Adsorption of Phenol Using 8-Hydroxyquinoline Treated and Untreated Tea Waste

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Abstract

Phenol compounds found in wastewaters of various industries such as petroleum refining, coal conversion, plastic, textiles, iron and steel manufacturing units. Remediation of phenols and its derivatives from contaminated water before discharging is essential, as they are toxic for aquatic organisms. This work is an attempt to remove phenol from aqueous solution applying the adsorption technique using locally available and eco-friendly tea waste adsorbent. The batch adsorption experiment was performed on different concentrations. Langmuir and Freundlich isotherms were applied to confirm the adsorption model. The data obtained found to be best fitted to the Langmuir isotherm. The kinetic study for the adsorption process were performed by checking various models and the data obtained show that the pseudo-second-order model fit well for both 8-HQ treated and untreated powdered tea waste adsorbent.

Keywords: Phenol; 8-hydroxyquinoline; Adsorption; Kinetics; Langmuir and Freundlich isotherm

Introduction

Water is an essential resource for the existence of all life forms. Freshwater is important for human and aquatic organisms and for all activities of all living beings; but they are limited due to the increasing population, urbanization and climate changes. This scarcity was due to water pollution that caused by the discharge of untreated or partially treated industrial effluents into the natural ecosystem, posing serious problems. Thus, these industrial effluents, containing several organic and inorganic chemicals as -phenols, formaldehyde, dyes, and heavy metals are the major water pollutants [1].

Aromatic hydrocarbons are one of the common contaminants of groundwater originating from coal gasification, oil refining process, wood treatment process, fires of forests automobile exhausts and disposal of oils and fuels. Many of these compounds are reported, to be toxic, carcinogenic and tend to accumulate in the aquatic organisms even present in low concentrations. The presence of heteroatom in them makes them more soluble than their homocyclic analogs [2-5]. One of the aromatic organic compounds is phenol (C_6H_5O) white crystalline solid that is volatile. It consists of phenyl (C_6H_5-)(-OH) groups which was first extracted from coal tar. It is an important industrial commodity as a precursor to many materials and useful compounds. Their major use involves its conversion to plastic or relates materials [6,7].

Beside their usage phenol and its chemical derivative has a toxic effect on the aquatic organisms and humans. Since phenol and its derivatives are harmful to living even at low concentrations, they known as dubious pollutants. Phenols and its deriv atives removal study have been reported by various researchers [8-10].

Several methods for organic pollutants removal from wastewaters, such as precipitation, solvent extraction, and adsorption are usually applied. Adsorption is one of the respective methods for wastewater treatment due to its several advantages such as high efficiency, low cost, simple application and easy recovery of adsorbent [11]. Recently, researchers reported the potential use of tea waste generated from the cafeteria as an adsorbent for removal of heavy metal from aqueous solution [9,12-14].

In this work tea waste collected from the local cafeteria used as an adsorbent for the removal of phenol from aqueous solution. Collected tea wastes were used as an untreated and 8-Hydroxyquinoline treated powder for the potential removal process.

Materials and Method

The following chemicals and materials used in this work. Hydrochloric acid, HCl, Sodium hydroxide, NaOH, Phenol, C_6H_5OH, and 8-Hydroxyquinoline (99% Sigma Aldrich), Graduated cylinder, Oven drier, Digital electronic balance, Potentiometer (microprocessor pH meter, pH 211, HANNA), mortar and Pastel, sieve 150μm size, UV-Vis. Spectrophotometer (JENWAY 6705) and Scanning electron microscope (Model JSM 6510LV, JEOL Japan).

Experimental procedure

Preparation of adsorbent: The tea waste used as an adsorbent was collected from different cafeterias of Jimma town,

Southwestern, for the removal of phenol from aqueous solution. The collected tea waste washed with tap water followed by drying under sunlight. Then the dried tea waste was powdered to mesh size 150μm and washed with distilled water until neutral pH was observed then kept for drying in an oven at 110°C. The dried tea waste was now separated into two halves, then one half was treated with an 8-HQ solution; while other part left untreated. Both parts of tea waste were kept in the sample bottle separately for the further experiment.

Preparation of stock solution: A saturated solution of 8-HQ was prepared by adding an appropriate quantity in 1000ml of distilled water, sonicating for 2hr and then stirred with a magnetic stirrer for another 2hr. The solution was then filtered to remove the undissolved 8-HQ. Four standard solutions (10ppm, 15ppm, 20ppm, and 25ppm) were prepared by adding 0.01gm, 0.015gm, 0.02gm and 0.025gm of phenol to 1L of distilled water respectively.

