Removal of Phenol From Aqueous Solution By Agriculture Waste

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Abstract
Using agriculture waste products waste Tea (WT) and activated carbon waste Tea (WT-GAC) as biosorbent for phenol from aqueous solution was studied. Adsorption in this way more economical in comparison with other conventional methods which are usually costly. Batch kinetics and isotherm studies were carried out under varying experimental conditions of contact time, phenol concentration, adsorbent dose and PH value. It was observed that the adsorption process is instantaneous and attained equilibrium within 10 minutes for activated carbon waste Tea and 30 minutes for waste Tea at phenol concentration (100-600) mg/L. the adsorption of phenol increase with increasing the solution pH value till pH 7 then it decrease with increasing pH value. The Freundlich and Langmuir models were used for the mathematical description of adsorption equilibrium and it was found that data fitted very well to the Freundlich models.

Keywords: phenol, adsorption, Agricultural, waste product.

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Introduction
There is a growing concern about widespread contamination of surface and ground water by various organic compounds due to the rapid development of chemical and petrol chemical industries over the past several decades, so many industrial wastes contain organics which are difficult or impossible to remove conventional biological treatment processes [1].

Pollution by phenols is an important environmental issue. Phenol being a basic structural unit for a variety of synthetic organic compounds, wastewater originating from many chemical plants and pesticide and dye manufacturing industries contain this chemical wastewater, from other industries such as paper and pulp; gas and coke manufacturing, rubber and petroleum also contain different types of phenols. It is important to remove phenols and aromatic compounds from contaminated industrial aqueous streams before discharged into any water body [2]. Human consumption of phenol contaminate water can cause severe pain leading to damage of the capillaries ultimately causing death. Their presence in water supplies is noticed as bad taste and order [3].

There are many methods such as oxidation, precipitation, solvent extraction and adsorption for removing phenols and its derivatives from aqueous solution [1].

Rodrigo (2004) investigated the adsorption of phenol on gold electrodes at the potential of zero charge. The results show that the adsorption process occurs in two distinct and successive steps the first one is the physical adsorption on the phenol oxygen and the aromatic ring pointing towards the bulk of the solution. This is followed by a second step consisting of the reorientation of the molecule to a horizontal configuration [4]. Senkurk (2009) studied the adsorption capacity of some natural material for phenol such as bentonite modified with cationic surfactants. Adsorption studies were performed in batch system and the affects of various experimental parameters such as solution pH, contact time, initial phenol concentration and temperature were evaluated upon phenol adsorption on to organobentonite, maximum phenol removal was observed at pH 9.0. Equilibrium was attained after contact time of 1 h [5]. A study of Antonio.(2006) found the removal of phenol by using a strong base anion exchanger. It was observed that its removal capacity was higher than that of other known adsorbents [6]. The potential of rice husk and rice husk ash was studied by.Mavi (2004). Batch kinetics and isotherm studies were carried out under varying experimental contact time, phenol concentration, adsorbent and pH the study showed that rice husk ash is very affective than rice husk for phenol removal [1]. A study by.Nagda (2007) found the removal of phenol by tendu leaf refuse from bidi industry waste to remove phenol from aqueous solution. Adsorption equilibrium of tendu leaf refuse and chemically carbonized tendu leaf refuse was reached with 2 hr for phenol concentration 25 mg/L and 1 h for phenol concentration 200mg/L. The studies showed that the rice husk ash can be used an efficient sorbent material for removal of phenol [2]. The potential of water hyacinth ash for phenol adsorption
was studied using batch kinetic and isotherm studies. The studies were carried out under varying experimental condition. The Freundlich and Langmuir adsorption models were used for the mathematical description equilibrium and it was found that the experimental data fitted very well to the Langmuir model [3]. Recently interest has turned to using various biomasses and agricultural waste as biosorbent, which have the advantage of low cost and increased tolerance of environmental conditions. Biosorption can be defined as a process in which solids of natural origin are employed for separation of pollutants from an aqueous environment. Many natural material were used as biosorbent for phenol removal like human hair, chicken feather, peanut shell, tamarind nutshell and waste tea, presented with cheap viable options [2]. Consumption of tea in Iraq is about 12000 ton/year. The objective of this study was to investigate waste tea and activated carbon prepared from waste tea as adsorbent for adsorption of phenol. The effect of initial phenol concentration, contact time, pH and adsorbent dosage on the adsorption of phenol were studied.

