STUDY OF ADSORPTION FOR PHENOLIC COMPOUNDS FROM COCONUT SHELL AS ACTIVITED CARBON

Elham Saad Falah **Osama Ali Sharif** **Ahmad Muftah Dabah**

Elham.s.falah@gmail.com osama0602@gmail.com ahmad.eldabah@gmail.com

Higher Institute Of Sciences and Technology- Alkhums, Libya
Department of Chemical Engineering
Abdualati Ibrahim Al-Tabib

tabiblibya2017@gmail.com
Applied Research and Development (ARDO), Tripoli, Libya

Abstract

The presence of phenolic compounds in water and wastewater has been of great public concern and it is one of the most frequent contaminants at hazardous-waste sites. Phenol is usually formed due to the photo degradation of pesticides and these phenols have considerable solubility in water. There are very toxic to flora and fauna and therefore, pose serious environmental problems. In the present study, two organic phenolic compounds (4- Nitrophenol & m-cresol) were used to determine their adsorption capacities by using activated carbon. This work was carried using a fixed bed column. The effects of process variables such as bed height, flow rate and breakthrough have been investigated. The results have been used to predict the effect of parameter changes on the system by using the bed depth service time (BDST) model at various depths in column (Z=30, 40 and 50 cm), (4-Nitrophenol: Q = 50 mL/min, Breakthrough 10%, and m-Cresol: Q = 50 mL/min, Breakthrough 20%).

Key-words: Adsorption, Coconut Shell, Activited Carbon, 4-Nitrophenol, m-Cresol.

الملخص

وجود المركبات الفينولية في المياه ومياه الصرف هو أحد أكثر الملوثات شيوعًا حيث أن هذه المركبات لها قابلية كبيرة للذوبان في الماء وهي مركبات شديدة السمية للنباتات

والحيوانات ، وبالتالي فهي تسبب مشاكل بيئية خطيرة. في هذا البحث، أجريت دراسة بطريقة الامتزاز لإيجاد كفاءة حبيبات الكربون المنشط (GAC) من قشرة جوز الهند، لمعالجة المياه الملوثة من المركبات الفينولية (4-نيتروفينول و م- كريزول) لتحديد قدراتهم على الامتصاص باستخدام الكربون المنشط، حيث تم تنفيذ هذا العمل باستخدام مفاعل ذو الحشوة الثابتة وكذلك دراسة تأثير متغيرات العمليات مثل ارتفاع الطبقة الحشوة ومعدل التدفق والاختراق واستخدمت هذه النتائج للتنبؤ بتأثير تغيير المعاملات على النظام باستخدام نموذج وقت خدمة عمق السرير BDST علي ارتفاع مختلف في العمود (50,40,30سم) ومعدل التدفق (4-نيتروفينول: 50 مل / دقيقة ، اختراق 10٪) ومعدل التدفق (م- كريزول: 50 مل / دقيقة ، اختراق 20٪).

1. Introduction

The major aim of wastewater treatment is to remove as much of the suspended solids as possible before the remaining water, called effluent, is discharged back to the environment. As solid material decays, it uses up oxygen, which is needed by the plants and animals living in the water. Phenolic compounds are toxic to human and aquatic life, creating an oxygen demand in receiving waters. Chronic toxic effects, due to the phenolic compounds pollution reported in humans, include vomiting, anorexia, difficulty in swallowing, liver and kidney damage, headache, fainting and other mental disturbances [1]. These organic compounds are considered as priority pollutants since they are harmful to organisms at low concentrations, and can be toxic when present at elevated levels and are suspected to be carcinogens [2]. Phenolic compounds are commonly produced in wastewater streams generated by petrochemical, oil refineries, coal conversion, steel plant, paint and phenol producing industries [3, 4] The removal or destruction of phenolic compounds has become a significant environmental concern as less than 1 mg/L Phenolic compounds are required for wastewater discharged [5]. It is well known that phenolic compounds are toxic while some of these continents are carcinogenic. Adsorption processes play a good roles in pollution prevention with application for product recovery, purification and removal (and recycle) of contaminants from air and water streams. It is a physical process in which dissolved molecules or small particles (adsorbate) are attracted and become attached to the surface of something larger (adsorbent). The attraction is similar to that of a magnet on a refrigerator, but on an atomic or molecular scale. Energy differences and electrical attractive forces which known as Van der Waals forces, cause molecules of the adsorbate to physically fasten and stick onto the adsorbent. Adsorption occurs when molecules diffusing in the fluid phase are held for a period of time by forces emanating from an adjacent surface. The surface represents a gross discontinuity in the structure by the surrounding atoms like those in the body of the structure. The amount of material adsorbed depends on a number of factors including the degree of attraction, the surface area exposed to mobile particles, the concentration of the contaminants the pH and temperature of the liquid. Typically, the strongest adsorbents are micro porous or finely divided solids (clays, charcoal, powdered metals) and liquids (fine droplets like aerosols). The rate of adsorption is controlled by transfer of species within the adsorbent particle because diffusion through solids is naturally slower than in fluids, Therefore the process continues until a characteristic equilibrium is attained at the adsorbent surface between the adsorbate in fluid phase and adsorbent on the solid or adsorbent properties. [6]

