



## Phenol Adsorption on Magnetic Biochar Derived From Olive Pomace: Equilibrium, Kinetic and Thermodynamics

### Pirinadan Elde Edilen Magnetik Biyokömür ile Fenol Adsorpsiyonu: Denge, Kinetik ve Termodinamik

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#### ABSTRACT

In this study, magnetic biochar obtained from pyrolysis of pretreated olive pomace by iron chloride was used as adsorbent to remove phenol and the adsorption capacity of phenol was revealed. Batch experiments were performed as a function of pH, contact time, adsorbent dosage, temperature, and phenol concentration. Moreover, adsorption kinetics and thermodynamics of phenol adsorption onto magnetic biochar were also evaluated in the study. The optimum conditions for maximum adsorption capacity were obtained at pH of 5.7, dosage of biochar 0.14 g and 60 minutes contact time. In this study, three adsorption isotherms, namely Langmuir, Freundlich and Temkin, were applied to fit the equilibrium data of adsorption of phenol onto magnetic biochar. Results showed that correlation coefficients ( $R^2$ ) for three isotherm models decreased with the temperature increment from 20°C to 40°C and the most suitable isotherm model for adsorption was Freundlich. As for kinetics of the adsorption process, the best described model was found as pseudo-second order. In adsorption thermodynamics part, the negative  $\Delta H^\circ$  and  $\Delta G^\circ$  values demonstrated that adsorption was exothermic, feasible and was more spontaneous at lower temperatures.

#### Key Words

Adsorption, magnetic biochar, olive pomace, phenols.

#### ÖZ

Bu çalışmada, demir klorür ile işlem görmüş pirininin pirolizinden elde edilen manyetik biyokömür, fenol gideriminde adsorban olarak kullanılmış ve fenolün adsorpsiyon kapasitesi ortaya konmuştur. Çalışmada, fenolün adsorpsiyonu farklı pH, temas süresi, adsorban dozu, sıcaklık ve fenol konsantrasyonlarında denenmiştir ve en uygun koşullar optimum olarak seçilmiştir. Ayrıca, fenol adsorpsiyon kinetiği ve termodinamiği de çalışma kapsamında değerlendirilmiştir. Maksimum adsorpsiyon kapasitesi için optimum koşullar, pH 5.7, biyokömür dozu 0.14 g ve 60 dakika temas süresinde elde edilmiştir. Bu çalışmada, fenolün manyetik biyokömür üzerinde adsorpsiyonu için Langmuir, Freundlich ve Temkin adlı üç adsorpsiyon izotermi uygulanmıştır. Sonuçlar, üç izoterm modeli için 20°C'den 40°C'ye çıkıldığında korelasyon katsayılarının ( $R^2$ ) sıcaklık artışıyla azaldığını ve adsorpsiyon için en uygun izoterm modelinin Freundlich olduğunu göstermiştir. Adsorpsiyon işleminin kinetiğine gelince, en iyi model yalnızca ikinci mertebe olarak bulunmuştur. Adsorpsiyon termodinamik kısmında, negatif  $\Delta H^\circ$  ve  $\Delta G^\circ$  değerleri, adsorpsiyonun ekzotermik, uygulanabilir ve düşük sıcaklıklarda daha spontan olduğunu göstermiştir.

#### Anahtar Kelimeler

Adsorpsiyon, magnetik biyokömür, pirina, fenol.

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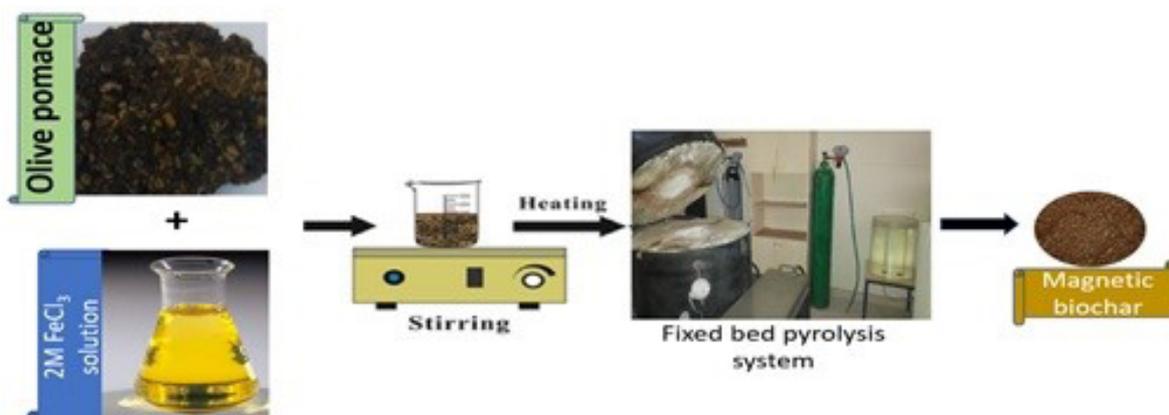
## INTRODUCTION

In recent years, phenolic compounds are becoming indispensable part of our lives since they are being used in many applications. Adhesives, foams, emulsifiers, detergents, insecticides, dyes, explosives etc., includes phenolic compounds and all these products have economic importance in several industries like food, petrochemical, agriculture etc. [1]. However, phenolic compounds are one of the most important toxic compounds for environment and human health also. They are water soluble that means easily reaching to the wastewater through various types of industrial applications. Therefore, phenolic compounds are considered as among priority contaminants in wastewater as even at low concentrations have toxic effects on organisms and human. Capillaries can be damaged if water polluted by phenolic compounds is consumed. Moreover, phenolic compounds' toxicity and resistance into the environment can increase if chlorine, which exist into drinking water, joins to the structure of phenolic compounds [2]. Additionally, phenol compounds are reactive due to chemical reactions either at benzene ring or hydroxyl group and it is highly resistant to biological decomposition due to presence of stable benzene ring [2, 3]. Therefore, it may be accumulated in the tissues before excreting by body metabolic pathway [3].

