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Adsorption of Phenol from Aqueous Solution Using Activated Carbon prepared from Coconut Shell

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Abstract

Adsorption separation of phenol from aqueous solution using activated carbon was investigated in this work. The adsorbent was prepared from coconut shell and activated by physical activation method. The coconut shell was first carbonized at 800°C under nitrogen atmosphere and activated by CO_2 at the same temperature for one hour. The prepared activated carbon was characterized by Scanning Electron Microscope (SEM) and BET Surface Analyzer and by the determination of iodine number as well as Boehm titration. The iodine number indicates the degree of relative activation of the adsorbent. The equilibrium adsorption isotherm phenol from aqueous solution was performed using liquid phase batch adsorption experiments. The effect of experimental parameters including solution pH, agitation time, particle size, temperature and initial concentration was investigated. The equilibrium data was analyzed using Langmuir and Freundlich adsorption model to describe the adsorption isotherm and estimate the adsorption isotherm parameters. The results indicate the potential use of the adsorbent for removal of phenol from the aqueous solution.

Keyword: Adsorption separation, Phenol, Activated carbon and Coconut shell

1. Introduction

Phenol is the major pollutants in the wastewater from various industries. The phenolic pollution is commonly observed in the chemical and pharmaceutical industries like petrochemical industries, petroleum refineries, coal gasification operations, liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills and pharmaceutical industries. It is a highly corrosive and nerve poisoning agent[1]. Phenol adsorption, a standard method to study the capacity of activated carbon to remove organics from water, was used to determine the adsorption capacity of activated carbons and to study the conditions for regeneration after its use. Phenol adsorption kinetics and equilibrium for activated carbon have been studied, and experiments were performed to determine the way that phenol is adsorbed onto the granules [2].

It is well-known that activated carbon is the general adsorbent due to the large range of applications. One of the largest uses of activated carbons is in the purification of potable water where it is used for the removal of natural organic compounds which adversely affect the taste and odor of water[3]. Numerous works are being continuously published concerning its use as adsorbent for treatment of potable water, purification of air, retention of toxins by respirators, removal of organic and inorganic pollutants from flue gases and industrial waste gases and water, recuperation of solvents and hydrocarbons volatilized from petroleum derivatives etc[4],[5]. Thus, activated carbon has played an important role in the chemical, pharmaceutical and food industries.

Activated carbon can be prepared from almost any organic material rich in carbon and preferably with low content in inorganic matter. Taking into account the large volume of activated carbon required to attend the increasing world demand, biomass derivatives are very interesting raw materials because they are abundant and inexpensive (generally agricultural residues) and they are obtained from renewable sources [6]. Within the large range of biomass derivatives used as activated carbon precursors (woods and components, fruit shells, pulp and stones, bagasse, etc.), coconut shell is one of the most employed for industrial purposes, mainly due to its large availability in several regions of the world[7]. Coconut shells have little or no economic value and their disposal is not only costly but may also cause environmental problems. Coconut shell is suitable for preparing microporous activated carbon due to its excellent natural structure and low ash content[8],[9].

The methods for preparing an activated carbon can be divided into two categories: physical activation and chemical activation. In the physical activation, a raw material is first carbonized and the carbonized material is secondary activated by steam or carbon dioxide, air or their mixtures, i.e., there are two steps: carbonization step and activation step [10]. This research work presents a detailed study about the production of highly porous granular activated carbons from coconut shell using either physical activation with CO_2. For determination of characteristics of produced activated carbon, determination of Iodine value by the adsorption of iodine solution by activated carbon, Boehm titration for the determination of the parameters describing surface acidity such as pH as well as the presence of acidic and basic functional groups on the activated carbon surface and the determination of BET (Brunauer-Emmett-Teller) surface area based on physical adsorption of gas molecules on the surface of activated carbon produced from coconut shell with physical activation process have been studied during this research work. Adsorption characteristics of phenol from aqueous

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solution by the produced activated carbon have been the principle interest throughout the research work.

Bangladesh is a topical country where the availability of raw material required for preparation of activated carbon is abundant and are very cheap. Activated carbon is extensively used in wastewater treatment. It is also used for treating both industrial and municipal liquid waste. There is a good prospect of removing contaminants such as phenol from different solution in sectors like petrochemical, pharmaceuticals, textile dyeing, liquefaction processing industries etc. Therefore, the preparation and use of activated carbon for removal of phenol from aqueous solution is important, economical and environment friendly for our country.

2. Experimental Methods

2.1 Preparation of Raw material

At first, the coconut shells were cleaned. After that by using a hammer, the coconut shells were crushed. Coconut shells were crushed until it met the desired level of size. The resulting particles were sieved and particles having sizes between 4-14 US mesh (5-10 mm) were considered as samples for preparation of activated carbon. Then the samples were washed at least 3 times with distilled water. After that the washed coconut shell samples were dried at 110℃ for 24h in a vacuum dryer to remove moisture. After drying, the coconut shell samples were collected and stored in a desiccator.

