Study the Adsorption Phenomena of Phenol from Industrial Wastewater using Commercial Powdered Activated Carbon by using Isotherm Models

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Abstract

Adsorption studies for phenol removal from aqueous solution onto commercial Powdered Activated Carbon were carried out. Batch kinetics and isotherm studies were carried out under varying conditions of contact time, initial phenol concentration, adsorbent dose and pH. The adsorption of phenol increases with increasing initial phenol concentration and decreases with increasing the solution pH value. The equilibrium data in aqueous solutions was well represented by the *Langmuir* and *Freundlich* isotherm models. Kinetics of adsorption followed a first order rate equation. The studies showed that the Commercial Powdered Activated Carbon can be used as an efficient adsorbent material for the removal of phenolics from water and industrial wastewater.

Keywords: Powdered Activated carbon, Adsorption, Phenol, Isotherm, Aqueous system.

دراسة ظاهرة إمتزاز الفينول من المياه الصناعية باستخدام مسحوق الكاربون المنشط التجاري بواسطة موديلات متساوي درجات الحرارة

الخلاصة

دراسات الأمتزاز لإزالة الفينول من المحاليل المائية بواسطة مسحوق الكاربون المنشط التجاري قد تم دراستها في هذا البحث، دراسات الحركيات الكيميائية (*Batch kinetics*) ومتساوي درجات الحرارة (*isotherm*) قد تم إنجازها تحت ظروف مختلفة من زمن الاتصال (*contact time*) وتركيز الفينول البدائي والجرعة الممتزة (*adsorbent dose*) والأس الهيدروجيني (*pH value*). إمتزاز الفينول يزداد مع زيادة تركيز الفينول البدائي ويقل مع زيادة قيمة الأس الهيدروجيني للمحلول. بيانات الاتزان للمحاليل المائية قد تم تمثيلها بصورة جيدة بواسطة موديلات متساوي درجات الحرارة (*isotherm*) للانكمير (*Langmuir*) وفرينـدليش (*Freundlich*). حركيات الإمتزاز تتبع معادلة الحالة من المرتبة الأولى. الدراسة أوضحت بأن مسحوق الكاربون المنشط التجاري يمكن ان يستخدم كمادة ممتزة فعالة لإزالة الفينول من الماء و المياه الصناعية.

Nomenclature

Abbreviations		Symbols	
CPAC	Commercial Powdered Activated Carbon	b	*Langmuir* constant (l/mg)
		C_e	Equilibrium concentration of the adsorbate (mg l^{1})
PAC	Powdered Activated Carbon	k	*Freundlich* constant (mg/g)
EPA	Environmental Protection Agency	K_a	Ionic constant of the weak acid

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1/*n*   *Freundlich* constant (l/mg)
$Q^°$ *Langmuir* constant (mg/g)
q_e Amount adsorbed at equilibrium (mg/g)

Greek Litters

j_{ions} Ionic fraction of phenolate ion

Subscript

e   Equilibrium

Introduction

Many industrial wastes contain organics which are difficult, or impossible, to remove by conventional biological treatment processes [1]. Phenols as a class of organics are similar in structure to the more common herbicides and insecticides in that they are resistant to biodegradation. Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications [2]. In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste [3-6]. Phenolics constitute the 11th of the 126 chemicals which have been designated as priority pollutants by the United States Environmental Protection Agency [1]. Stringent US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg l^{-1} [7]. Activated carbon is an effective adsorbent primarily due to its extensive porosity and very large available surface area. There are many methods such as oxidation, precipitation, ion exchange and solvent extraction to remove phenolic materials from aqueous solution. However, in water treatment the most widely used method is adsorption onto the surface of activated carbon [8]. Activated carbons are widely used as an adsorbent for the removal of a wide range of pollutants from various hosting matrices and not those incorporated in the crystal lattice because of their high adsorption capacity, fast adsorption kinetics and ease of regeneration. Several researchers have been reported the adsorption theory and applications of the solid phase extraction to remove phenol from wastewater. Activated carbons are complex and heterogeneous material made of wood, coconut shells, coal, etc with unique adsorptive characteristics mainly influenced by the porous structure, surface area and chemical structure of the surface [9, 10].

