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Removal of mixture of phenolic compounds from aqueous solution by tire char adsorption

Abeer M. Abdul Ameer
Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad, Iraq

Abstract. The article presents the results of the pyrolysis products from waste tires. Pyrolysis was meted out at (400-800°C) for 2 hr in absence of oxygen. The yield of char range from (0.479 - 0.3104). By chemical treatment of char with NaOH solution the modified char was produced. The physical and chemical properties were studied (optimum temperature, proximate analysis and Boehm titration for surface functional groups) for original and modified chars. Isotherm for pure and multicomponent system for three components (phenol, 4-aminophenol and 4-chlorophenol) were studied. The Langmuir and Freundlich models were used to describe the sorption of phenolic compounds for single-solute isotherms and the modified extended Langmuir and extended Freundlich gave information results for competitive system. Langmuir model was the best fit for experimental results. The capability of the studied char to adsorb phenols were in the order: 4-chlorophenol > 4-aminophenol > phenol.

1. Introduction
Phenolic compounds coming from a different industrial origin like oil refineries, units of petrochemical and phenols which are mostly utilized as a medium in the industries like plastics, dyes, insecticide, leather, etc. [1]. Removal them from wastewaters is of specific advantage as a result of very toxic substances [2].

Waste tires are one of the most important types of solid wastes is ensuing from the increase in vehicle monarchy and transport volume around the world. These junk tires act a significant ecological drawback as a result of their volume, complex and indistinctive disposal [3]. There are some ways to recycle and employ ground tires, because of the presence of carbon black in tire char can be used as an adsorbent to get rid of inorganic and organic materials from wastewater was studied for several centuries [4]. Tire rubber it is cheap and readily available [3].

Different water treatment technologies are used to remove phenolic pollutants, for instance, biological degradation, chemical oxidation or sorption and others [5]. The sorption technique is widely used for wastewater treatment because of its convenient operation, its effectiveness and comparatively low cost [6].

For improving the surface characteristic chemical modification by acidic, basic or polymers sometimes increase its sorption qualification. The product is described by increased or decreased surface area and change the functional groups and increase sorption sites which enhance chemical bonding contaminants [7,8].

The objective of this work was to study the performance of original and modified chars for removal of phenol, 4-chlorophenol and 4-aminophenol in the case of pure and competitive adsorption from aqueous solutions. Also, this study contains knowledge and understanding the properties and structure of these adsorbents.
2. Materials and method

2.1 Reagents
Three phenols: P(-OH), 4-PCP (-Cl), and 4-PMP (NH2) were utilized. Table 1 list main properties of phenol compounds.

| properties          | Phenol | PCP     | PMP    |
|---------------------|--------|---------|--------|
| Symbol              | P, PCP | PCP     | PCP    |
| Molecular formula   | C6H6O  | C6H5Ocl | C6H7NO |
| MWT                 | 94     | 128.555 | 109.128|
| pKa at 25           | 9.89   | 9.37    | 5.75   |
| Solubility at 25 g/l| 93     | 27      | 15     |
| Log Kwo             | 1.5    | 2.39    | -      |

2.2 Char Production and Characterization
The carbon from char was obtained in this study from scrap tires. The scrap tires were cut in to small particles 1-1.5mm after that pyrolysis made at (400-800 °C) without oxygen for 2 hours [11] finally char produce.

2.3 Modification of char
The modified Char were intended by basic treatments of char. For the, 1g of char was initially put in a flask and (20 ml) of Sodium hydroxide (5N) the solution was left in contact on the shaker for 24 h. Through this time, by shaker, the solution was berserk best structure homogenization. After that, filtration was used to separate the solid and liquid phases and the product was washed with deionized water until (pH 7) was obtained. Then the modified char was produced [12].

2.4 Characterization of char

2.4.1 Boehm titration
By using Boehm titration method [13] can be known as the nature of surface if acid or base.

2.4.2 Thermal analysis
The optimum temperature for pyrolysis was determined under vacuum from 400-800°C with heating rate 10°C/min.

2.4.3 Proximate analysis
Moisture, volatile matter, ash and fixed carbon were determined by The ASTM D3172-07 method

2.4.4 Regeneration efficiency
Experiments on sorption –desorption was performed with batch method. Desorption studies were done in 40 mL of solution mix with 1g char kept at a constant temperature of 25°C and put on a rotary shaker at 150 rpm for 1hr. For desorption, the char -phenols was washed with distilled water and then added to 5M NaOH solution with agitation at 150 rpm for 1 h. The produced char is separated by filtration, then washed with distilled water, dried at 110 °C for 1 h, and kept for reuse.

