Available online at http://ijcpe.uobaghdad.edu.iq and www.iasj.net
Iraqi Journal of Chemical and Petroleum Engineering
Vol.20 No.1 (March 2019) 23 – 29
EISSN: 2618-0707, PISSN: 1997-4884

Adsorption of Phenol from Aqueous Solution using Paper Waste

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Abstract

The exploitation of obsolete recyclable resources including paper waste has the advantages of saving resources and environment protection. This study has been conducted to study utilizing paper waste to adsorb phenol which is one of the harmful organic compound byproducts deposited in the environment. The influence of different agitation methods, pH of the solution (3-11), initial phenol concentration (30-120ppm), adsorbent dose (0.5-2.5 g) and contact time (30-150 min) were studied. The highest phenol removal efficiency obtained was 86% with an adsorption capacity of 5.1 mg /g at optimization conditions (pH of 9, initial phenol concentration of 30 mg/L, an adsorbent dose of 2 g and contact time of 120min and at room temperature). The well-known Langmuir and Freundlich adsorption models were studied. The results show that the equilibrium data fitted to the Freundlich model with R^2=0.9897 within the concentration range studied. The main objective of this study is finding the best mixing and conditions for phenol removal by adsorption via paper waste.

Keywords: adsorption, isotherm model, phenol, untreated waste office paper, ultrasonic wave device

Received on 28/11/2018, Accepted on 20/01/2018, published on 30/03/2019

https://doi.org/10.31699/IJCPE.2019.1.4

1- Introduction

Phenol is critical poisons existing in wastewater as aromatic semi-volatile hydrocarbons. Several industries such as rubber, textile, pharmaceutical, pulp and paper, pharmaceutical industries, plastics, coke manufacturing, ferrous industries and petroleum refineries may discharge a significant amount of phenol [1]. Phenol is easily absorbed into the body through skin, stomach, and lungs. Further, phenol can cause conflict with the brain control of regular breathing patterns [2]. Thus, it is considered as hazardous pollutant since it causes adverse effects on health and the environment.

According to the United States Environmental Protection Agency (USEPA), the acceptable concentration of phenol in surface water should be less than 1.0 mg/L and in drinking water should not exceed 0.002mg/l [3]. In addition, the presence of phenol into drinking water sterilized by chlorine compounds results in the establishment of phenol compounds leading to serious problems to health and environment. Phenol gives undesirable taste and odor to drinking water. Thus, wastewater containing phenol must be treated to prevent health and environmental risks [4].

Phenol removal from wastewater has been carried out by various methods such as chemical oxidation [5] membrane filtration [6], biodegradation [7], electrocoagulation [8], photodegradation [9], solvent extraction [10] and adsorption [11]. Adsorption is an effective method among these technologies.

It is considered as a suitable technique for phenol removal from wastewater because of its insensitivity to poisonous and toxic wastes. In addition, adsorption has the merits of flexibility, the simplicity of design, ease of operation [12].

Recently, researchers have been focusing on using of natural adsorbents instead of conventional adsorbents [13]. Likewise, they have used effective and low-cost adsorbents from different raw materials derived from waste stuff to remove phenol such as Miswak's Root [14], sawdust [15], coal fly ash [16], forest waste [10], lignitic coals [17], banana peels [2] and rice straw [18[. A considerable amount of paper waste is daily produced and used for different purposes. And it is burned to create heat and the only amount of it is recycled for paper industries. The sorption ability of cellulosic material makes the waste paper a possible green to be used as a low-cost adsorbent for phenol removal. Recently, using ultrasonication for extraction and refining processes has gained great attention. However, more information is required about the removal of organic pollutants from wastewater by adsorption coupled with ultrasonication method [19].

Adsorption isotherm models have been applied to explain adsorption data such as Langmuir and Freundlich model. The Langmuir isotherm assumes that adsorption on a surface is limited to a single molecular layer with a finite number of identical sites. All site can take in only one adsorbate molecule [20]. The Langmuir isotherm equation is considered the first theoretically developed isotherm model and it keeps an essential location in physisorption and chemisorption theories[21].

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The Freundlich isotherm explains that the adsorption occurs on heterogeneous sites with non-uniform distribution of energy level, and it proposes reversible adsorption and possible adsorption on multilayers [22].