Different techniques, such as chemical oxidation, biodegradation, membrane filtration, solvent extraction and adsorption, have been adopted for removing phenol from aqueous solutions and/or wastewaters. However, adsorption's low cost, regeneration possibility and high uptake capacity is making it more favored method [4]. Although various adsorbents, either natural or synthetic, have been used in adsorption studies of phenolic compounds, nowadays, adsorbents which are naturally available in the environment are gaining importance by virtue of low-cost [2]. Biochar is carbonaceous solid produced by pyrolysis of biomass at high temperature in oxygen free environment and it can be generated from various agricultural wastes having high production amounts such as fruit wastes, coconut shell, scrap tires, sawdust, rice husk, olive pomace (OP) etc. [5]. It is one of the robust ways for storing carbon which is derived from plants. Furthermore, its potential for water contamination remediation is high since diverse functional groups inhabiting stable porous structure generation can benefit aqueous contaminant removal from solution [6].

Olive pomace (OP) biochar has been used as adsorbent by virtue of its high binding efficiency, low cost and high production amount [7]. OP biochar was used for removal of many different kinds of heavy metal like Ni (II), Cu(II), Pb(II), Zn(II), Cr(VI), Cd(II) and As (III) [7-11]. In addition to removal of heavy metal, these also were used for methylene blue, crystal violet and Remazol brilliant blue R dyes [12, 13]. In a study about pyrolysis char of OP using as adsorbent [14, 15], adsorption capacity was found as 8.76, 7.75 and 8.77 mg g<sup>-1</sup> for Pb, Zn and Cu, respectively. Although various studies about heavy metal adsorption with OP biochar have been conducted, adsorption of phenolic compounds with OP biochar have not been studied yet. Furthermore, limited number of studies were reported about removal of phenolic compounds by using biochar [5,6,9]. 2,4,6-trichlorophenol was removed from stock solution by biochar produced from sugarcane bagasse and pentachlorophenol was adsorbed by rice straw biochar. Additionally, biochar obtained from pyrolysis of municipal wastewater biosolids were used for removal of halogenated phenols, adsorption capacity of sewage sludge biochar was found high for sulfonated methyl phenols [16]. Biochar obtained from Chinese herb residue [17], pine fruit shells [4] and *Hizikia fusiformis* [5] are other biochar adsorbents used in phenolic compounds' removal studies in the literature.

There are some modification approaches to increase biochar adsorption capacities; these can be stated as carriage of metals, oxides or ions, mixing biochar with reducing or oxidizing salts, modifying biochar by organic compounds. Among these approaches, magnetic biochar can be successfully generated by chemical co-precipitation of iron oxides and it can provide effective absorptivity, ready separation and easy recycling [6]. There only few studies exist in the literature about adsorption with magnetic biochar and these are mainly about heavy metal adsorption. For instance, Han et al. [6] and Xin et al. [18] studied Cr (VI) adsorption by magnetic biochar derived from peanut hull, Reddy et al. [19] and Yap et al. [20] conducted a study about Pb (II) and Cd (II) adsorption with magnetic biochar obtained from pine bark waste and coconut shell. Therefore, in this study, magnetic biochar produced from OP was used as adsorbent to remove phenol and the adsorption capacity of phenol was revealed. Moreover, the effects of contact time, pH, adsorbent dosage, temperature, and phenol concentration were studied to reveal kinetic, thermodynamics and equilibrium characterization of phenol adsorption onto OP magnetic biochar.



**Figure 1.** Preparation process of magnetic biochar from OP.

## MATERIALS and METHODS

### Preparation of OP char and OP magnetic biochar

In this study, OP chars and magnetic biochar was obtained from pyrolysis of OP taken from Ernar Inc.-Mersin. Firstly, OP chars were pyrolyzed in fixed bed pyrolysis system at 600°C, 5°C/min heating rate. Secondly, OP magnetic biochars were obtained by following these steps: Firstly, OP samples were dried and grounded and then, 50 g of dried and grounded OP were mixed in 400 mL of 2M iron chloride solution for half an hour and kept at 70°C for half an hour (Figure 1). After that, pre-treated biomass was then separated from the solution and pyrolyzed at 600°C, 5°C min<sup>-1</sup> heating rate (Figure 1). By this method, 10g Fe<sub>2</sub>O<sub>3</sub> were attached to 1 g biochar.

### Batch adsorption experiments

Prepared OP chars and OP Fe<sub>2</sub>O<sub>3</sub>- magnetic biochars were used in adsorption experiments of the phenols. Firstly, phenol solutions having different concentrations were prepared and measured in accordance with phenol analysis [21] to obtain standard curve. In the phenol analysis, ammonium hydroxide solution, phosphate buffer solution, 4-aminoantipyrine and potassium ferricyanide solution were used and the test results were determined by using spectrophotometry at 500 nm wavelength.

Secondly, in this study, the effects of different parameters including contact time, initial concentration of phenol, pH of the solution, adsorbent temperature and the adsorbent dose were investigated and ultimately, the adsorption of isotherms, kinetics and equilibrium were determined. In the decision step of contact

time for both OP chars and OP magnetic biochars, 20 mL phenol solution (initial phenol concentration: 60 mg L<sup>-1</sup>, pH: 5.7, temperature: 20°C, adsorbent dosage: 0.1g) were added into beakers and adsorption study of phenol was conducted at 200 rpm and at different contact time (from 10 to 90 min.). In this step, adsorption capacity of OP and OP magnetic biochars were compared to each other to evaluate the effect of applied FeCl<sub>3</sub> modification to the OP. In order to evaluate effects of pH values, adsorption process was conducted with 20 mL phenol solutions at different pH values (2.9, 3.6, 7, 9.4 and 11.3) at selected optimum contact time by keeping other experimental conditions fix. The pH of the solution was adjusted with 0.1 M hydrochloric acid or 0.1 M sodium hydroxide. After determination both pH and contact time, 0.005 – 0.30 g adsorbent per 20 mL were added into beakers including 60 mg L<sup>-1</sup> phenol solutions to adjust optimum adsorbent dose. Finally, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg L<sup>-1</sup> initial phenol solution concentrations and effects of temperatures at 20°C and 40°C were studied at selected contact time, adsorbent dosage and pH value.