Materials and Methods

Preparation of biosorbent

Waste tea was collected from the local resource, washed with boiled water thoroughly until it became colorless. The waste tea (WT) mixed with distilled water then it dried at room temperature. The fraction with a particle size ranging between 4-6 mm was retained for the whole of handling. Granual activated carbon from waste tea (WT-GAC) was prepared by pyrolysis of waste tea in electrical oven. Many experiment were made to establish best temperature and time conditions. It was found that 300°C for 2 h as suitable condition. It was noticed that by increasing time and temperature some of (WT-GAC) turned to ash, on the contrary by reducing time and temperature the transfer was not accomplished. After cooling the sample stored until used. The specific surface area of the WT-GAC was 4.14 m²/gm and for WT was 0.73 m²/gm samples were analyzed with surface area analyzer B.E.T Method by ministry of oil (petroleum R&D center).

Chemicals

The test solutions were prepared by diluting of stock solution of phenol to the desired concentrations. A stock solution was obtained by dissolving 1.0 g of phenol (obtained by Fluka AG, Chemische Fabrik CH-9470 Buchs) in 1L distilled water. Desired solutions of phenol were prepared using appropriate subsequent dilutions of the stock solution. The rang in concentration of phenol prepared from standard solution varied between 100mg/L to 600 gm/L. The pH of the solution was adjusted to the required value with 0.1N HCL and 0.1 N NaOH solutions.

Adsorption studies

Adsorption studies were performed in batch method. The batch adsorber which is shown in fig (1). is an agitated vessel in which a batch of liquid adsorbat is contact with a batch of adsorbent for a period of time followed by discharge of the slurry from the vessel and filtration step to the solids from liquid.
The adsorption of phenol on (WT) and (WT-GAC) using 100/ml of aqueous phenol solution of varying concentration and known amount of WT(4,2,1) gm and WT-GAC(1, .75, .5) gm were add to each flask. The flasks were maintained at room temp. (20±1 °C) under constant stirring on a magnetic stirrer. Samples were removed under different time intervals, filtrated and analyzed for phenol with. High-Performance Liquid Chromatograph (HPLC)-model LC-2010 AHT, Japan. There after in order to monitor phenol removal, biosorption capacity at equilibrium time (Qe) will be determined according to the following equation:

\[ Q_e = \frac{(C_o - C_e) \times V}{M} \quad \text{(mg/g)} \quad \text{--- (1)} \]

Where \( C_o \) and \( C_e \) are respectively the initial and equilibrium liquid phase concentration of the adsorbate (mg/L), \( V \) the solution volume (L), and \( M \) is the mass of the dried adsorbent (g) [7,8].

The uptake was calculated from the difference between the initial and final concentration per weight of adsorbent.

\[ \text{Uptake} = \frac{(C_o - C_e)}{M} \quad \text{------- (2)} \]

Results and discussion

The adsorption of phenol in aqueous solution on WT and WT-GAC were examined by various physiochemical parameters such as pH contact time, and the amount of adsorbend and adsorbate.

Effect of PH on phenol removal

In any adsorbate- adsorbent system, pH of the system affects the nature of surface charge of the adsorbent. The adsorption of phenol by WT and WT-GAC were studied at various pH values [3, 5, 7, 9]. Several 100 ml portions of 600 mg/L of phenol were adjusted to assigned pH with Sodium hydroxide or hydrochloric acid and were mixed with 0.75 g WT-GAC and 4 g WT with stirring for 10 min for WT-GAC and 0.75 hr to WT. Adsorbed amount decreased with increasing pH value fig.(2). Which can be attributed to the phenol ionization to form phonate ions and at the same time the presence of hydroxyl ions on the adsorbent prevents the uptake of phonate ions. Similar behavior has been reported during the adsorption of phenol onto bentonite and Tendu leaf refuse [5, 2].