2- Materials and Experimental Work

2.1. Phenol

Phenol is a crystalline and colorless to light pink material (phenol changes pink on exposure to light and air). Phenol used in this study has been supplied by Loba Chemie Pvt. Ltd. (Laboratory reagents & fine chemicals).

The chemical and physical properties of phenol are shown in Table **1**.

Table 1. Characteristics of phenol

Chemical formula	C_6H_5OH
Molecular weight	94.11 g/mol
Solubility (5% in water)	clear, colorless solution
Appearance	white crystals or crystalline flakes
Stabilizer	max 0.15%
Normal boiling point	181.84 °C

2.2. Adsorbent

Paper waste (A4) was collected from a local office. According to the label on the package, the paper characterized as flat, smooth, multi-purpose paper, elemental chlorine free fiber, acid-free and moisture retention capacity. It was cut into small pieces (4*2 mm) by suitable paper shredder and then kept in dry place.

3- Phenol Adsorption Study

The adsorption capacity of the adsorbent was studied on a laboratory scale liquid phase batch. The experiments were conducted at a fixed amount (1gm) of waste paper which was positioned into 125-mL flasks containing 20 mL phenol solution.

The initial concentrations of phenol solution at rang from30 to 90 mg/L were prepared. The pH of phenol solutions during the interaction with the adsorbent was found to be ranging of (3–11). Three different devices were used to agitate the solution which are the laboratory shaker, the mechanical agitator, the magnetic stirrer and ultrasonication device with an agitating speed of 250 rpm and for 15 0 min to meet the environmentally relevant conditions.

The experiments were done at a temperature of 25°C. At the end of mixing time, the samples were withdrawn, filtered by filter papers to remove the suspended adsorbent and analyzed using UV- Visible spectrophotometer (UV-160 A Shimadzu). Phenol adsorbed by paper waste was found by calculating the difference between the initial concentration (C_o) and the equilibrium concentration (C_e).

The effect of pH, phenol concentration, adsorbent dose and contact time on the phenol adsorption was studied.

$$q_e = (C_o - C_e)*V/m \quad (1)$$

$$R\% = [(C_o-C_e)/C_e]*100 \quad (2)$$

Where q_e is the adsorption capacity, C_o represent the initial concentrations of phenol and C_e equilibrium concentrations of phenol (mg/L), respectively; V represents the volume of the phenol solution (mL) and m is the mass of adsorbent (g)

Computer interfaced UV-Visible spectrophotometer (GBC Cintra 6 series V-3656) was used for samples analysis at an absorbance value of 270 nm. Treated water samples of 2 mL were placed in a quartz cell and analyzed to measure phenol concentration. Phenol concentration was estimated using the phenol concentration-calibration curve shown in Fig. **1**. The calibration curve was prepared using different known phenol concentrations. A straight line with a slop of 0.0139 was obtained to determine unknown phenol concentration remaining in the solution. Then, the percentage removal of phenol was calculated by Eq. (2).

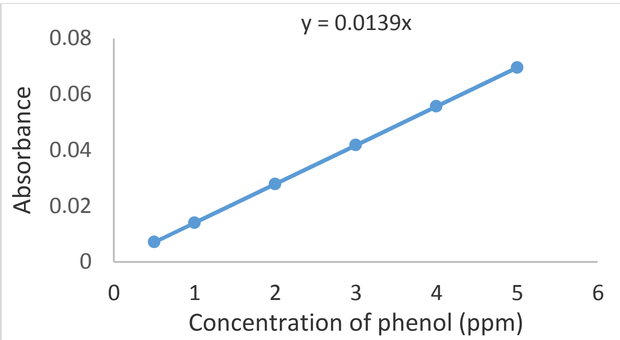

Fig. 1. Calibration curve of phenol adsorption

3.1. Effect of Mixing Techniques

To study the effect of mixing methods on the adsorption of phenol, the Erlenmeyer flasks containing the adsorbent and adsorbate solution were agitated at 200 rpm for 200 min at room temperature.

The adsorption experiments were carried out using 30 ml of 30 ppm phenol solution containing 1 g of paper waste and a pH of 8.

