased from 10 to 60 mg/l, the removal efficiency will be decreased from 88.59% to 75.95%, in the contact time of 90 min.

Surveying the correspondence of results with linear adsorption isotherms

Langmuir model is one of the most widely used

models, which is valid for monolayer adsorption onto a completely homogeneous surface.[35] In the Langmuir equation (Eq. 2), q_e (mg/g) is the rate of the adsorbed phenol per weight unit of the prepared activated carbon, q_{max} (mg/g) is the maximum adsorption capacity of the prepared activated carbon, C_e (mg/l) is the equilibrium concentration, and K_L is the Langmuir constant.[36]

Langmuir model:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (2)$$

Freundlich is a widely used isotherm model that assumes a heterogeneous adsorption surface with sites that have different energies of adsorption.[37] In this model, K_F and n are the Freundlich constants characteristic of the system. K_F ($mg^{1-1/n}$ $l^{1/n}$ g^{-1}) and n are indicators of adsorption capacity and adsorption intensity, respectively (Eq. 3).[38] The results showed that the found data are in accordance with Freundlich model ($R^2 = 0.9958$).

Freundlich model:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Redlich-Peterson model contains three parameters and integrates the features of the Langmuir and the Freundlich isotherms (Eq. 4).[39]
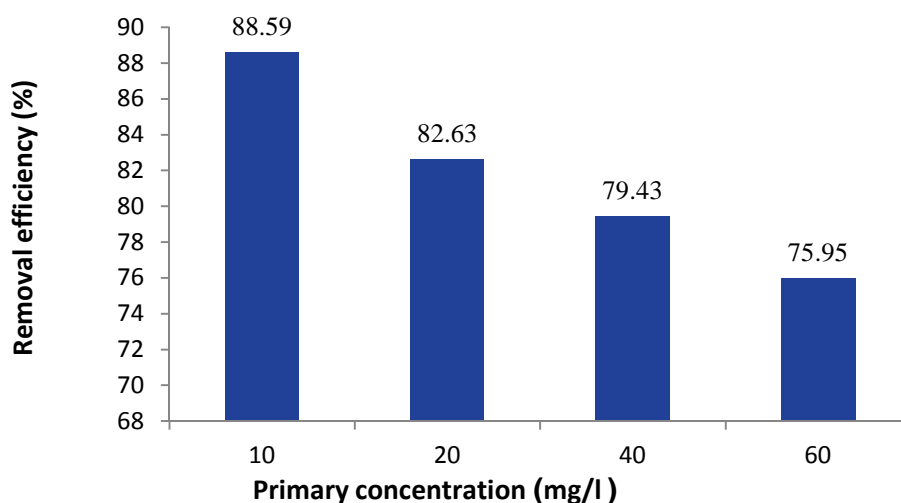
Figure 5. Effect of different concentration on parachlorophenol removal (the amount of adsorbent 0.4 g/l, pH = 3 and 30° C)

Redlich-Peterson model:

$$q_e = \frac{K_r C_e}{1 + a_r C_e^{\beta}} \quad (4)$$

The Temkin equation (Eq. 5) shows the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherm. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage.

Where in this model A is the Temkin isotherm constant (L/mg), b_T is the Temkin constant related to the variation of adsorption energy (J/mol), R is the universal gas constant [8.314 J/(mol K)], and T is the absolute temperature (K).[40]

Temkin model: $q_e = \dfrac{RT}{b_t} \ln(a_t C_e)$ (5)

Parameters calculated related to adsorption isotherms are provided in table 1. Different models of adsorption isotherms are shown in figure 6.

Conclusion

The special surface of produced activated carbon in this study was 111.702 m²/g and the total volume of the internal diameter of the hole was 0.124 ml/g. The percentage of parachlorophenol removal achieved at a higher temperature in lower pH. Results of this research showed that the produced activated carbon from used tires can be used as an effective and low-cost adsorbent for removing parachlorophenol from aqueous solutions.