Powdered Activated Carbon (PAC) is one type of activated carbon with effective diameter less than 50 µm. Its apparent density ranges from 0.36 to 0.74 g/cc, and is dependent on the type of materials and the manufacturing process. The primary advantages of using PAC are the low capital investment costs and the ability to change the PAC dose as the water quality changes. The latter advantage is especially important for systems that do not require an adsorbent for much of the year [11].

The objective of the present study is to describe the potential of Commercial Powdered Activated Carbon (CPAC) to adsorb phenolic pollutants using phenol as a model component. Batch kinetics and isotherm studies were conducted to evaluate the adsorption capacity of CPAC. The influences of various factors, such as initial pH, and initial pollutant concentrations on the adsorption capacity were also studied.

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Methods

Several models have been published in the literature to describe experimental data of adsorption isotherms. The *Langmuir* and *Freundlich* isotherm models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions at different pH values [12].

In 1918 *Langmuir* used a simple model of the solid surface to derive an equation for an isotherm. He assumed that the solid has a uniform surface, that adsorbed molecules don't interact with one another, that the adsorbed molecules are localized at specific sits, and that only a monolayer can be adsorbed [10].

Langmuir assumed that the surfaces of most solids are not uniform, and the desorption rate depends on the location of the adsorbed molecule. The force between adjacent adsorbed molecules is often substantial. There is much evidence that adsorbed molecules can move about on the surface. This mobility is much greater for physically adsorbed molecules than for chemisorbed once and increases as T increases [10].

The linear form of the *Langmuir* isotherm model can be represented by the following relation [2]:

$$\frac{1}{q_e} = \frac{1}{Q^o} + \frac{1}{bQ^o}\frac{1}{C_e} \qquad .....(1)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg l^{-1}), and Q° (mg/g) and b (l/mg) are the *Langmuir* constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$ [2].

The *Freundlich* isotherm can be derived by modifying the *Langmuir* assumption to allow for several kind of adsorption sites on the solid, each kind having a different heat of adsorption. The *Freundlich* isotherm is often applied to adsorption of solutes from liquid solutions onto solids.

The linear form of the *Freundlich* isotherm model is given by the following equation [2]:

$$\ln q_e = \ln k + \frac{1}{n}\ln C_e \qquad .....(2)$$

Where k (mg/g) and $1/n$ (l/mg) are *Freundlich* constants related to adsorption capacity and adsorption intensity, respectively, of the adsorbent. The values of k and $1/n$ can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$ [2].

Experimental Work
Materials

The chemicals used as supplied from local markets. The characteristics of the activated carbon and phenol are presented in Table (1) and (2) with their purities, physical properties such as density were measured experimentally and compared with values in the literature [1, 2].

Procedure

The CPAC used in this study was purchased from local market. The CPAC was used in the batch experiments. Prior to use, the carbons were washed several times with deionised water. Afterward they were dried in an oven at 110 °C for 24 h and stored in a desiccator until used.

Batch adsorption experiments were carried out by allowing an accurately weighted amount of CPAC

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to reach equilibrium with phenol solutions of known concentrations (based on earlier studies and our pretest results). Initial concentrations of phenol were held between 100 and 500 mg l^{-1}. The pH was adjusted using dilute HCl or NaOH solutions. Known weights of CPAC (0.3 mg) were added to glass backer bottles each containing 100 ml solution. The backers were agitated on a shaker at an 80 rpm constant shaking rate at 25℃ for 24 h to ensure equilibrium was reached. At the end of the equilibrium period the contents of the backers were filtered, centrifuged for 10 min at 5000 rpm using a 4124 Bestell centrifuge (Haraeus-Christ, Germany) and the supernatant was subsequently analyzed for residual concentration of phenol. The concentration of phenol was determined with photometric method [12]. At the end, after the preparation of samples according to the standard methods, the residual phenol concentrations were measured using spectrophotometer equipment (spectrophotometer DR-2000, HACK). The absorbance of the colored complex of phenol with 4-aminoantipyrine was read at 500 nm [12]. Finally the suitability of the *Freundlich* and *Langmuir* adsorption model to equilibrium data were investigated for phenol - adsorbent system in three different pH. All experiments were run in duplicates to ensure reproducibility.