Preparation of treated tea waste adsorbent: 10gm of dried tea waste powdered was taken into round bottom flask and treated with 8-HQ solution then kept into water bath shaker for 24hrs, after that the solution was taken out from the shaker. The solution was then filtered with filter paper and the filtrate washed until excess 8-HQ was removed.

Calibration of phenol: 1gm of powdered tea waste was weighted and added into four shaking bottles; followed by addition of 100ml of (0.01M, 0.015M, 0.02M, and 0.025M) in each shaking bottle. The sample was shaken for 65min before filtration. The filtered sample was calibrated by UV-Vis spectrophotometer. Maximum absorption was obtained at 285nm.

Adsorption isotherm

In a solid-liquid system, adsorption results in the removal of solutes from solution by accumulating at a solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at a constant temperature, can be described by an adsorption isotherm according to the general Eq. (1): In this study, the extent of phenol adsorption capacity at equilibrium, q_e (mg/g), was calculated

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

$$q_t = \frac{(C_o - C_t)V}{W} \tag{2}$$

The percentage of phenol removal was calculated using, Eq. (3):

$$(\%)\ Adsorption = \frac{C_o - C_e}{C_o} \times 100 \tag{3}$$

C_o corresponds to the initial concentration of C_6H_5OH, and C_e (mg/g) corresponds to the concentration of phenol at equilibrium. V (L) is the volume of the solution, and W (g) is the mass of the dry adsorbent.

Result and Discussion

Calibration of phenol

Calibration curve was plotted for the solution of phenol at different concentrations shows the maximum peak at 285 nm. At the same wavelength, the different absorbance of the C_6H_5OH solution formed due to the concentration difference, as shown in Figure 1 (a & b).
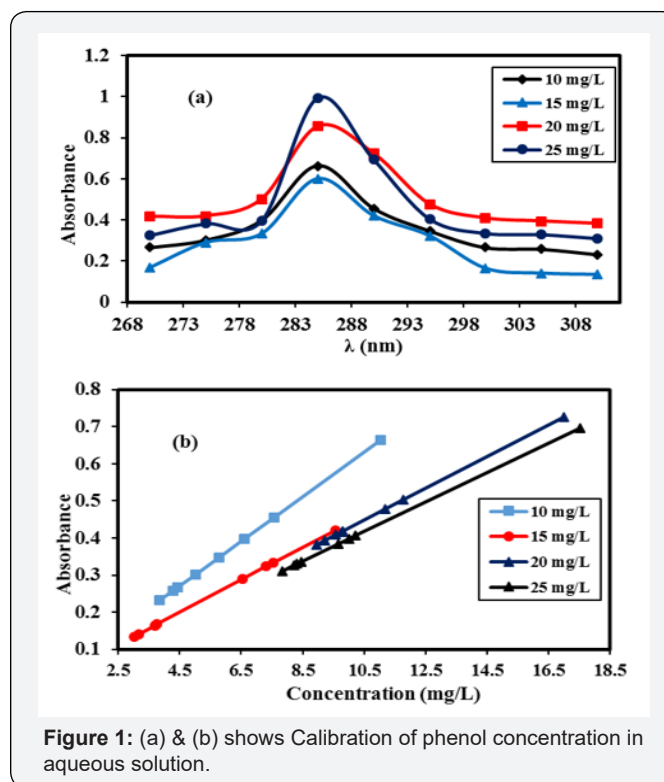

Figure 1: (a) & (b) shows Calibration of phenol concentration in aqueous solution.
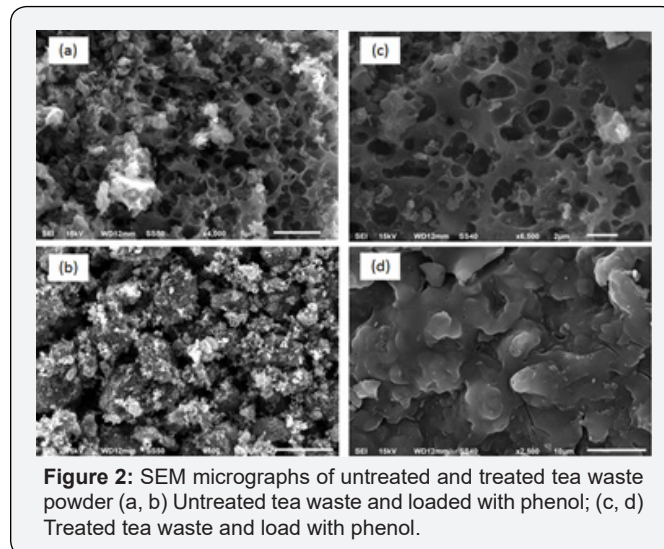
SEM micrograph