3.2. Effect of pH on phenol Adsorption

The pH of the solution is one of the most important parameters and it plays a major role in the adsorption process. The experiment was carried out in the pH range of 3-11 adjusted by 0.3N HCl and 0.3N NaOH. The adsorption experiments were executed using 30 ml of 30 ppm phenol solution containing 1 g of paper waste. The solutions were agitated for 150 min at 250 rpm at room temperature.

3.3. Effect of Phenol Concentration

The effect of initial phenol concentration on the equilibrium uptake was studied by differing the initial phenol concentration in the range of 30-90 ppm.

The adsorption experiments were carried out using 30 ml of phenol solution containing 1 g of paper waste and solution pH 9. The solutions were agitated for 150 min at 250 rpm at room temperature.

3.4. Effect of Adsorbent Dose

To investigate the effect of adsorbent dose, different amounts of adsorbent (0.5-2,5 g) were used. The adsorption experiments were achieved using 30 ml of 30 ppm phenol solution and solution pH 9. The solutions were agitated for 150 min at 250 rpm at room temperature. In this study and adsorption capacity was determined using Eq.(1).

3.5. Effect of Contact Time on Dye Adsorption

The effect of contact time on the phenol removal was conducted on phenol solution with an initial concentration of 30 ppm. The flasks were filled with 30 ml of the aqueous solutions of pH 9 were shaken for a contact time ranging of (30-150) min at pH 9. The best values of solution pH and a dose of waste paper were used for this study.

3.6. Adsorption Isotherm

The adsorption isotherm is a commonly used method for representing the equilibrium states of an adsorption system. The adsorption isotherm gives information related to adsorbate and adsorbent, [23]. Generally, it describes using an isotherm just in what way the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [24]. The experimental data were suitable to Langmuir and Freundlich models using Eq.(3) and Eq(4) respectively.

$$q_e = K_f Ce^{1/n} \quad (3)$$

$$q_e = \frac{abCe}{1+bCe} \quad (4)$$

Where *qe* is the equilibrium amount absorbed in (mg/g)of sorbent (mg/g), K_f is the Freundlich adsorption coefficient (mg/g)(L/mg), C_e is the equilibrium concentration (ppm), n is considered a number which describes surface heterogeneity and sorption intensity.

If n is ranging between 2 and 10, this means good adsorption.

If the numerical value of 1/n less than one, this indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. a is the maximum adsorption capacity (mg/g) and (b*)* is the Langmuir fitting parameter (L/mg) [16].

It can be expected whether an adsorption system is unfavorable or favorable according to the value of R_L which is an important characteristic of the Langmuir isotherm.

It is a dimensionless constant referred to separation factor or equilibrium parameter and defined by (5):

$$R_L = \frac{1}{1+KL\ C0} \quad (5)$$

Where Co is the highest initial concentration, this parameter suggests the type of isotherm to be irreversible (RL = 0), favorable (0 < RL < 1) or unfavorable (RL > 1) [20]

4- Results and Discussion

4.1. Effect of Mixing Techniques

The removal efficiency of phenol by paper waste is studied by four different ways of mixing as shown in Fig. **2**. It shows that mixing technique plays an important role in the proportion of removal. The ultrasonic wave device and the mechanical device showed higher efficiency for phenol removal than the laboratory shaker, and less adsorption occurred using the laboratory shaker. This can be attributed to the advantages of using ultrasound including highly effective mixing and micro-mixing, high energy and mass transfer [25]. Also, the adsorption rate and adsorption capacity increased in the case of using magnetic and mechanical stirrers. The size of adsorbent reduced and the adsorption sites were simply attainable to the adsorbate molecules [26].

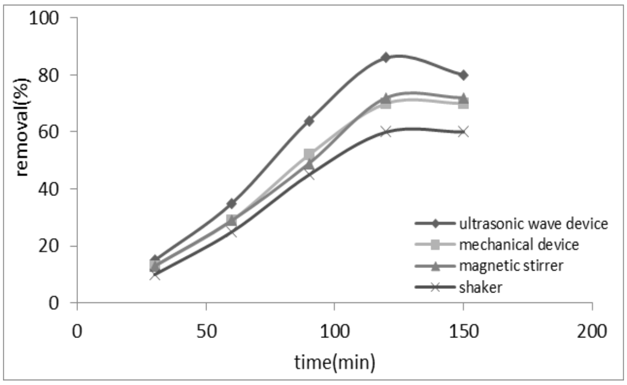

Fig. 2. Effect of different mixing techniques on the adsorption kinetics

4.2. Effect of pH

The adsorption of phenol mainly depends on the hydrogen ion concentration of the solution. Fig. **3** was shown the effect of changing pH on the adsorption capacity of phenol by paper.