Effect of contact time and initial concentration

The adsorption data for the uptake of phenol versus contact time at different initial concentration on WT is presented in figs (3,4,5). The results showed that the equilibrium time required for the adsorption of phenol on WT was almost 45 min. The higher sorption rate at initial period may be due to an increased number of vacant site on the adsorbent available at the initial stage. As time precedes the concentration is reduced due to the accumulation of phenol particle in the vacant sites. It was also seen that an increase in initial concentration resulted in increased phenol uptake similar results were obtained by.Nagda,(2007).Mahvi (2004) and.Uddin (2007) (1, 2, 3). From fig.s (6, 7,8) it was observed that the adsorption of phenol on WT-GAC was instantaneous and attained equilibrium within five minutes. The quick establishment of equilibrium indicate the high adsorption capacity of the WT-GAC. This is in agreement with results obtained by Abdul Hameed [10] and.Uddin [3].

Effect of adsorbent concentration
The effect of adsorbent concentration on phenol removal was studied where different amount of WT and WT-GAC were contacted with fixed initial phenol concentration. The results were shown in figs (9,10). The percentage removal of phenol increased with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent dosage. The same results obtained by Nagada (2007) and Mahvi [3, 1].

**Adsorption equilibrium**

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values which express the surfaces properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. Equilibrium data can be analyzed using commonly known adsorption isotherm which provide the basis for the design of adsorption system. The most widely used isotherm equation for modeling of the adsorption data is Langmuir equation which is valid for monolayer sorption on to a surface with a finite number identical site and is given by equation (3)

$$Q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \quad \text{(3)}$$

Where $Q_e$ (mg/gm) and $K_L$ (mg/L) are the equilibrium adsorption capacity of adsorbent and the equilibrium concentration in the aqueous solution respectively. $q_o$ is the maximum adsorption capacity corresponding to complete monolayer on the surface bond (mg/gm) and $K_L$ is the Langmuir constant related to energy of adsorption (L/mg).

The linearized form of Langmuir equation can be written as

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o K_L} \quad \text{(4)}$$

The Langmuir constants $q_o$ and $K_L$ can be calculated from the slope and the intercept of the straight line by plotting $\frac{C_e}{q_e}$ versus $C_e$ [3, 1].

The Freundlich model is an empirical equation based on sorption on heterogeneous surface it is given as

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad \text{(5)}$$

The value of $K_f$ and $n$ are the Freundlich constants that indicate adsorption capacity and adsorption intensity can be calculated from the slope and the intercept of the straight line by plotting $\ln q_e$ versus $\ln C_e$ [3, 1]. Figs (11- 22) show the Langmuir and Freundlich curves for phenol adsorption on WT and WT-GAC. The isotherm constants and correlation coefficients are shown in table (1). It was observed that the equilibrium data were well represented by the Freundlich equation when compared to the Langmuir equation i.e for a given system only one of the models can be true description of physical reality with the exclusive of all other models [3, 8, 10]. The correlation factor $R^2$ is close to the unity for WT and WT-GAC. The higher value of $K_f$, the Freundlich constant showed easy uptake of phenol from aqueous solution. Also higher value
of n reflects the intensity of adsorption signifies that the surface of biosorbents is heterogeneous in nature and high enough for effective separation, this is in agreement with results obtained by Nagda [3].

Conclusions
In this study the adsorption of phenol from aqueous solution was investigated using waste tea and granual activated carbon from waste tea. The result showed that the equilibrium time required for the adsorption of phenol on WT was 0.75h and for WT-GAC was 10 min. The results indicated that adsorption amount of the adsorbent was considerably affected by initial pH it took place at Ph in the rang (3-7) then it decreased with increasing pH. The surface area of the WT-GAC was 4.14 m²/gm and for WT was 0.73 m²/gm. Equilibrium data were well represented by Freundlich isotherm equation.