Results and Discussion

Effect of pH

The adsorption of phenol by CPAC was studied at various pH values. Different initial concentrations of phenol were prepared based on the researches concerning the phenol concentration in industrial effluents [13] in the range of 100-500 mg l^{-1} and adjusted

to different pH values of 5, 7, and 11. CPAC was added to make its concentration 30 mg l^{-1} and adsorption was carried out until equilibrium. The results are displayed in fig.(1).

As was expected, the adsorbed amount decreases with increasing the pH value (Fig.(1)). This can be attributed to the dependency of phenol ionization on the pH value. The ionic fraction of phenolate ion (j_{ions}) can be calculated from [2]:

$$j_{ions} = \frac{1}{\left[1 + 10^{\left(pk_a - pH\right)}\right]} \quad \text{.....(3)}$$

Obviously, j_{ions} increases as the pH value increased. Accordingly, phenol, which is a weak acid (pK_a=10), will be adsorbed to a lesser extent at higher pH values due to the repulsive forces prevailing at higher pH values. Similar behavior has been reported by Halhouli et al. [8] for the adsorption of phenol by activated carbon [2]. In the higher range phenol forms salts which readily ionize leading negative charge on the phenolic group. At the same time the presence of OH ions on the adsorbent prevents the uptake of phenolate ions [1,3].

Effect of Initial Phenol Concentration

Fig.(2) shows the effect of contact time on the removal of phenol by CPAC. The results show that the equilibrium time required for the adsorption of phenol on CPAC is 6 h. It is also seen that the remaining concentration of phenol becomes asymptotic to the time axis after 6 h of shaking. However, for subsequent experiments, the samples were left for 24 h to ensure equilibrium. These results also indicate that the adsorption process can be considered very fast because of the largest amount of phenol attached to the adsorbent within the first 3 h of

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adsorption. The equilibrium time was independent of initial concentration of phenol. The phenol removal versus time curves is single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of phenol on the surface of the adsorbents [2].

As has been shown previously (fig.(2)) the adsorption of phenol onto CPAC increases as the initial phenol concentration increased. Adsorption equilibrium was reached within 6 h for phenolic concentrations 100-500 mg l^{-1}. This is also inconsistent with the results of fig.(3).

Increasing the initial phenol concentration would increase the mass transfer driving force and therefore the rate at which phenol molecules pass from the bulk solution to the particle surface. Hence a higher initial concentration of phenol enhances the adsorption process. This would results in higher adsorption [2]. On a relative basis, however, the percentage adsorption of phenol decreases (fig.(1)) as the initial phenol concentration increases. Similar results reported by other researcher [2].

Effect of CPAC Dose

Fig.(4) shows the removal of phenol as a function of carbon dosage by CPAC at the solution pH of 7. Carbon dosage was varied from 10 to 150 mg l^{-1}. It is evident that for the quantitative removal of 400 mg l^{1} of phenol in 100 ml, a minimum carbon dosage of 150 mg l^{-1} CPAC is required for 97% removal of phenol. The data clearly shows that the CPAC is effective for the removal of phenol. The results also clearly indicate that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible [1].

Adsorption Isotherms

The three equilibrium curves that were obtained at the three pH values in this study are well represented by the *Freundlich* and *Langmuir* isotherm models (fig.(5) and fig.(6)). When the *Langmuir* and *Freundlich* isotherm model were applied to these data, a very good fit was obtained at all pH values (fig.(6) and fig.(5)).

The *Langmuir* constants $Q^{°}$ and *b* and *Freundlich* constants *k* and $1/n$ at various pH values are displayed in Table (3). It is obvious that the parameters $Q^{°}$ (6.41 at pH of 5 to 4.7 at pH of 11) and *k* (0.27 at pH of 5 to 0.135 at pH of 11), which are related to the adsorption capacity, increase with a decrease in the pH values [2-4]. This is consistent with the experimental observation. R^{2} values, which are a measure of goodness-of-fit (Table (3)), show that both the *Langmuir* and *Freundlich* isotherm models can adequately describe the adsorption data.

Conclusions

In this study, the ability of commercial Powdered Activated Carbon to adsorb phenol from aqueous solution was investigated as a function of pH and initial phenol concentration. CPAC adsorption capability was strongly dependent on the pH of the solution. The adsorption capacity was increased with a decrease in the pH and an increase in the initial phenol concentration. The adsorption of phenol was increased with increasing contact time and became almost constant after 6 h. The adsorption phenomenon of phenol to CPAC was expressed by the *Langmuir* and *Freundlich* adsorption models. Consequently, the experimental data showed that both the *Langmuir* and *Freundlich* isotherm models can

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adequately describe the adsorption data.