This figure shows the removal percentages of phenol from solution increased in the range 40%, 60%, 77%, 81% as pH changed in the range 3, 5, 7, 9, respectively. And then the removal percentages reduced to 73% with pH equals 11.

Hence, pH of 9 is the favorite. When pH ≤ 9, the phenolic compounds present as unionized acidic compounds and thereby the electrostatic attractions increase between the phenol and adsorption sites [10].

Phenol is a weak acid with acid dissociation value (pK_a) equals to 9.8 and it dissociates into phenoxide ion when pH > pKa. Up to pH 9, the concentration of the negatively charged phenoxide ion increases and the electrostatic repulsions occur between the negative surface charge of the paper and the phenoxide anions in solution [27][28].

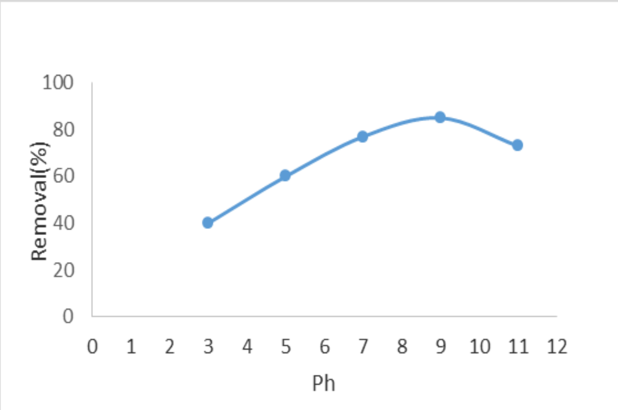

Fig. 3. Effect of pH solution on phenol removal efficiency

4.3. Effect of Initial Phenol Concentration

The effect of phenol concentration on the removal efficiency by paper waste was studied at five different phenol concentrations (i.e. 30, 50, 70, 90, 120 ppm) and the results are shown in Fig. **4**, where, pH was fixed at 9 and ultrasonic device was chosen as it gave best results.

The results show that increasing the initial phenol concentration decreased the removal efficiency from 87% to 69%. This effect is related to the increase in phenol concentration which leads to the saturation of unoccupied sites on the adsorbent surface at higher phenol concentrations[11].

In other words, decreasing the pollutant concentration in the wastewater increases the chance of adsorbate molecules to react with the available active sites on paper waste so, the adsorption rate increases [29] [3].

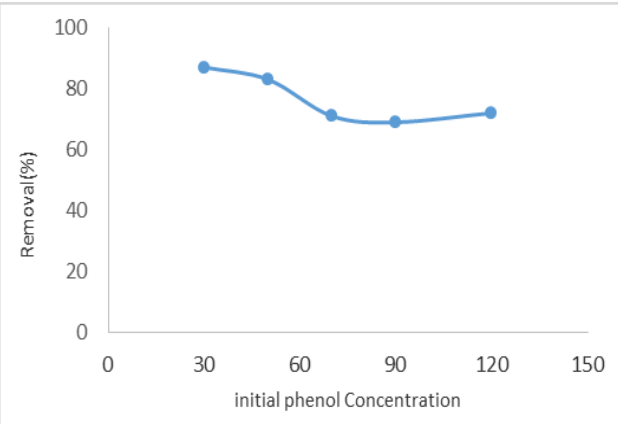

Fig. 4. Effect of initial phenol Concentration on removal efficiency

4.4. Effect of Adsorbent Dose

The effect of adsorbent dosage on the adsorption of the phenol was studied at pH of 9, initial phenol concentration of 30 ppm and using an ultrasonic device. The results of the phenol adsorption are shown in Fig. 5. It is found that the removal of phenol increased from 44% to 88% when the adsorbent dose increased from 0.5 to 2 g. This can be explained as increased in the adsorbed phenol molecules are due to increasing the number of active sites [30]. When the adsorbent dose beyond 2 g/L has no significant effect on the adsorption of phenol. This is due to the adsorption of the all phenol molecules present in the solution by the waste paper;[2].