In this study, the adsorption capacity was determined using the following equation 1:

$$q_e = \frac{(C_o - C_e)V}{m}$$

(Equation. 1)

where,  $q_e$  : adsorption capacity ( $\text{mg g}^{-1}$ ),

$C_o$  : initial concentration of phenol in the solution ( $\text{mg L}^{-1}$ ),

$C_e$  : final equilibrium concentration of phenol ( $\text{mg L}^{-1}$ ),

$V$  : liquid volume inside the reactor (L), and  $m$  is the adsorbent mass (g).

### Adsorption isotherms

Adsorption isotherm reflects the relationship between the amount of a solute adsorbed at constant temperature and its concentration in the equilibrium solution. Moreover, equilibrium study on adsorption provides information on the capacity of the adsorbent; so, they are important for understanding of adsorption system. There are several isotherm equations available for analyzing experimental adsorption equilibrium data. In this study, three adsorption isotherms: Langmuir, Freundlich and Temkin were applied to fit the equilibrium data of adsorption of phenol onto OP magnetic biochar.

### Langmuir Isotherm Model

The one of the most widely used isotherm equation for modeling of the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites and is given by Equation 2 [22].

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o K_L} \frac{1}{C_e}$$

(Equation 2)

where,  $q_o$  : maximum adsorption capacity ( $\text{mg g}^{-1}$ ),

$K_L$  : langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption ( $\text{L mg}^{-1}$ ),

$C_e$  : equilibrium concentration ( $\text{mg L}^{-1}$ ),

$q_e$  : equilibrium adsorption capacity of adsorbent ( $\text{mg g}^{-1}$ ).

### Freundlich Isotherm

Freundlich Isotherm is mainly indicated adsorption equilibrium of multi-phase adsorption onto surface and is an equation based on sorption on heterogeneous surface. Equation of this isotherm is given by Equation 3 [23].

$$\log q_e = \log K_F + (1/n) \log C_e$$

(Equation 3)

where,  $K_F$  : Freundlich constants indicating adsorption capacity

$n$  : adsorption intensity constant

### Temkin Isotherm

The Temkin isotherm model contains a factor that explicitly takes into account the adsorbent-adsorbate interactions. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interactions. The adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy. The Temkin adsorption isotherm expression is given by Equation 4 [24].

$$q_e = \frac{RT}{b} \ln(A) + \frac{RT}{b} \ln(C_e)$$

(Equation 4)

where,  $B (=RT/b)$ : temkin constant related to heat of adsorption,

$A$ : equilibrium binding constant related to maximum binding energy ( $\text{L g}^{-1}$ ),

$C_e$ : equilibrium concentration of phenol ( $\text{mg L}^{-1}$ ),

$R$ : universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ),

$T$ : absolute solution temperature (K).

## RESULTS and DISCUSSION

### Effect of contact time

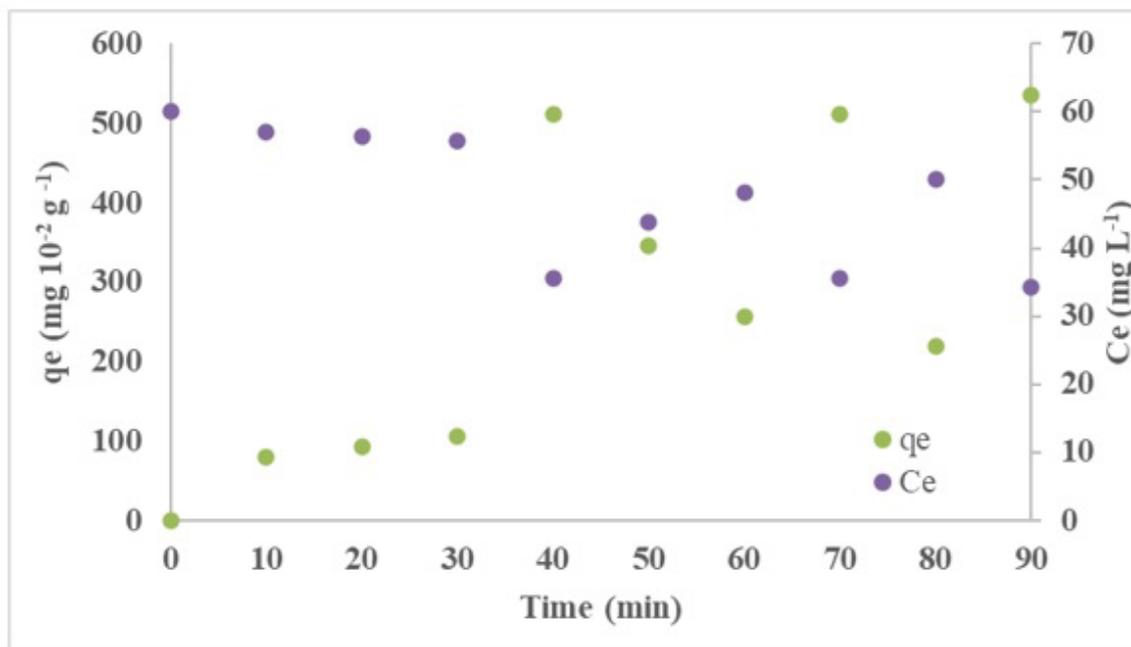
Contact time is one of the vital parameters in adsorption studies. In the study, different contact time values at constant initial phenol concentration were tried to find appropriate duration for the removal of phenol (Figure 2). Different phenol removal trends were observed in the case of using OP biochars and OP Fe<sub>2</sub>O<sub>3</sub>-magnetic biochars (Figure 2). While phenol adsorption on non-modified OP biochars has no regular kinetic stage, phenol adsorption on magnetic biochar was achieved by two stage kinetic behavior. In phenol adsorption process of OP magnetic biochars, firstly, phenol adsorption increased up to 60 minutes, then lower adsorption capacity was observed during 60-90 minutes. Accordingly, it indicates that accessible sites are higher in initial adsorption stage as compared to second stage. In the study, the highest phenol removal capacity and the lowest phenol concentration after adsorption was achieved at 70 min. and 60 min. for OP biochars and OP magnetic biochars, respectively (Figure 2). At the optimum contact times for OP biochars and OP magnetic biochars, adsorption capacity of phenol was found higher in the experiments conducting with OP magnetic biochars (max. q<sub>e</sub> for OP char: 5.1 mg g<sup>-1</sup>; max. q<sub>e</sub> for OP magnetic char: 7.06 mg g<sup>-1</sup>). Therefore, the optimum contact time was selected as 60 min. and the other experiments were conducted by using OP magnetic biochars.