It can be concluded that CPAC can be used for removal of phenol and other harmful compounds in effluents.

Acknowledgment

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Table (1) Properties of the Commercial Powdered Activated Carbon

Property	unit	value
Density	g/cm^3	0.495
Ash	wt%	4
Moisture	wt%	2.8
Solubility in water	wt%	0.37
Solubility in acid	wt%	1.2
Solubility in methanol	wt%	0.26
Volatile matter	wt%	7.1
Surface area	m^2/g	540
Iodine number	mg/g	500
Nominal size	mm	38-75
pH	-	8.1

Table (2) Physical properties of Phenol.

Component	M.wt.	Density		Refractive index		Boiling point ^{o}C	Purity %	Supplier
		Exp.	Lit.	Exp.	Lit.			
Phenol	94.113	1.588	1.587	1.5423	1.5395	181.8	99.5	Merck

Table (3) Parameters of *Freundlich* and *Langmuir* isotherm models

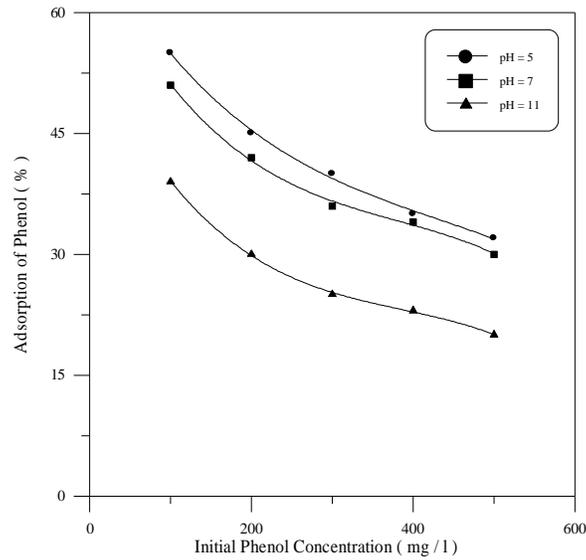| pH	*Freundlich* constants		R^2	*Langmuir* constants		R^2
	k	1/n		Q^o	b	
5	0.27	0.51	0.998	6.41	0.009	0.993
7	0.21	0.53	0.993	6.39	0.007	0.997
11	0.14	0.54	0.989	4.7	0.006	0.992

Figure (1) Relationship between initial phenol concentration and its percent adsorption for various pH values.
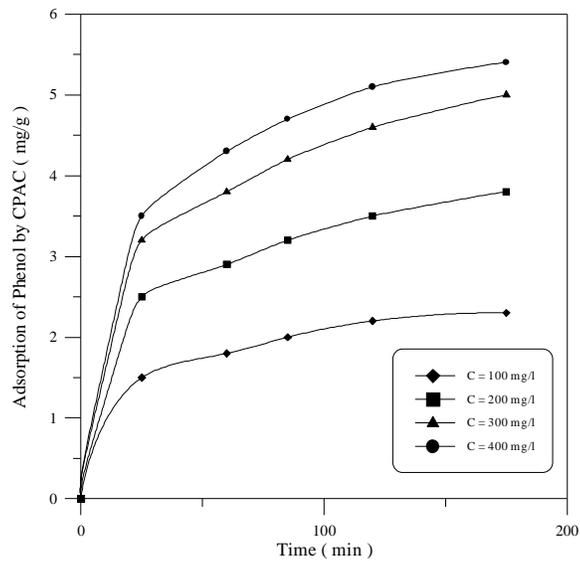

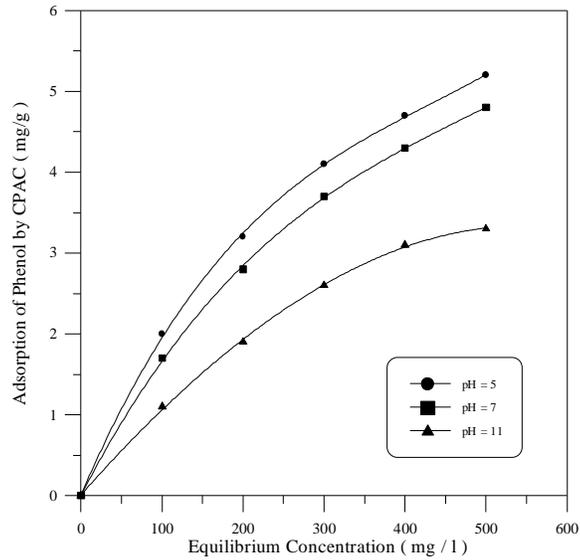**Figure (2) Effect of contact time for the removal of phenol by CPAC in various phenol concentrations.**