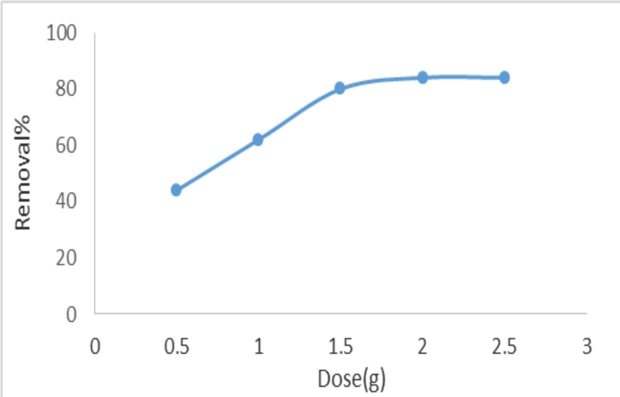

Fig. 5. Effect of Adsorbent Dose on removal efficiency

4.5. Effect of Contact Time

Time is an important parameter affecting the adsorption of phenol on an adsorbent. Fig. **6** shows that phenol removal increased from 15% to 80% with increasing time from 30 to 120 min and the adsorption reached an equilibrium at about 120 min which is the maximum adoption [31]. The performance of adsorption and the adsorption capacity highly increase over time until the equilibrium is attained. It was stated that the reason behind their findings was the formation of a layer of phenol on the adsorbent [14].

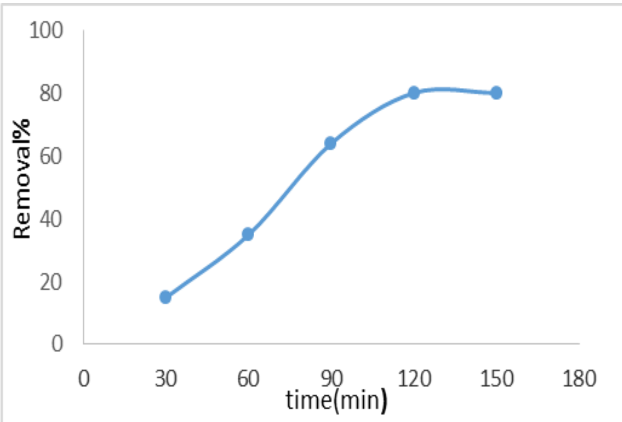

Fig. 6. Effect of time on removal efficiency

5- Adsorption Isotherm

The information obtained from adsorption isotherm is required for designing the adsorption equipment and describing the nature of the interaction between adsorbent and adsorbate molecules at equilibrium [23].

Two isotherm models namely Freundlich and Langmuir models were applied on the adsorbate-adsorbent interaction.

They give an equilibrium relationship between the adsorbate adsorbed on the adsorbent and adsorbate remaining in the solution [1].

The results show that the experimental equilibrium data (shown in **Table 2** and **Fig. 7**, **Fig. 8** and **Fig. 9**) were accepted to the Freundlich and Langmuir isotherm equations; but Freundlich isotherm model provides higher R^2 than Langmuir isotherm model.

The isotherm constants calculated from the model are shown in **Table 2**.