### Effect of initial pH value of phenol solution

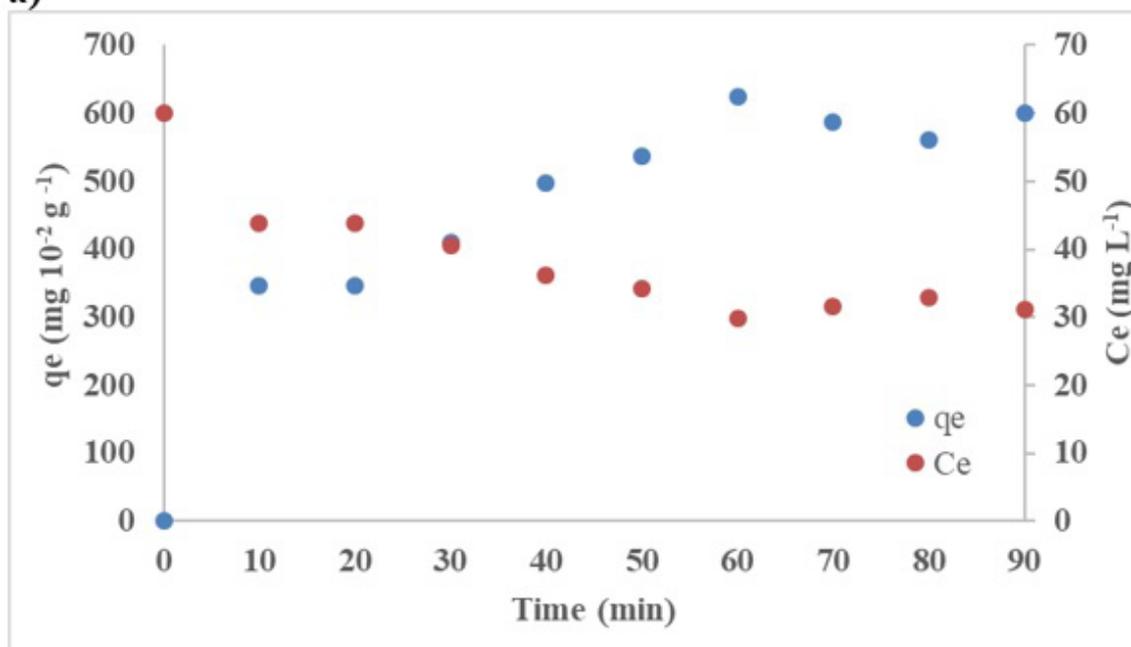
It is well known fact that pH has an important role during adsorption since surface charging of magnetic biochar was affected from initial pH values [4]. Moreover, phenol ionization degree depends on initial pH of solution [4, 25]. Adsorption capacity based on different pH values were illustrated (Figure 3). Phenol adsorption increased from pH 2.9 to 5.7; however, it diminished after 5.7 which is original pH of stock solution. The reason of decrement of phenol adsorption capacity at alkaline pH values can be connected to electrostatic repulsion between OP magnetic chars' negatively charged surface and C<sub>6</sub>H<sub>5</sub>O<sup>-</sup> ions. Furthermore, negative ions on OP magnetic biochar can repress phenol ions' dispersion and phenol adsorption [26, 27]. Therefore, original pH of the stock phenol solution was selected as optimum pH for adsorption experiments.

### Adsorption Isotherms

All three isotherms graphs were drawn for both 20°C and 40°C based on equations given in materials and methods section to calculate both isotherm constant and capacity values (Figure 4 and Table 1). Figure 4 (a), (b), (c) shows the Langmuir, Freundlich and Temkin curves at 20°C and Figure 4 (d), (e), (f) shows the Langmuir, Freundlich and Temkin curves at 40°C for phenol adsorption onto OP magnetic biochar, respectively. According to R<sup>2</sup> values of Langmuir model, the phenol adsorption with OP magnetic biochar was favorable at 20°C. Moreover, K<sub>L</sub> values increased with increment of the solution temperature from 20°C to 40°C; therefore, more adsorption of phenol onto OP magnetic biochar has been determined at higher temperature. Although this result can be attributed that the adsorption process is endothermic, K<sub>L</sub> values alone are not sufficient parameters to explain the relationship between adsorption and temperature [28]. Furthermore, all three isotherms R<sup>2</sup> values decreased with the increment of temperature (Table 1). As for Freundlich isotherm, while n value was found smaller than 1 at 20°C, it was higher than 1 at 40°C (Table 1). This result indicates that the adsorption is favorable over the entire ranges of concentration studies at 20°C, but the adsorption is favorable especially at high concentration for 40°C [29]. The value 1/n is a heterogeneity factor and more heterogeneous surface is obtained when 1/n value closes to the zero. Therefore, in this study, surface heterogeneity increased with increasing temperature since lower 1/n value was obtained at 40°C as compared to 20°C [30]. In Temkin isotherm, the constant of phenol adsorption, B, is directly related to the coverage of phenol onto OP magnetic biochar due to adsorbent-adsorbate interaction. It decreased from 2.89 to 1.10 with the increment of the temperature (Table 1). This can connect that the heat of adsorption of phenol onto OP magnetic biochar decreases with increasing temperature from 20°C to 40°C and the sorption is exothermic. Furthermore, the R<sup>2</sup> value of the Temkin isotherm was lower at 40°C as compared to 20°C.