2.5 Adsorption equilibrium studies

2.5.1 Single isotherm
Experiments of the batch were administered in a shaker using 5 flasks containing 40 ml of phenolic compounds solution at the different initial concentration (50, 100, 150, 200, and 250 ppm). The adsorbent (0.02 g) was added to every flask and closed it. The shaker was operating at 130 rpm and after
24 h separating the adsorbent from the solution by filtration and centrifuge device then concentration was measured by UV for pure compound.

2.5.2 multicomponent isotherm
The steps for multicomponent isotherms like pure isotherms, but the initial concentration of phenolic compounds (75, 120, 150, 195 and 225 ppm) with equal concentration. concentration was measured by Hplc.

2.6 Adsorption modelling

2.6.1 Single component modelling
Two isotherm models were utilized to the experimental data, Freundlich, Langmuir. The Freundlich model is an empirical equation, and it is widely to describe much adsorption data for nonlinear sorption model with heterogeneous adsorbent surfaces. This model is expressed as

\[ q_e = K_F C_e^{1/n} \]  

Where, \( q_e \) is the solid-phase equilibrium concentration (mg g\(^{-1}\)); \( C_e \) is the aqueous phase concentration of equilibrium (mg L\(^{-1}\)); \( K_F \) is the Freundlich equilibrium parameter (mg g\(^{-1}\))(L mg\(^{-1}\))\(^{1/n}\), \( n \) represents the exponential parameter it ranges between zero and one [14]. The Langmuir model has a theoretical basis, and it is generally the most straightforward non-linear isotherm model on monolayer sorption. The Langmuir equation is:

\[ q_e = \frac{q_m q_i}{1 + b C_e} \]  

Where, \( q_e \) and \( q_i \) are the solid-phase equilibrium concentration and uptakes at saturation (mg/g); \( C_e \) is the aqueous phase equilibrium concentration (mg/L).

2.6.2 Multicomponent model
Interaction and competition among the adsorbate molecules play a very important role within sorption method. The sorption mechanism will be difficult for these systems. So for understanding the mechanism, different single component isotherm models are modified to multi-component systems, to realize the interaction between the pollutant molecules Various isotherm models such as modified Langmuir extended model and extended Freundlich, were studied. Therefore, the current study reviews the different isotherm models used for multicomponent adsorption. [15, 16].

**modified Langmuir extended model:**

\[ \frac{q_i}{q_m} = B_{ii} C_i / (1 + \sum_{j=1}^{n} B_{ij} C_j) \]  

Where \( B_{ii} \) related to the amount of species i that adsorbed without competition with species j and \( B_{ij} \) related to the amount of species j that adsorbed with competition with species i.

**Extended Freundlich model:**

\[ \frac{q_i}{q_m} = k_i C_i^{n_i+n_i} / (\sum_{j=1}^{n} k_{ij} C_j^{n_{ij}}) \]  

Where \( q_e \), is the amount of component i sorbed per unit mass of adsorbent, \( C_i \) the concentration of equilibrium for component i and \( C_j \) the concentration of equilibrium for other component, \( q_m \) and \( n_i \) parameters gained from Freundlich model for each species. \( k_{ij} \) linked to the amount of species j that sorbed with competition with species i.
3. Result and discussion

3.1 Effect of temperature on the waste tire rubber
Char Temperature was done from (400 to 800°C) without of oxygen at 10 °C/min (Figure 1). Porous structure of char will damage at high temperature [17]. Also, increasing the temperature lead to rise the ash and fixed C contents, and for lowering of volatile materials content [18]. Figure 1 shows the product yields for tire rubber was pyrolysis at various temperatures. We observe by increasing the activation temperature from 400°C-600°C the yield% of Char decreases from (0.479 - 0.3208) while adsorption uptake increase from (27.75, 38.5, 48) mg/g to (42, 47 and 69) mg/g for P, PMP, PCP respectively. While, when temperature increased from (600-800) °C can be seen that slightly decrease in yield% from (0.3208-0.3104) and adsorption uptake (42, 47 and 69) to (40.5, 45.5 and 67.5) for phenolic compounds. Therefore, temperature pyrolysis at 600 °C is the optimum temperature in this study.

![Figure 1. Effect of temperature on char.](image)

3.2 Single adsorption isotherm
The adsorption isotherm for single component system of phenol, parachlorophenol and par aminophenol onto char and modified char of size 1.5mm at 25 °C are shown in figures (2,3). From results listed in table 2 it is clear that R² value for langmuir isotherm higher than Freundlich therefore, the Langmuir isotherm had the best fit. This means that the sorption of phenols by char is of the mono-layer type.
Figure 2. Adsorption isotherm of (a-PCP, B-PMP and C-phenol on tire char at (25°C).
Figure 3. Adsorption isotherm of (a) PCP, (b) PMP, and (c) phenol on modified char at (25°C).
Table 2. Adsorption isotherm parameters for tire char systems