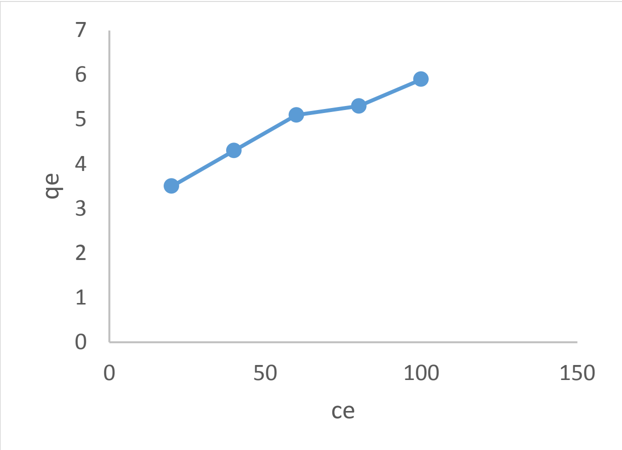

Fig. 7. Adsorption isotherm model of phenol

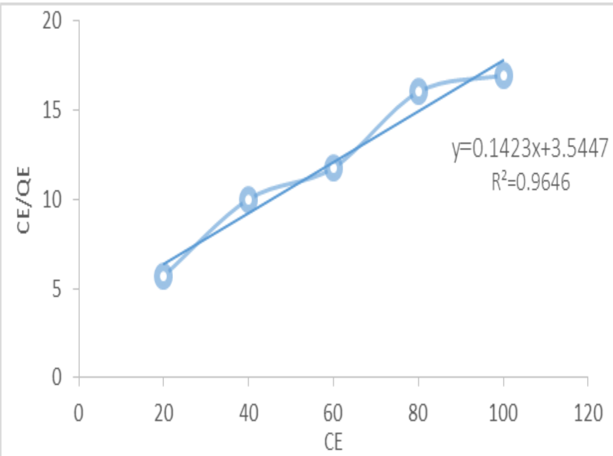

Fig. 8. Langmuir adsorption isotherms for phenol adsorption

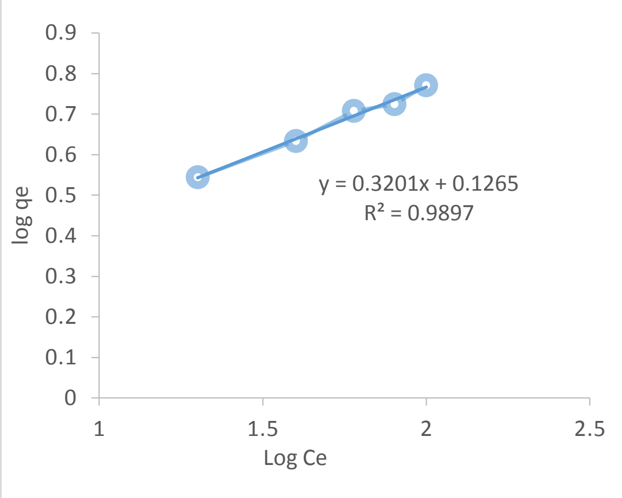

Fig. 9. Freundlich adsorption isotherm for phenol adsorption

Table 2. Isotherm constants for phenol removal by waste paper

Langmuir isotherm			Freundlich isotherm		
Q_m	k_L	R^2	k_f	n	R^2
7.0274	0.0401	0.9646	1.338	3.124	0.9897

6- Conclusions

Recently, high costs and environmental respects concomitant with using of commercial adsorbents has led to a major value of research effort aiming to develop novel cheap adsorbents resulting from renewable resources. In our work, paper waste can be used as an effective adsorbent for phenol elimination from aqueous solution. It was found that the amount of phenol adsorbed depended on several parameters such as the type of agitation techniques, pH, adsorbent dosage, initial phenol concentration and contact time. The final outcomes obtained from this work were well submitted by Freundlich isotherm. The high removal efficiency of 86.4% was obtained using ultrasonic wave device, pH of 9, initial phenol concentration of 30 ppm, a paper waste dose of 1 g, and contact time of 120 min)

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امتزاز الفينول من مياه الصرف الصحي باستعمال المخلفات الورقية

الخلاصة

إن استغلال المصادر القابلة للتدوير ومنها المخلفات الورقية له مميزات في حماية البيئة ومواردها. وقد أجريت ا لدراسة على استخدام المخلفات الورقية لامتصاص الفينول الذي يعد واحد من المنتجات العضوية الضارة على البيئة. تمت دراسة تأثير اختلاف طرق الخلط ودرجة الحموضة من المحلول(3−11) ، تركيز الفينول الأولي (30−120 جزء في المليون) ، كتلة المادة المازة(0.5−2.5 جم) ووقت الاتصال (30−150 دقيقة).

أعلى كفاءة لإزالة الفينول تم الحصول عليها كانت 86% وسعة الامتزاز قدرها 5.1 ملغم / غم و الظروف المثلى (درجة الحموضة 9 ، تركيز أولي الفينول 30 ، جرعة ممتزة من 2 جم وزمن الاتصال 120 دقيقة وفي درجة حرارة الغرفة) . تمت دراسة ملائمة نماذج امتزاز لانجميور وفروندليتش اثناء الاتزان .أظهرت النتائج ملائمة فروندليتش مع معامل تصحيح (R^2=0.9897) ضمن الحدود المدروسة.