Figure 2: SEM micrographs of untreated and treated tea waste powder (a, b) Untreated tea waste and loaded with phenol; (c, d) Treated tea waste and load with phenol.

Figure 2 (a & b) depict the SEM micrographs for tea waste untreated powder before and after phenol adsorption it is evident from the figure that the surface is porous for both treated and untreated tea waste powder. However, apparently this porosity was

shown disappeared in Figure 2 (c & d). This may be due, to the fact that diffusion of phenol on to the surface of the adsorbent might have occurred for adsorption [9].

Effect of Initial concentration on contact time for the adsorption of phenol

Figure 3: Effect of initial concentration on contact time for the adsorption of phenol at 303K; (a) untreated and (b) 8-HQ treated tea waste.
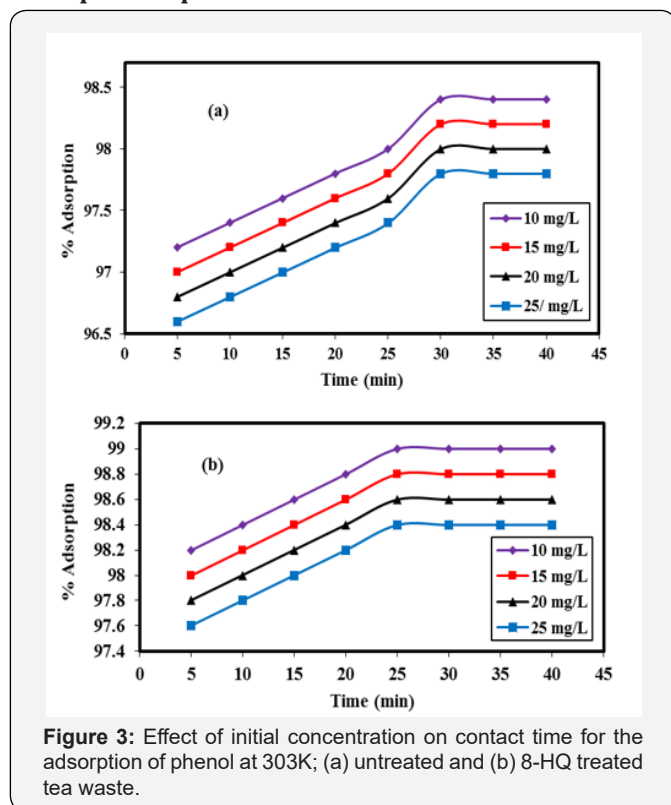
Time is one parameter that has an influence on surface property of an adsorbent. This effect of time was observed at which adsorbent and solution exist together. As the solution stays for a longer time by shaking with an adsorbent, the number of particles of solute adsorbed to the surface increases. More attachment of solute particles to the adsorbent surface increases the percent of adsorption. Also, modification of the surface increases the percent of adsorption by increasing the surface of the adsorbent. Figure 3 below is showing time influence and difference of percent adsorption of treated and untreated tea waste.

Adsorption isotherm study

Adsorption isotherm is a basic requirement for the design of an adsorption system. The adsorption mechanism was investigated using Langmuir and Freundlich models. The two models differ from each other in their assumption concerning of existence of fine adsorption capacity [15]. Langmuir isotherm describes quantitatively for the formation of a monolayer on the outer surface of the adsorbent and after that, no further adsorption takes place, Figure 4a. The Langmuir isotherm is valid for monolayer adsorption onto the surface contain a fine number of the identical site [16-20].