In the present study, two organic phenolic compounds (4-Nitrophenol and m-cresol) were used to determine their adsorption capacities by using activated carbon. The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost and land, simple design and easy operation, no effect by toxic substances and superior removal of organic waste constituents as compared to the conventional biological treatment processes. Activated carbons of high porosity, high surface are frequently used in industry for purification and chemical recovery operations as well as environmental remediation can be produced from a number of precursor materials including coal, wood and agricultural wastes. Recognizing the economic drawback of activated carbon, such as high cost, many investigators have studied the feasibility of using cheap, commercially available materials as potential adsorbents such as the low rank coal. [7]

The overall aim of this study was to determine the capability of modified coconut shell adsorbent for adsorption of 4-Nitrophenol and m-cresol. To determine the breakthrough point for a dynamic column operated under different bed depths and flow rates in order to evaluate its performance.

2. Experimental section

2.1 Materials and Method

2.1.1Adsorbent (Activated Carbon)

Coconut shell is suitable for preparation of micro porous activated carbon due to its excellent natural structure, high carbon and low ash content. [8] Activated carbon particle size fraction from (0.5mm to 2mm) was sieved. The activated carbon was washed by distillated water and kept in distillate water an overnight and finally dried in an oven.

I. Product Description:

Activated Carbon is a carbonaceous material of porous carbon element made from anything, which carbonizes under combustion (direct or indirect fire/heat). The innumerable pores of Activated Carbon make it highly useful for absorption of gases, liquids, vapors, solvents, dispersions and colloids. Activated Carbon comes in granular or powdered form, thus giving different pore sizes (micropores, mesopores/medium and macropores), suitable for differed target substances. coconut shell charcoal activated carbon is generally microporous with high absorptive capacity and an ideal liquid or gas filter agent. Activated Carbon can be made out of wood, but coconut shell is a cheaper and widely available raw material considered as farm waste by-product.[9]

II. Raw Material:

Coconut shell charcoal activated carbon is sourced from mature coconut shells. Coconut shell is an important raw material used to produce **charcoal briquette**. And coconut shell charcoal have wide applications in many fields because of its features and advantages. In Malaysia, coconut is the fourth important industrial crop after oil palm, rubber and paddy in terms of total planted area and it is an important export country of coconut products. Due to its high carbon content and hardness, coconut shells are an excellent raw material source to produce activated carbon. Activated carbon manufactured from coconut shell is considered superior to those obtained from other sources. They typically have a tighter, more microporous pore structure and tend to be harder, more resistant to abrasion and lower in ash than similar grades of coal-based carbons. [10] Even Though, the Coconut shell is more cheap than others but, still have a few disadvantage like these shell has high alkaline and these alkaline will increase the potassium in the components you will used and this increase will make too many disease.

III. Manufacturing Process:

There are basically two steps:

(a) Carbonization (burning/pyrolysis) which produces mere charred coconut shell with poor absorptive power;

(b) Activation by selective oxidation of the charred shell in controlled atmosphere of steam and air that increases the absorptive capacity.

The process essentially involves the creation of internal pores of various widths, bulk density, size distribution and hardness that account for the powerful forces, which hold the absorbed molecules on the surface of the carbon. The surface area of the internal pore structure measures the absorptive capacity.[9]

2.1.2 Adsorbate:

Table (1) shows the physical properties of 4-Nitrophenol and m-Cresol.