2.2 Preparation of Activated Carbon

Activated carbon from coconut shell was produced applying physical activation method at the selected condition. In physical activation process, a two-step procedure was used in this work to synthesize activated carbon from coconut shell feeds: Carbonization and activation. In carbonization stage, the dried coconut shell samples were burned in the absence of air at 800℃. For maintaining absence of air condition, nitrogen was flowed continuously to retain inert atmosphere. Then the activation process was carried out by CO_2 at 800℃. Coconut shells were dried in an oven at 110^oC for 24 h to remove moisture. The dried coconut shells were placed into a one-end open cylindrical ceramic tube and filled the tube's one third with the samples (98.0g) and the rest was filled by packing materials. ¼ SS tube carrying nitrogen gas and thermocouple wire were placed into the ceramic tube through the packing materials and coconut shell samples to the closed end of the tube. Then the cylindrical ceramic tube was placed in a tubular furnace and heated up to 800℃ under N_2 atmosphere. N_2 were flowing continuously with the flow rate of 8.0 L/h controlling with a flow meter. After reaching 800℃, it kept for 1 hour. Then nitrogen was switched to CO_2 and the sample was kept at this temperature in flowing of CO_2 (8.4 L/h) for a specified period of time: 60 min (1 h). After completion of CO_2 activation, the gas was switched to nitrogen and the sample was cooled down to room temperature. Then the prepared activated carbon (26.754g) were collected and preserved into a vacuum box for further characteristics tests.

2.3 Characterization of prepared activated carbon

For characterization of activated carbon Iodine Value determination, Boehm Titration & BET surface analyses were done. Iodine value of activated carbon was determined by ASTM D 4607.The Boehm titration procedure was used to calculate the amount of surface acidic and basic functional. All experimental was carried out in a batch mode. The surface chemistry was determined with the use of four independent solutions of 0.1N HCl, 0.1N $NaHCO_3$, 0.1N Na_2CO_3 and 0.1N NaOH. In each adsorption experiment, 1.0 g adsorbent was added to 50 mL of the solutions with known concentration in a 250 mL round bottom flask under room temperature and the mixture was subjected to continuous stirring for 48 hr using a shaker with a speed of 150 rpm. 10 mL from each solution was taken and the excess of base and acid was titrated against 0.1N HCl first and then later against 0.1N NaOH. The amount of HCl that reacted with the absorbent was then used to calculate the number of surface basic sites while the amount of NaOH, Na_2CO_3 and $NaHCO_3$ reacted with the absorbent was used to calculate the number of surface acidic sites.BET surface was analysed by liquid N_2 adsorption and desorption.

2.4 Phenol Adsorption

Phenol solutions were prepared solid phenol granules to the desired concentrations. For equilibrium time identification, 200 ppm phenol solution was prepared. 0.5 g of activated carbon was added into 5 conical flasks each containing 250 ml 200 ppm phenol solution. Then the phenol solutions were put into a shaker. The concentration of phenol in solutions was determined by spectrophotometrically at 763 nm with UV-2600, UVvis spectrophotometer, Shimadzu. During the experiment folin reagent was used. The concentrations of phenol solutions were measured after 2h, 6h, 12h, 20h and 24h respectively.

Adsorption isotherm studies were performed by using batch technique in a shaker bath at constant temperature. The adsorption kinetics were determined at four different initial phenol concentrations (100, 200, 300 and 400 ppm) at room temperature. 0.5 g of adsorbent was added to each 250 mL phenol solutions and the concentration of phenol was measured after 24h which was the required time for reaching equilibrium concentration measured previously. The concentration of phenol in solutions was determined by spectrophotometrically at 763 nm with UV-2600, UV vis spectrophotometer, Shimadzu. During the experiment Folin & Ciocalteu's phenol reagent was used. From the absorbance reading, the concentration of the solution can be obtained with help of calibration curve.

3. Results and Discussion

Activated carbon prepared from coconut shells were achieved by physical activation process.Activated carbon yield = 27.3%.Iodine value of activated carbon was determined by ASTM D 4607.After 10 trials, the iodine value was found between 400-600.Theoretically the iodine value of physically activated carbon is about 600-1100. So, the iodine value is consistent with the theoretical value. BET surface area, S_{BET}=236.12 m^2/gm Total pore volume Vm = 47cm^3/gm. Surface chemistry of activated carbon was characterized by Boehm titration.

Table 1. Surface functional groups (in mmol.g^{-1}) of AC produced from coconut shell.

Carboxylic group	Lactonic group	Phenolic group	Acidic group	Basic group
0.021	0.023	0.056	0.120	0.102

The Boehm's technique was used to characterize the surface chemical property of the adsorbent.Several assumptions were made before the surface acidity and basicity could however be calculated. It was assumed that acidic group generally, could only be neutralised by NaOH, Na_2CO_3 and $NaHCO_3$ while all basic groups would be neutralised by HCl. Table 1 shows the summary of the properties of the surface functional groups through the Boehm titration. The concentration of acidic sites for the Activated carbon made from coconut shell is 0.1203 mmol.g^{-1}. The basicity groups value is 0.10232 mmol/g. So it indicates that surface chemistry of activated carbon has both acidic and basic characteristics.