The linear form of Langmuir isotherm is given by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{q_m b_L} + \frac{C_e}{q_m} \qquad (4)$$

Where q_e and q_{max} are equilibrium and maximum uptake capacity (mg/g) respectively, b_L is related to the free energy of adsorption and represent the Langmuir adsorption constant, C_{eq} is the equilibrium adsorbate concentration in morality. The Langmuir constant that is, related to the maximum capacity (q_{max}) and energy adsorption (b_L), was calculated from the slope & intercept of linear plot C_e/q_{eq} versus C_{eq}.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L that is given by (Table 1)

$$R_L = \frac{1}{1 + b_L C_O} \qquad (5)$$

Where b_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution. The values of R_L indicates the type of isotherm to be irreversible ($R_L=0$), favorable ($0<R_L<1$), linear ($R_L=1$), or unfavorable ($R_L>1$). The value of R_L is found to be 1.588×10^{-4} and 5.026×10^{-4} mg/L at 303K for untreated and treated tea waste adsorption experiment respectively. This indicates that adsorption of phenol is favorable on both 8-HQ treated and untreated tea waste adsorbent.

Figure 4: Adsorption isotherm model of phenol onto 8-HQ treated and untreated tea waste; (a) Langmuir (b) Freundlich.
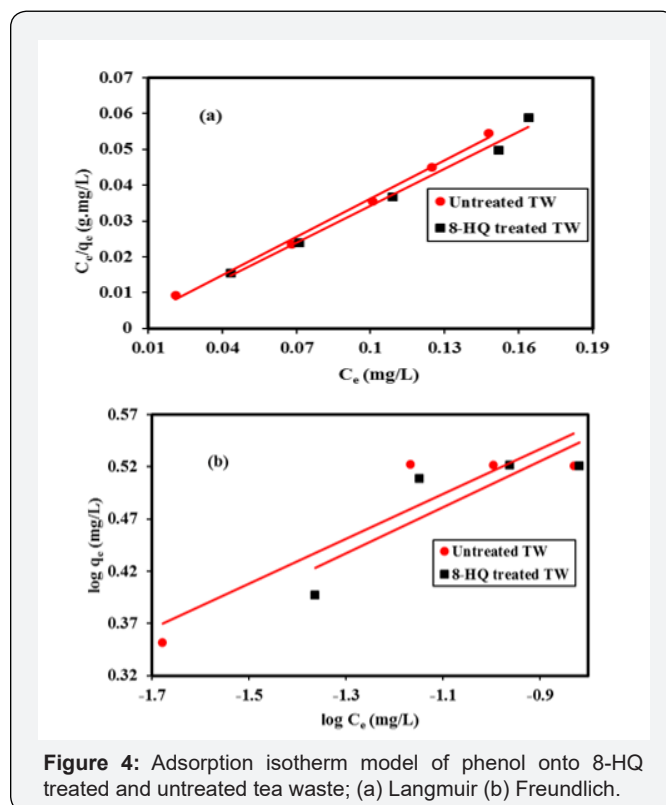
Freundlich adsorption isotherm, Figure 4b commonly used to describe the characteristic for the heterogamous surface [21-24]. The linear form of the Freundlich given as the following equation.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (6)$$

Where q_e is the adsorption density (mg/g), C_e is the concentration of the adsorbate in solution at equilibrium (mg/L); K_F and

1/n are the Freundlich constants. The plot of log q_e versus log C_e yields a straight line indicating to obey a Freundlich adsorption isotherm.

Table 1: Isotherm parameters for Phenol adsorption on modified and unmodified Tea Waste prepared adsorbent at room temperature.

Adsorption Isotherm & Constants	Values	
	UTW*	8-HQTW*
Langmuir		
qm (mg/g)	2.801	2.906
bL (L.mg-1)	629.234	1989.406
R2	0.997	0.995
RL.10-4(mg/L)	1.588	5.026
Freundlich		
n	0.381	0.394
Kf	2.073	2.063
R2	0.749	0.855

UTW*-Untreated Tea Waste; 8-HQTW*- 8-HQ treated Tea Waste.

This isotherm does not predict any saturation of the sorbent by the sorbate; thus, mathematically infinite surface coverage is predicted, indicating multilayer adsorption on the surface. Freundlich adsorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies indicate a multilayer sorption of the surface. The binding capacity and affinity between the adsorbent and phenol ions reach the highest value with high KF and 1/n. Favorability of adsorption gives by the magnitude of the exponent *n*. As can be seen from Table 1 and Figure 4b, treated tea waste is a good adsorbent for phenol adsorption.