|                   | Lungmuir isotherm (1) |       |
|-------------------|-----------------------|-------|
|                   | qm (mg/g)             | K_L  |
|                   |                       | R^2   |
| Original char     |                       |       |
| 4-pcp             | 308.2013              | 0.005257 | 0.96550 |
| 4-pmp             | 246.7326              | 0.003328 | 0.98892 |
| p                 | 184.6907              | 0.003856 | 0.99248 |
| Original char     |                       |       |
| Freunlich isotherm|                       |       |
| 4-pcp             | 4.458140              | 1.4671 | 0.94714 |
| 4-pmp             | 1.961119              | 1.3467 | 0.98225 |
| p                 | 1.799879              | 1.388165 | 0.985 |
| Modified char     |                       |       |
| Lungmuir isotherm |                       |       |
| 4-pcp             | 331.6641              | 0.006193 | 0.96345 |
| 4-pmp             | 290.2808              | 0.003125 | 0.9986 |
| p                 | 274.0545              | 0.002229 | 0.99877 |

Modulated char     |                       |       |
| Freunlich isotherm|                       |       |
| 4-pcp             | 6.392951              | 1.5559 | 0.95462 |
| 4-pmp             | 2.184106              | 1.341  | 0.9986 |
| p                 | 1.395844              | 1.24187 | 0.99985 |

3.3 Competitive adsorption isotherm

Interaction and competition among the adsorbate molecules plays a very important role with in sorption method.

The results of multicomponent adsorption of P,PCP,PMP as shown in table 3 and 4. These tables show that modified Langmuir extended correlates with correlation coefficients of (0.97532, 0.94974 and 0.94374) for PCP ,PMP,P respectively. While the extended Freundlich equations correlates with correlation coefficients (0.9744, 0.34277and 0.98984) for PCP ,PMP and P respectively. Therefore, modified extended Langmuir is the best analysis of isotherm data with higher R^2 for original and modified chars. Also modified char as the same of original with modified Langmuir extended had higher correlation coefficients as shown in table 3 and 4.

Table 3. Results of multicomponent isotherm correlated with Modified extended Langmuir equation.

| Adsorbate (original char) | qm_i | B_1  | B_2  | B_3  | Correlation coefficient |
|---------------------------|------|------|------|------|-------------------------|
| PCP                       | 308.2013 | 0.003392 | -0.171141 | 0.166001 | 0.97532 |
| PMP                       | 246.7326 | 0.001537 | -0.148075 | 0.120223 | 0.94974 |
| P                         | 184.6907 | 0.000337 | -0.042013 | 0.022443 | 0.94375 |
| Adsorbate (on modified char) | qmi | B_1  | B_2  | B_3  | Correlation coefficient |
| PCP                       | 331.6641 | 0.020529 | 0.121878 | -0.067500 | 0.94629 |
| PMP                       | 290.2808 | 0.005950 | 0.003853 | -0.006968 | 0.91835 |
| P                         | 274.0545 | -6.30942 | 5.805150 | 0.074205 | 0.98661 |
Table 4. Results of multi component isotherm correlated with extended Freundlich equation.

| Adsorbate (on orginal char) | Adsorbate (on modified) | ki  | ni  | $K_i$ | $k_i$ | $N_i$ | $N_i$ | $N_i$ | Correlation coefficient |
|----------------------------|-------------------------|-----|-----|-------|-------|-------|-------|-------|-------------------------|
| cp                         | 4.4581                  | 1.4671 | 52.1601 | -268.852 | 9714.29 | 7.484096 | 6.555833 | 2.34626 5 | 0.9744 |
| mp                         | 1.9611                  | 1.3467 | -21.3766 | 307.8384 | 0.102237 | -1.09923 | -1.92111 | 0.11739 8 | 0.34277 |
| p                          | 1.7998                  | 1.3881 | 395.642 | 167.6117 | -780.411 | -2.22211 | -1.67675 | 1.96783 | 0.98984 |
| Adsorbate (on modified)    | 6.3929                  | 1.5559 | -12.1706 | -9.04371 | 22.05701 | -1.13477 | -15.2320 | -0.90317 1 | 0.98811 |
| cp                         | 2.1841                  | 1.341  | 6518.57  | 6.838103  | 0.026183  | -64.1753  | -51.5701  | -49.7035  | 0.67398 |
| mp                         | 1.3958                  | 1.2418 | 1.76256 | -1.72829 | 1.351351  | -1.22388  | -1.117293 | 1.23566 | 0.98078 |
| p                          | 44                      | 7      | 4       | PCP     | PMP     | Ph        | q mg/g   | Ce ppm |

![Graph showing adsorption isotherm](image-url)
3.4 Effect of adsorbate nature

Conception adsorption on the surface of adsorbent and the effect of carbon surface chemistry with adsorbate nature is the important step. The capacities of sorption on adsorbats can be determined, the adsorption isotherms at (25 °C) were studied. The research was done by three adsorbats, (PCP,PMP and P) using tire char as an adsorbent. The isotherms showed that the higher adsorption capacity was for PCP, followed by PMP, and P as in (Figure2,3) for pure and figure 4 for multicomponent.