Table 1. Parameters and contents adsorption isotherms

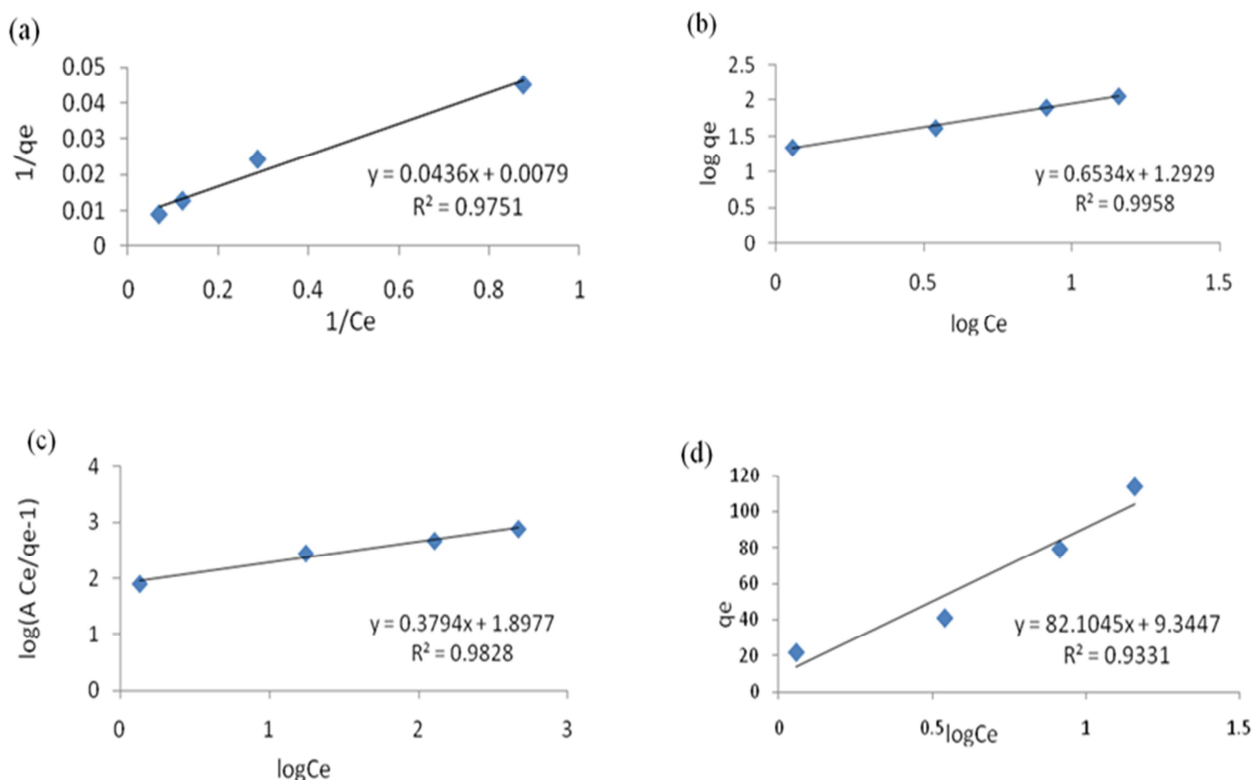| Parameter		Content
Langmuir	q_{max}	126.58
	B	181
	R^2	0.975
Freundlich	1/n	6534
	N	1.5304
	K_F	19.62
	R^2	0.9958
Redlich-Peterson	β	3794
	a_r	79.13
	K_r	130
	R^2	0.9828
Temkin	A	9.3447
	B	82.1045
	R^2	0.9331

Figure 6. Adsorption isotherms for parachlorophenol whit activated carbon produced from used tires: (a) Langmuir model, (b) Freundlich model, (c) Redlich-Peterson model, and (d) Temkin model

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

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