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**Figure (3) Relationship between equilibrium phenol concentration
and its adsorption for various pH values.**

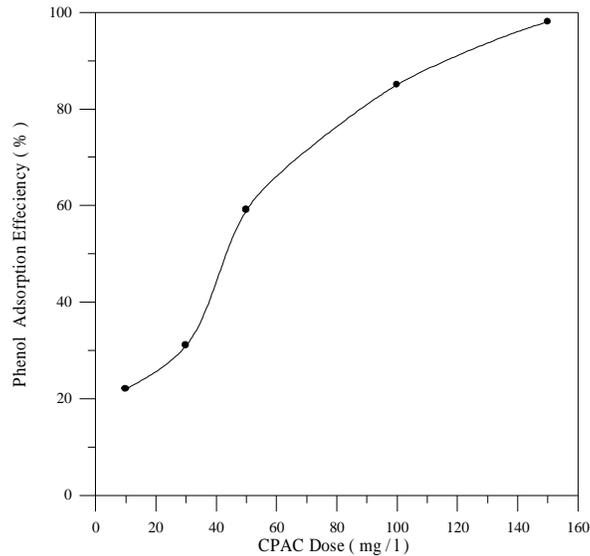**Figure (4) Effect of carbon dosage on the removal of phenol
by CPAC.**

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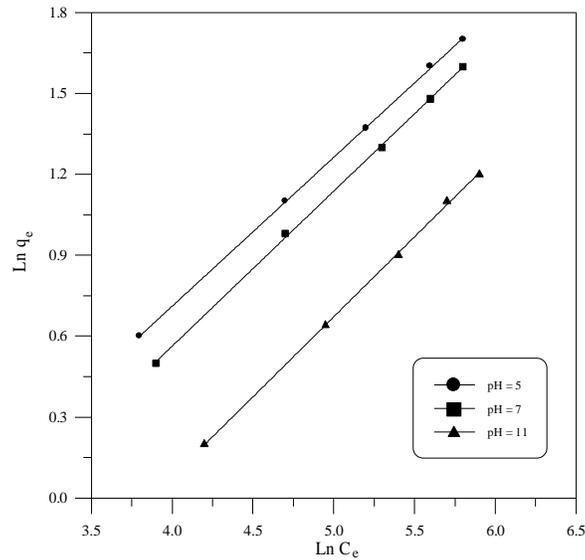by using Isotherm Models**

**Figure (5) Freundlich adsorption isotherm for phenol with
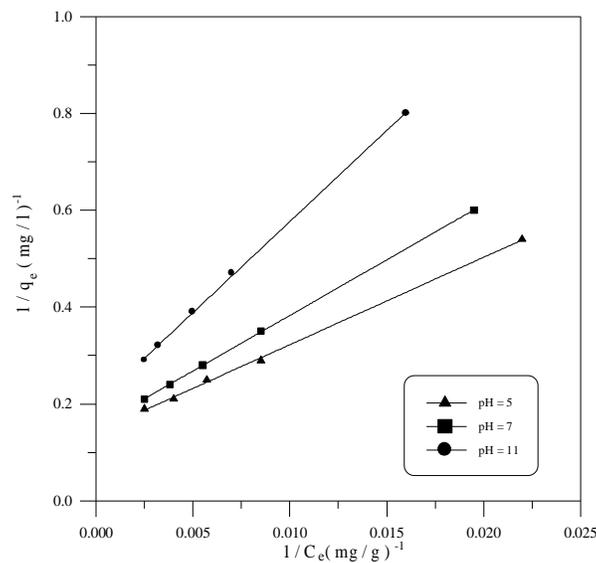CPAC at various pH values.**

**Figure (6) Langmuir adsorption isotherm for phenol with
CPAC at various pH values.**

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