"OH group on adsorption of phenol may be attributed to the capability of this group to form hydrogen bonding with water ":[19].The entrance of organic molecules block by molecules of adsorbed water to paramount some parts of the surface; this impact named "solvent effect" [20].

- PCP is more hydrophobic than PMP, and P as a result of value of log(kow) and high MWT made PCP higher adsorption capacity (Table 1). Also, solubility of phenols in water consider as significant effect on adsorption which water solubility of the phenolic compounds decreased with the adsorption capacity increased [21]. In the present study, for PCP, although of its solubility in water (i.e. 27 g L⁻¹) in (Table 1). But Other factors effect on the severity of the adsorptive/solvent interactions in the solution [12].

-At pH is 5.5 the phenolic compounds were partially separated, also by the high pKa magnitude in Table 1 [1 ,22]. For this reason, they were sorbed mostly by π–π interactions between electrons belong to the aromatic ring of compound and layers of the tire char at 600°C . Since "the chloro ring substituents is electron withdrawing groups [23] while the amino group is a donating electron group, that groups reduce electronic density in the aromatic ring of the phenols therefore the adsorption was higher for PCP ["[12].

3.5 Characterization of the studied carbons

Surface functional groups of the original and modified chars were showed in table 5. It is clear that e total acidic groups content for original char was form (5.45 mmol /g) while,modified char was 2.02 (mmol /g). However, it is vital to show that Boehm titration is not suitable for original char due to high acidic group. So, when acidic group reduced means increase basic groups lead to increase the sorption of aromatic compounds by an "electron acceptor–donor complex " [24].

| adsorbate type | Carboxylic group (mmol /g) | Lactonic group (mmol /g) | Phenolic group (mmol/ g) | Total acidic sites (mmol/ g) |
|----------------|---------------------------|-------------------------|--------------------------|-----------------------------|
| Orginal char   | 1.33                      | 0.92                    | 3.2                      | 5.45                        |
| Modified char  | 0.83                      | 0.09                    | 1.1                      | 2.02                        |
3.6 Proximate analysis
The proximate analysis of chars explains in table 6. The content of fixed carbon plays a vital function, increase in fixed carbon content means increase carbon surface for phenolic adsorption [25]. The volatile substance of char was considerably low. Higher volatility in char means increasing amounts of pyrolytic oil condensed on the char [26] or the raw tire. The produce char by pyrolysis had primarily fixed carbon content and ash, all the volatile matter removed nearly by pyrolysis process. After pyrolysis ash content kept largely in the char.

Table 6. proximate analysis of tire and char

| properties              | Original rubber | char | Modified char |
|-------------------------|-----------------|------|---------------|
| Moisture Content (weight %) | 1.02           | 0.4  | 0.31          |
| Volatile Content (weight %) | 61.6           | 4.16 | 1.1           |
| Ash Content (weight %)   | 2.87           | 2    | 5.2           |
| Fixed Carbon (weight %)  | 32             | 93.84| 95.9          |
| Bulk density mg/g        | -              | 0.4  | 0.361         |

4. Regeneration efficiency
Figure (5) represents the influence of initial phenols concentrations on the efficiency of regeneration for regaining the char sorption capacity compared to original char. It is clear that the regeneration efficiency slightly decreased for PCP, PMP and P. PCP regeneration efficiency decreased to (94.18 %) in the first cycle and next cycle 81.141% even reach in five cycles 48.4%. Further by increasing the number of the reused times lead to a decrease in the regeneration efficiency. Also, decrease in regeneration for PMP and P can be seen in figure (5). These are in agreement with [27] was found to facilitate the recovery of tire char. Thus, tire char has excellent recycle- ability and can be repeatedly used in phenols wastewater treatment.

Figure 5. Reusability of phenols on tire char (T=25°C, Con.=75ppm, pH=5.5).
5. Conclusions
In this paper, the ability of using local adsorbent of char was specified, and the results obtained in batch adsorption showed that the equilibrium isotherms for the phenolic compounds adsorption on to char and modified char were represented by liguunmer and freundlich equations. The coefficients of determination show that langmuirs equation fit the experimental data more than freundlichs equation fore pure, while for multicomponent the equation fit. Also it may conclude that for single and multicomponent system the adsorption capacity in the order p-chlorophenol > p-aminophenol > phenol. Preferential adsorption of PCP could be explained by the electron-withdrawing for -Cl group and higher molecular weight. For yield of char decrease with increase temperature.

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