Table (1): physical properties of 4-Nitrophenol and m-Cresol [11].

Properties		
Chemical formula	4-C6H5NO3	C7H8O
Molar mass	139.110 g/mol	108.14 g/mol
Appearance	Colorless or yellow pillars	colorless liquid to yellowish liquid
Melting point	113 to 114 °C (235 to 237 °F; 386 to 387 K)	11 °C (52 °F; 284 K)
Boiling point	279 °C (534 °F; 552 K)	202.8 °C (397.0 °F; 475.9 K)
Solubility in water	10 g/L (15 °C) 11.6 g/L (20 °C) 16 g/L (25 °C)	2.35 g/100 ml at 20 °C 5.8 g/100 ml at 100 °C

2.2 Fixed Bed Experiments

A small scale pilot plant was constructed to determine the column characteristic of the adsorption system. Figure (1) shows the fixed bed adsorber. In this study burette were used and it was made of inert materials (grade glass). Column breakthrough data were obtained in a 1cm ID and length 66cm. The adsorbent should be kept submerged in water before the run. The adsorbate solution in tank (10 L) distribute to the adsorber column by used calibrated rot meter, it was used to control the flow rate through the column, then samples were taken from sampling point at appropriate time intervals by a syringe to record the value of outlet concentration phenolic compounds; finally the effluent was discharged into the drain.

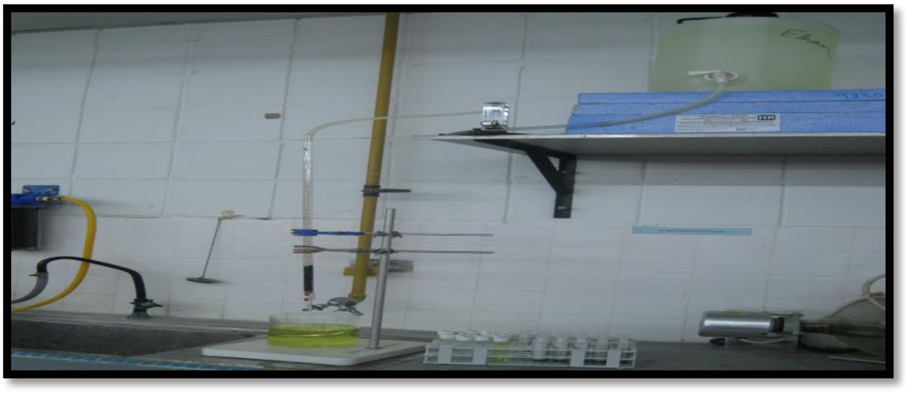

Figure (1) Fixed Bed Adsorber.

2.2.1 Adsorption Kinetics In Fixed Bed Adsorber

A simple approach to fixed bed absorbers has been proposed, to correlate the service time (t) with the process variable. The column experiments were carried out under fixed initial adsorbate concentration (40 mg/l) for flow rate at room temperature (25 °C). A series of experiments were carried for each phenolic compound in their single form. Breakthrough curves were recorded during each column experiment at various depths in column (Z=30, 40 and 50 cm), at flow rate (F=50 ml/min) was studied. All the runs carried at room temperature (22°C) and distillate water was used.

2.2.2 Mathematical Model

Various models are available for the design of fixed bed adsorption column, out of them MTZ, HETU and BDST model are the most commonly used which are discussed as following. [12]

2.2.3 Bed Depth Service Time

In continuous flow experiments, it is essential to predict the exhaustion rate of adsorbent bed on how long the bed will last before regeneration is necessary. In this the service time of a fixed bed adsorbent, treating a solution of single adsorbate can be expressed as a function of operational variable as equation (1):

$$t = \frac{N_0}{C_0 U} Z - \frac{1}{K_A C_0} Ln\left[\frac{C_0}{C_b} - 1\right] \qquad (1)$$

Where: Cb is the breakthrough phenolic compounds concentration (mg/L), N0 the sorption capacity of bed (mg/L), U the linear velocity (cm/min), and *K*a is the rate constant (L/mg. min).