Adsorption kinetics

To evaluate the kinetics of the adsorption process, the experimental data were compared to those predicted by two kinetic models, the pseudo-first order and pseudo-second order. The pseudo first order equation can be expressed, as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (7)$$

Where q_e and q_t the amount of adsorbate in mg at equilibrium at any time t, k_1 is the first order rate constant (min^{-1}). Rate constant, k_1 and theoretical q_e was calculated from the slope and intercept from the plot of log (q_e- q_t) versus t, Figure 5a

Pseudo-second order equation expressed as follow.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (8)$$

Where k_2 is rate constant of second order adsorption. The linear plot of $\frac{t}{q_t}$ versus time gives $\frac{1}{q_e}$ as slope and $\frac{1}{k_2 q_e^2}$ as intercepts, the linear plot pseudo-second-order model is shown in Figure 5b, Table 2 below.

Adsorption of phenol onto tea waste show rapid initial adsorption rate flowed by slower rate. Initially, the adsorption site is abundantly available, and phenol interacts easily, hence the higher rate of adsorption was observed. However, after initial periods

lower adsorption may be due to slower diffusion of adsorbate into the interior adsorbent. The two kinetics models mentioned above has been used to understand the adsorption kinematics and correlation coefficient, R^2. The linearity of these plots indicates the capacity of the two models. The correlation coefficient adsorption kinematics is 0.895 for untreated and 0.922 for treated adsorbents for pseudo first order and 1.00 1.00 for second order respectively. The correlation coefficient shows that the pseudo-second-order models fit better to the experimental data for both treated and untreated tea waste.
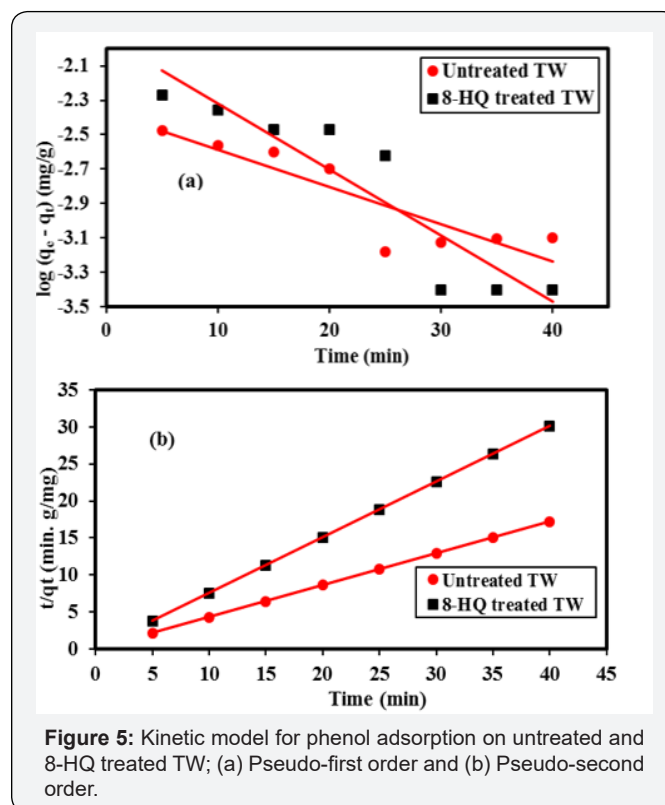

Figure 5: Kinetic model for phenol adsorption on untreated and 8-HQ treated TW; (a) Pseudo-first order and (b) Pseudo-second order.

Table 2: Values of kinetic parameters on the adsorption of Phenol on modified and unmodified Tea Waste prepared adsorbent at room temperature.

Kinetic Model & Constants	Values	
	UTW	8-HQTW
Pseudo-first order		
qe (cal)	0.862	0.661
k1	0.049	0.088
R2	0.895	0.922
Pseudo-second order		
qe (cal)	2.375	1.338
k2	37.72	17.722
R2	1	1

Conclusion

Adsorption of phenol from aqueous solution was investigated experimentally using tea waste as an adsorbent. The batch experiment revealed that the equilibrium adsorption attained at 30 and

25 minutes. The isothermal data were examined by employing two isotherm models, Langmuir, and Freundlich where the experimental data fitted very well to the Langmuir isotherm model indicating chemisorption of the adsorbate on powdered tea waste surface. Results of kinetics study indicate that the pseudo-second-order kinetics can simulate the adsorption process with a high accuracy for the adsorption of phenol from aqueous solution.

Acknowledgment

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