a)



b)

Figure 2. Effect of contact time on phenol adsorption capacity and equilibrium concentration of a) Char b) OP magnetic biochars.

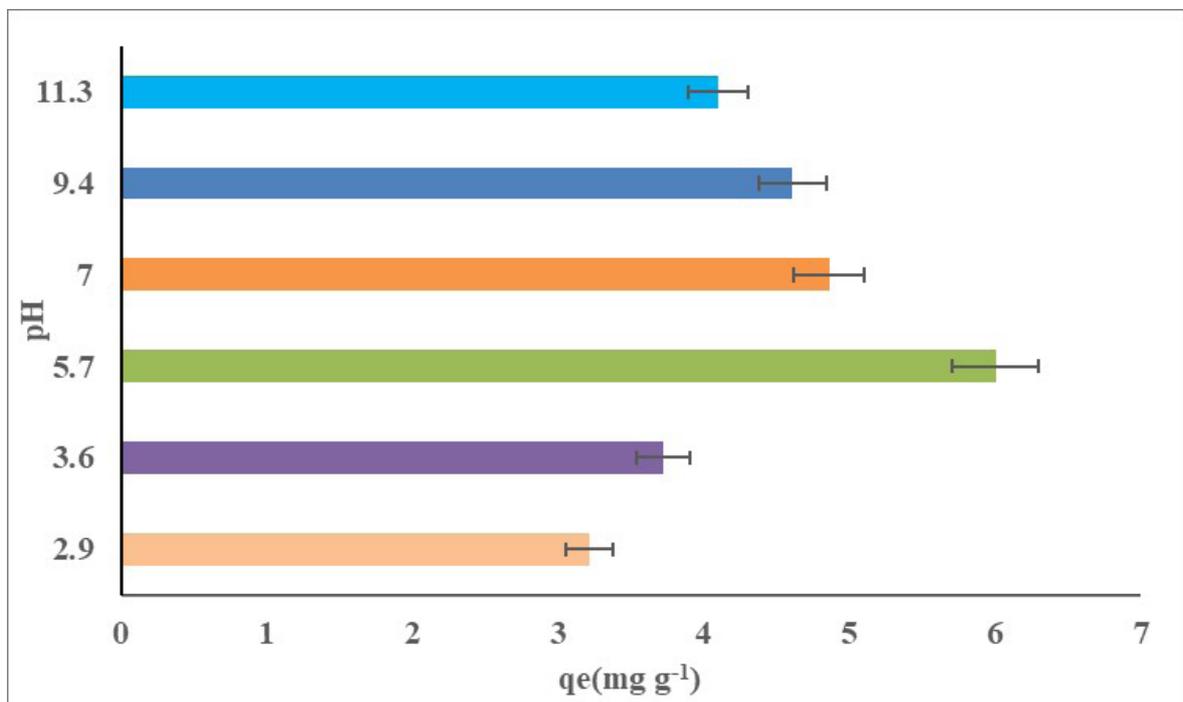
According to Table.1, when the correlation coefficients of the three isotherm models are compared at 20°C, the correlation coefficients in three isotherms are high (0.7093,0.9533 and 0.8573). According to these values, the adsorption data are found to be fit Freundlich model at 20°C. Furthermore, the correlation coefficients of the Freundlich and Temkin isotherms were close to each other. When the temperature was increased from 20°C to 40°C, correlation coefficients for three isotherm models decreased and found as 0.316, 0.5326 and 0.5376, respectively. Although the highest correlation coefficient at 40°C was found for Temkin isotherms, difference between correlation coefficient of Freundlich and Temkin isotherms was not too high (Table 1). Therefore, in this study, the most suitable isotherm model for adsorption of phenol onto OP magnetic biochar can be stated as Freundlich and adsorption process is exothermic. Therefore, lower temperature values are sufficient for phenol adsorption onto OP magnetic biochar since mostly physical forces, like Van der Waals forces, dominate the adsorption process [23]. Moreover, findings in the section of adsorption thermodynamics also supported that phenol adsorption on OP magnetic biochar is exothermic.

Adsorption isotherms were carried out by varying the initial concentration of the adsorbate from 20 to 100 mg L<sup>-1</sup>. Figure 5 (a) and (b), illustrates the equilibrium isotherms of adsorption phenol onto OP magnetic biochar, which describes the specific relationship between the adsorption capacity of adsorbent and the solution concentration of phenol at 20°C and 40°C.

Adsorption capacity, decreased with increase of the temperature. This phenomenon can be explained that the active binding sites were damaged and the binding forces between the phenol molecules and OP were weakened [31]. In this case, the tendency of the  $q_e - C_e$  graph drawn at 20°C is more favorable than 40°C, suggesting that the mechanism can be exothermic.

### Adsorption Kinetics

The study of adsorption kinetics study is important to understand the behavior of adsorbate adsorption on adsorbent, and to contribute to economical adsorption technology. Kinetic models are used to examine the rate of the adsorption process and potential rate-controlling step. In this study, the kinetic data obtained from batch studies have been analyzed by using pseudo-first order and pseudo-second order models.