Equation (1) can be represented as equation (2):

$$\mathrm{t} = \mathrm{m_x Z} + \mathrm{C_x} \qquad (2)$$

Where:

$$m_x = \frac{N_0}{C_0 U} \quad \text{And} \quad C_X = -\frac{1}{K_a C_0} ln\left[\frac{C_0}{C_b} - 1\right]$$

Thus a plot between service times against bed depth can be used to test the model. The amount of metal retained in the column depends on the influent metal concentration and can be calculated from the area above the breakthrough curve Eq. (3).[12] The adsorption capacity of the bed *q* can be determined from a plot of ln[(*C*0/*C*t)−1] against *t* at a given condition.

$$\mathrm{q} = \frac{\mathrm{Q*C0}}{\mathrm{1000*M}} \int_{\mathrm{o}}^{\mathrm{t}} \left[1 - \frac{\mathrm{Ct}}{\mathrm{C0}}\right] \qquad (3)$$

Where:

q represents the amount of phenolic compounds retained (mg of phenolic compounds per g of adsorbent), Ct and Co are the phenolic compounds concentrations at the column effluent and influent (mg/L) respectively, Q is the flow rate (mL/min), M is the mass of adsorbent in the column (g) and t is the adsorption time (min).

3. Results and Discussion

3.1 Effect of Organic Flow Rate and the Bed Depth

Figures (2) and (3) show the influence of the feed flow rate on breakthrough curves for the phenolic compounds. Generally the breakthrough point time decreases with increasing of flow of fluid through the bed. As the liquid flow rate increases, liquid distributions are improved and the resistance to mass transfer through the external liquid film is reduced which causes an improvement of the performance of the bed. Whereas increasing in the velocity of the liquid causes decreases in contact time, which results in a decrease of the capacity. It is also evident from these Figures that the break point time increases with increased bed height.

Accumulation of phenolic compounds in the fixed-bed column is largely dependent on the quantity of sorbent inside the column. The sorption breakthrough curves obtained by varying the bed heights from 50 to 30 cm at 50 mL/min flow rate and 40 mg/L initial phenolic compounds concentration onto Coconut Shell -GAC are given in Figures (2) to (3).

Both bed capacity and exhaustion time increased with increasing bed height, as more binding sites available for sorption, also resulted in a broadened mass transfer zone. The increase in adsorption with that in bed depth was due to the increase in adsorbent doses in larger beds which provide greater service area (or adsorption sites). This states that bed height (Z) and service time t of a column bears a linear relationship. Model is termed the Bed Depth Service Time (BDST) model and stated that the service time t of a column is given by equation (1). The column service time was selected as time when the effluent phenolic compounds concentration reached 40 mg/L. The plot of service time against bed height at a flow rate of 50 mL/min, as shown in Figures (4) and (5) was linear ($R2$ = 1.00) indicating the validity of BDST model for the present system. Thus, the bed capacity will change with the service time . The rate constant, KA, calculated from the intercept of BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase .If KA is large, even a short bed will avoid breakthrough, but as KA decreases a progressively longer bed is required to avoid breakthrough .The BDST model parameters can be helpful to scale up the process for other flow rates without further experimental run. Equation (2) is easier to use in its simplified form.

A plot of service time t versus bed depth Z should yield a straight line with a slope equal to m_x which represent the time required to exhaust a unit length of the adsorbent in the column under the test conditions. The intercept on the ordinate C_X is the time required for the adsorption curve front to pass through the critical bed depth. The main fixed bed variables studies in this section include bed height and flow rate.