References
6- Manuel Carmona, Antonio be Lucas (2006) chemical Engineering Journal 117 “ Combiend adsorption and ion exchang equilibrium of phenol on Amberlite IRA-420”
Table (1) Freundlich and Langmuir's equation constants

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<th>Type</th>
<th>Models</th>
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<th>$1/n$</th>
<th>$q_o$</th>
<th>$k_L$</th>
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Figure (1) Batch adsorber apparatus
Figure (2) Effect of pH on the removal of phenol

Figure (3) Effect of contact time on phenol uptake by 4 gm WT
Figure (4) Effect of contact time on phenol uptake by 2 gm WT

Figure (5) Effect of contact time on phenol concentration by 1 gm WT
Figure (6) Effect of contact time on phenol uptake by 1 gm WT-GAC

Figure (7) Effect of contact time on phenol uptake by 0.75 gm WT-GAC
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Figure (8) Effect of contact time on phenol uptake by 0.5 gm WT-GAC

Figure (9) Effect of adsorbent dosage on the removal of phenol on WT-GAC
Figure (10) Effect of adsorbent dosage on the removal of phenol on WT

\[ y = -0.0002x + 0.0636 \]

\[ R^2 = 0.7408 \]

Figure (11) plot of \( \frac{C_e}{q_e} \) vs \( C_e \) for determination of Langmuir constant at 4gm WT

\[ y = -0.0002x + 0.0636 \]

\[ R^2 = 0.7408 \]
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Figure (12) plot of \((C_e/q_e)\) vs \((C_e)\) for determination of Langmuir constant at 2gm WT

\[ y = -0.0001x + 0.0421 \]
\[ R^2 = 0.7979 \]

Figure (13) plot of \((C_e/q_e)\) vs \((C_e)\) for determination of Langmuir constant at 1gm WT

\[ y = -7E-05x + 0.028 \]
\[ R^2 = 0.9636 \]
Figure (14) plot of (ln$q_e$) vs (ln$C_e$) for determination of Freundlich constant at 4gm WT

$y = 1.7522x - 0.1538$
$R^2 = 0.9823$

Figure (15) plot of (ln$q_e$) vs (ln$C_e$) for determination of Freundlich constant at 2gm WT

$y = 1.6988x + 0.3883$
$R^2 = 0.9784$
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\[ y = 1.6877x + 0.7441 \]
\[ R^2 = 0.9975 \]

Figure (16) plot of \((\ln q_e)\) vs \((\ln C_e)\) for determination of Freundlich constant at 1gm WT

\[ y = -4E-05x + 0.0086 \]
\[ R^2 = 0.0544 \]

Figure (17) plot of \((C_e/q_e)\) vs \((C_e)\) for determination of Langmuir constant at 1gm WT-GAC
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Figure (18) plot of \( \frac{C_e}{q_e} \) vs \( C_e \) for determination of Langmuir constant at 0.75 gm WT-GAC

\[
y = -5 \times 10^{-5} x + 0.0131 \\
R^2 = 0.6332
\]

Figure (19) plot of \( \frac{C_e}{q_e} \) vs \( C_e \) for determination of Langmuir constant at 0.5 gm WT-GAC

\[
y = -7 \times 10^{-5} x + 0.0178 \\
R^2 = 0.8192
\]

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\[ y = 3.807x - 5.5121 \]
\[ R^2 = 0.4702 \]

Figure (20) plot of \((\ln q_e)\) vs \((\ln C_e)\) for determination of Freundlich constant at 1gm WT-GAC

\[ y = 2.1435x - 0.3599 \]
\[ R^2 = 0.9831 \]

Figure (21) plot of \((\ln q_e)\) vs \((\ln C_e)\) for determination of Freundlich constant at 0.75gm WT-GAC
$y = 2.3299x - 1.5012$

$R^2 = 0.9956$

Figure (22) plot of $(\ln q_e)$ vs $(\ln C_e)$ for determination of Freundlich constant at 0.5gm WT-GAC