**Figure 3.** Adsorption capacity of OP magnetic biochar with respect to different initial pH values.

The pseudo-first order equation of Lagergren is expressed as follows [32]:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (\text{Equation 5})$$

where  $q$ : amounts of phenol adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min),

$k_1$ : the rate constant of pseudo-first-order sorption ( $\text{min}^{-1}$ ).

The pseudo-second-order kinetic rate equation is expressed as follows [33]

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (\text{Equation 6})$$

where  $k_2$ : rate constant of pseudo-second order sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

The graphs of linearized form of the pseudo first and second order equations were shown in Figure 6 (a-b). Moreover, rate constants and phenol adsorption capacities for both adsorption kinetics were given at Table 2. Results showed that the pseudo-second order equation provided better correlation for the adsorption data since  $R^2$  value were higher at this kinetic. Moreover, obtained results in this study also matched with other studies about phenol adsorption in the literature [2-6]. Kinetic data followed closely to the pseudo-second-order model for phenol adsorption with both water hyacinth ash and biochar prepared from the pine fruit shells [3,6]. Accordingly, the  $q_e$  values were calculated based on equation in Figure 6 and they found as 4.58 and  $7.06 \text{ mg g}^{-1}$  for pseudo first and second order kinetic models, respectively.

### Adsorption Thermodynamics

Thermodynamic parameters such as standard Gibbs free energy change ( $\Delta G^0$ ), standard enthalpy change ( $\Delta H^0$ ) and standard entropy change ( $\Delta S^0$ ) were calculated by using the following equations:

$$\ln K_d^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (\text{Equation 7})$$

where  $K_d$ : equilibrium constant

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (\text{Equation 8})$$

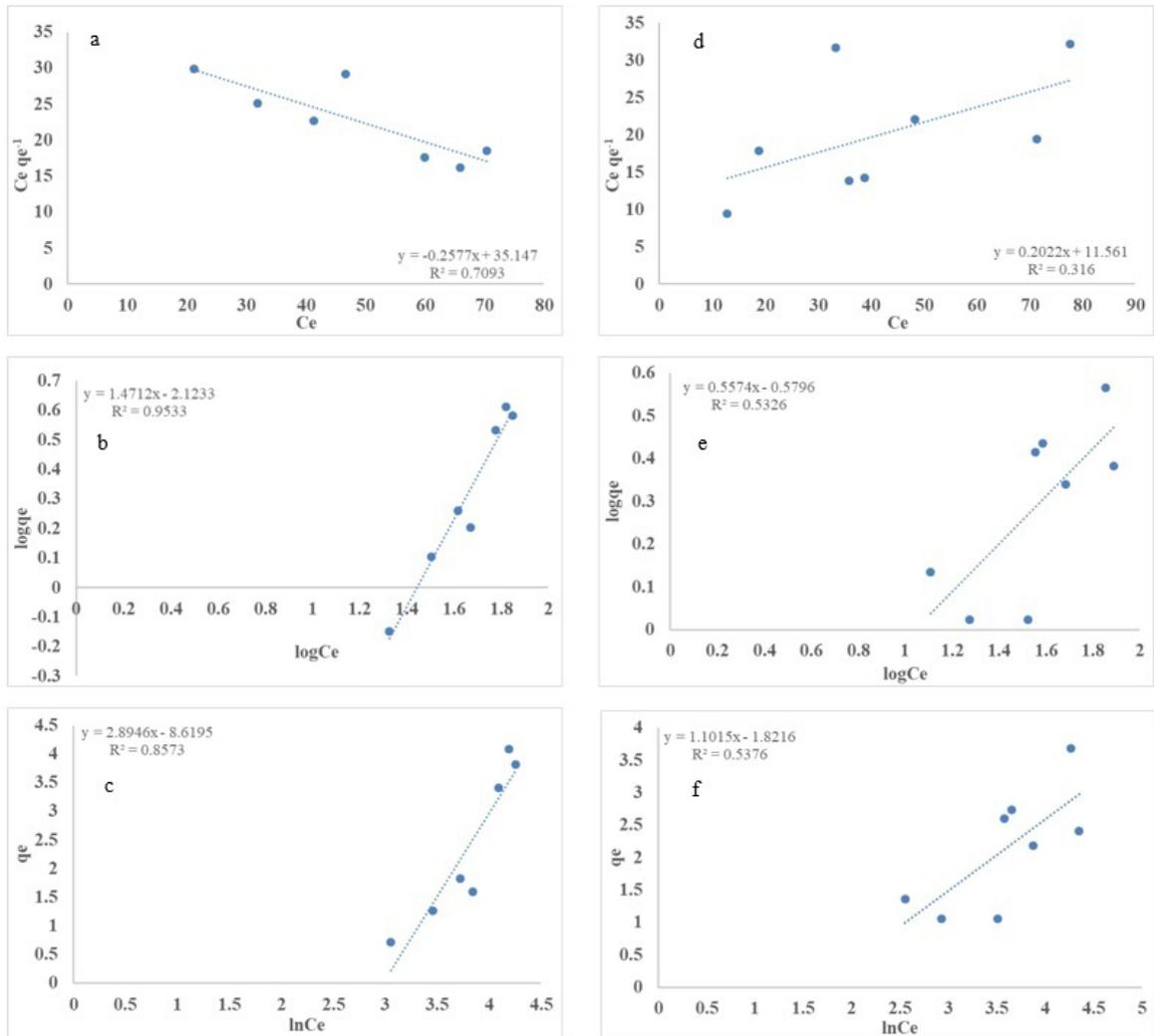
$\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  were calculated from a plot of  $\ln(K_d)$  versus  $1/T$ . The thermodynamic parameters of the phenol adsorption onto OP magnetic biochar are given in Table 3.  $\Delta G^0$  value for both temperatures were found as negative that confirms feasible and spontaneous phenol adsorption onto OP magnetic biochar [34]. Mostly,  $\Delta G^0$  values for physi-sorption is between -20 and 0 kJ/mol and chemisorption is between -80 and -400 kJ/mol [34]. In this work,  $\Delta G^0$  was -47.9 and -48.3 kJ/mol that indicated that phenol adsorption with OP magnetic biochar is mainly dominated with physical adsorption. Addition to  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  are one another critical thermodynamic parameters which give information about adsorption process. In this study, negative  $\Delta H^0$  value was obtained, which demonstrated the exothermic nature of the adsorption process [27]. As for  $\Delta S^0$ , positive value was found, so it can be explained by increment in randomness at the solid-liquid interface during the adsorption process [27].