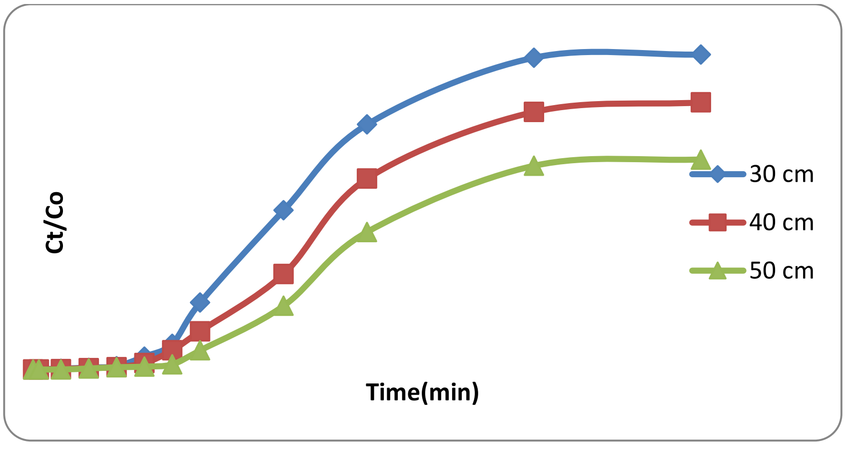

Figure (2) Breakthrough Curves for 4-Nitrophenol onto Coconut Shell-GAC for different bed depths, Q =50 Ml/Min, Co=40ppm.

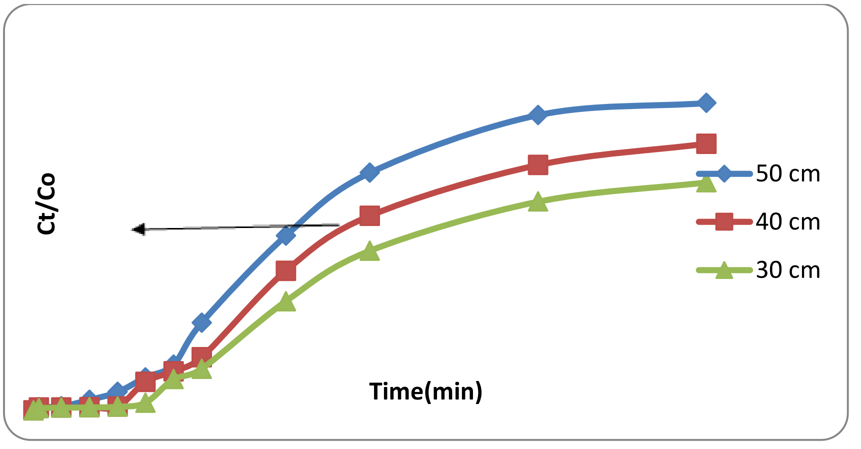

Figure (3) Breakthrough Curves for m-Cresol onto Coconut Shell-GAC for different bed depths, Q =50 ml/min, Co=40 ppm.

3.2. Effect of bed height

Equation (2) is the equation of straight line relating service time **t** to bed depth Z and may be used directly to test the BDST model. Figures (4) and (5) show how this relationship was confirmed for the adsorption of the solute of phenolic compounds onto GAC for various bed depths. The experimental data for the adsorption of phenolic compounds onto Coconut Shell -GAC fit the BDST model very well.

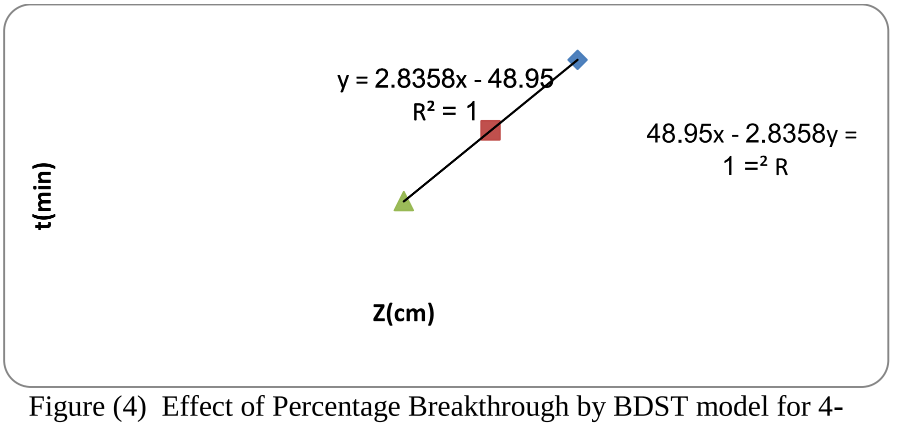

Figure (4) Effect of Percentage Breakthrough by BDST model for 4-Nitrophenol onto Coconut Shell-GAC (CO=40 mg/L, 50 mL/min)