**Table 1.** Isotherms parameters for adsorption of phenol onto OP magnetic biochar at 20°C and 40°C.

	Langmuir isotherm parameters			Freundlich isotherm parameters			Temkin isotherm parameters		
	$q_0$ ( $\text{mg g}^{-1}$ )	$K_L$ ( $\text{L mg}^{-1}$ )	$R^2$	$n$	$K_f$	$R^2$	$B$	$A$ ( $\text{L g}^{-1}$ )	$R^2$
20°C	3.88	0.0073	0.7093	0.68	0.0075	0.9533	2.89	0.05	0.8573
40°C	4.94	0.017	0.316	1.79	0.26	0.5326	1.10	0.18	0.5376

**Table 2.** Kinetic parameters for adsorption of phenol onto OP magnetic biochar at initial phenol concentration.

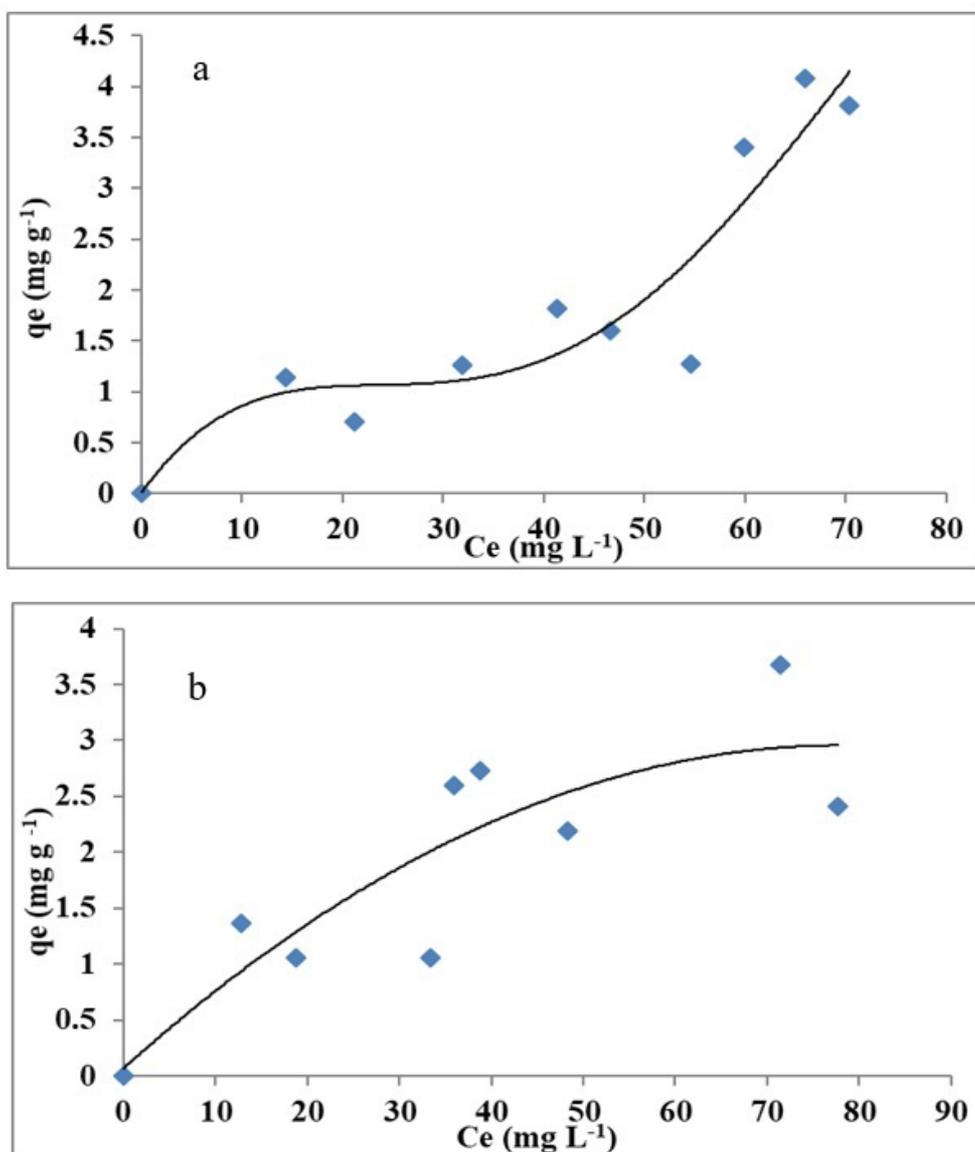
Pseudo-first order kinetic model			
$C_0$ ( $\text{mg L}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$r_1^2$
60	4.58	0.0297	0.9053
Pseudo-second order kinetic model			
$C_0$ ( $\text{mg L}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$r_2^2$
60	7.06	0.0086	0.9701