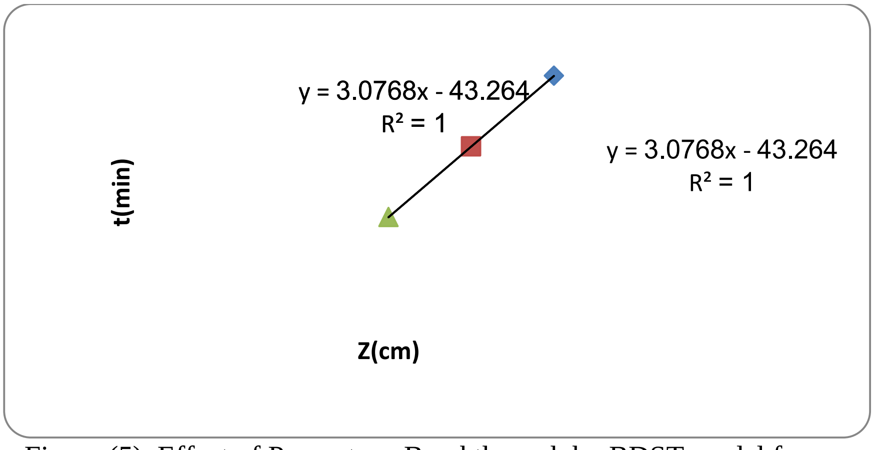

Figure (5) Effect of Percentage Breakthrough by BDST model for m-Cresol onto Coconut Shell-GAC (CO=40 mg/L, 50 mL/min)

Table (2) Compares Bed depth service time (BDST) parameters at different percentage breakthrough for the adsorption of Phenolic compounds with copper onto pretreated Aspergillus niger biomass.

Table (2) Comparison Bed depth service time (BDST) parameters at different% breakthrough for the adsorption of Phenolic compounds with cooper.

Adsorbate	Adsorbent	Vol. Flow Rate (mL/min)	Breakthrough%	Slope m_x (min/cm)	Intercept C_x(min)	N0 (mg/L)	Ka (mg/L.min)	Correlation Coefficient (R2)	References
4-Nitrophenol	Activated carbon (Coconut Shell)	50	10	2.8357	-48.94	17.84	0.0030	1.00	Present work
m-Cresol		50	20	3.0768	-43.26	19.33	0.0031	1.00	
Copper	pretreated *Aspergillus niger* biomass	1.6	9.9	237	−31.2	5960	0.008	0.99	Mausumi .M. *et al.* 2010)
Copper		5.2	9.9	73.2	−20.4	5960	0.0111	1.00	

4. Conclusion

This research work has revealed some latent facts about the usefulness and effectiveness of granular activated carbon produced from waste agricultural materials. From the experimental information gathered, it has been shown in this study that From the set of experimental and theoretical analysis on adsorption of phenolic solute compounds the following conclusions can be made.

1- granular activated carbon of (0.5-2 mm) particle size produced from coconut shell can effectively remove organic pollutants from distillate water

2- The sorption of phenolic compounds by coconut shell pellets a fixed bed column was studied.

3- The experimental results:

   A. (4-Nitrophenol: Volumetric Flow Rate = 50 mL/min, Breakthrough 10%, N0 = 17.84 mg/L and Ka 0.0030 mg/L.min).

   B. (m-Cresol: Volumetric Flow Rate 50= mL/min, Breakthrough 20%, N0 =19.33 mg/L and Ka 0.0031 mg/L.min) showed that adsorbent removes the phenolic compounds effectively and the change in the column operating parameters, such as bed height.

4- A bed depth service time model (BDST) has been applied as a quick design method for a fixed bed and has been successfully applied to the adsorption system where the variables studied include bed height and flow rate.

5. Recommendations For Future Work

1. The first recommendation is to increase the porosity of the coconut shell adsorbent by treated it by moisture and NaOH. It is regenerated by treatment with NaOH and moisture under conditions resulting in impregnation sufficient to restore the activated carbon to more than its original adsorptive capacity for the phenolic compounds
2. uses less than the size used in this purely, because the Grain size of carbon has effect on absorbance of the chemical compounds.
3. determine the breakthrough point for a dynamic column operated under different bed depths, also studying effect of

different flow rate and effect of particle size in order to obtain on good results.

6. References

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