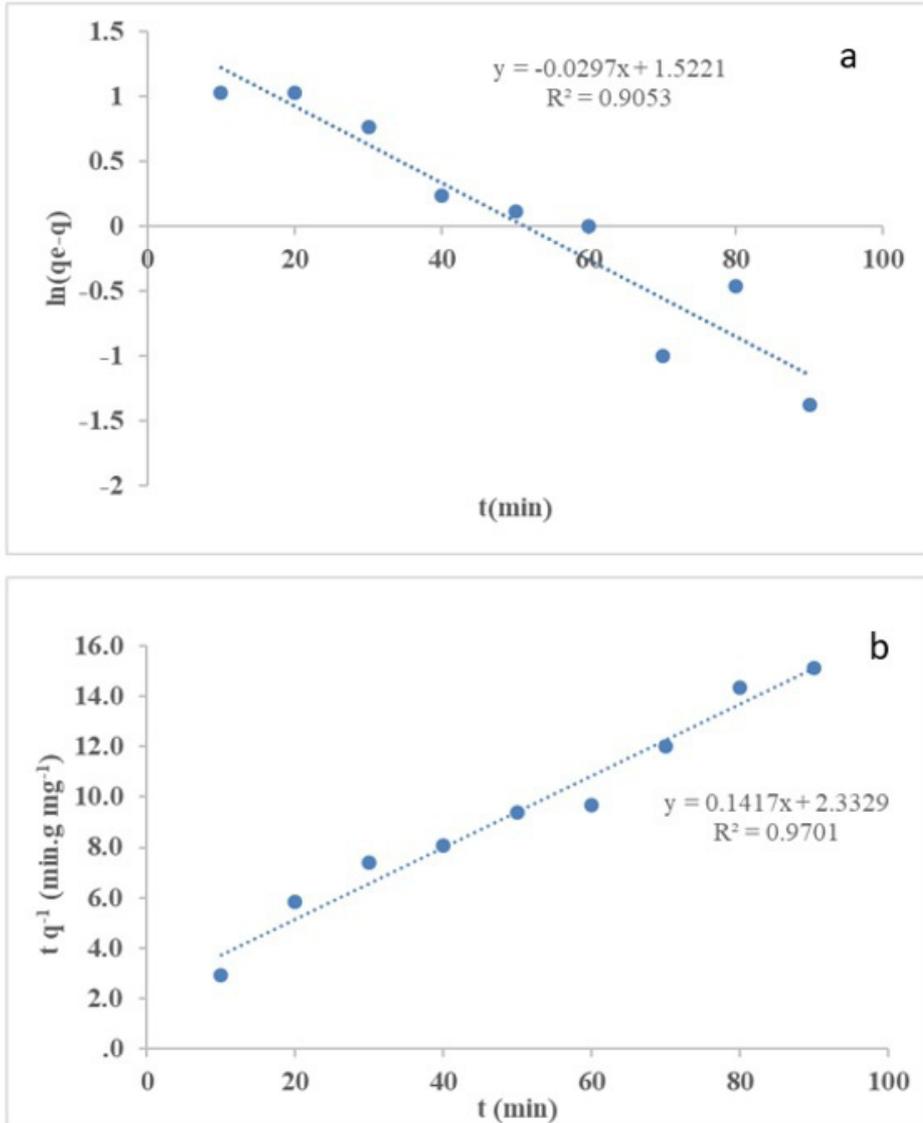


**Figure 4.** Langmuir isotherm (a), Freundlich isotherm (b) and Temkin isotherm (c) models at 20°C and Langmuir isotherm (d), Freundlich isotherm (e) and Temkin isotherm (f) models at 40°C for adsorption of the phenol onto OP magnetic biochar.

**Table 3.** Thermodynamic parameters of adsorption of phenol onto OP magnetic biochar.

Temperature (°C)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol)	$\Delta H^\circ$
20	-47.9	66.08	-27.6
40	-48.3		

**Figure 5.** Equilibrium isotherms for phenol adsorption onto OP magnetic biochar at 20°C (a) and 40°C (b).



**Figure 6.** Pseudo-first order (a) and pseudo-second order (b) kinetics for the adsorption of phenol onto OP biochar.

Adsorbent regeneration by desorption of phenol compounds from adsorbate can be achieved with several techniques, such as thermal regeneration, chemical regeneration, ultrasound and bioregeneration [35]. Among these techniques, chemical regeneration is much preferred by researchers in the studies about phenol desorption from pyrolysis chars [35-37]. Cancino et al. [36] conducted desorption experiments with water, ethanol and sodium hydroxide solutions and results showed that the highest recovery efficiency (10%) belongs to ethanol solutions. In another study conducted by Liu et al [37], results showed that adsorbate can be used to adsorb phenolic compounds at least three cycles after desorption with sodium hydroxide. Similarly, Ozkaya [35] indicated that phenol can be recovered with sodium hydroxide and first-order kinetic model is more suitable as compared to diffusion model in the desorption study of phenolic compounds with sodium hydroxide. Therefore, it is recommended usage of chemical regeneration techniques for phenol desorption from OP magnetic biochars for the future studies.

### Conclusion

The adsorption of phenol using OP magnetic biochar was investigated. The adsorption of phenol was found to be dependent on the pH solution, initial phenol concentration, contact time and temperature. The equilibrium adsorption data were best represented by the Freundlich isotherm, indicating adsorption on a heterogeneous surface and the adsorption capacity was found to be 7.06 mg g<sup>-1</sup> at 20°C. The results of the Freundlich isotherm model suggested that the adsorption process was dominated by physisorption mechanisms. The adsorption kinetic was described well by the pseudo-second-order model. The negative  $\Delta H^\circ$  and  $\Delta G^\circ$  values demonstrated that the adsorption was exothermic, feasible and more spontaneous at lower temperatures. Moreover, adsorption capacity of phenol with OP magnetic biochar was found as comparable with the literature. To conclude, OP magnetic biochar can be stated among the effective alternatives for phenol adsorption since it provides ready separation and easy recycling from solution by low cost.

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