SEM images of activated carbon prepared from coconut shells were obtained and are shown in Figure 1 and Figure 2. It is apparent that the activated carbon prepared from coconut shells has porous structure.

3.1 Phenol Adsorption

The effect of time for adsorption process was carried out to determine the equilibrium point. Figure 3 shows a plot of the amount of phenol adsorbed (mg/g) versus contact time for 200 ppm phenol concentrations at 25^{o}C. From the plot, it is found that the adsorption was rapid up to 800 min and later on became slow, and finally the systems reached equilibrium around 1440 min (Figure 3).Therefore, the maximum time of adsorption was restricted up to 1440 min. So, the time required to reach equilibrium is 24hr.

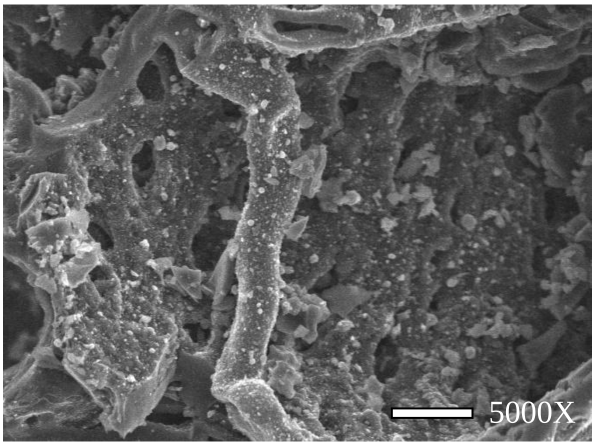

Figure 1: SEM image of Activated Carbon magnified by 5000 times

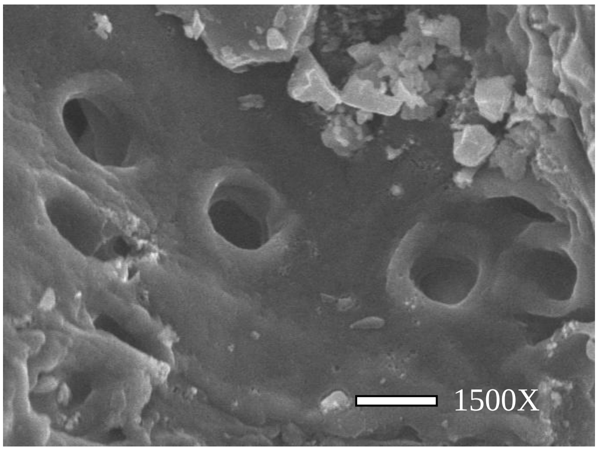

Figure 2: SEM image of Activated Carbon magnified by 1500 times

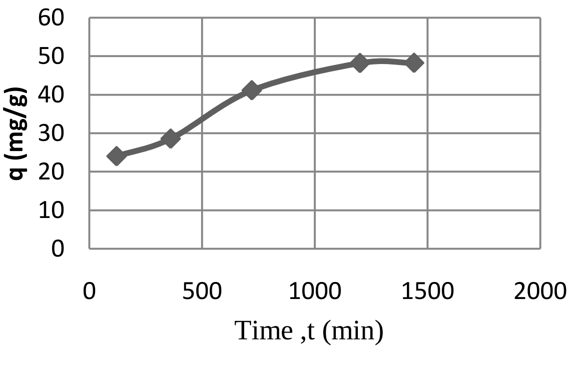

Figure 3: Adsorbed amounts of phenol at 25^{o}C as a function of time for 200ppm initial concentration (V=250 mL; m=0.5 g).

3.2 Kinetic Modeling

The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transport process. In order to investigate the adsorption process of phenol onto activated carbon, the adsorption rate data were analyzed using pseudo first-order and pseudo second-order kinetic models.The linearized forms of these equations are represented as

$$\log (q_e-q_t) = \log q_e- \frac{k_1}{2.303}\, t \text{-------------------------} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e} \text{ ---------------------------------------} \quad (2)$$

where, q_e and $q_t$are the amount of phenol adsorbed (mmol/g) at equilibrium and at time t (min), k_1 is the first order equilibrium rate constant (1/min), k_2 the pseudo second order rate constant (g/mg min). The pseudo first order and second order rate constants were evaluated from the linear plots of $\log(q_e-q_t)$ versus t, and t/q_tversust, respectively. The plots of pseudo second order and pseudo first order kinetic model are shown in Figure 4 and Figure 5 respectively.

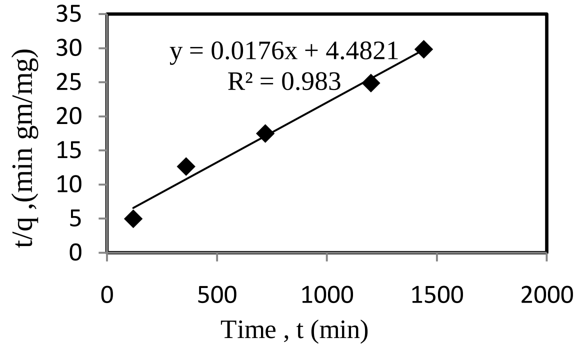

Figure 4: Kinetics of phenol adsorption according to the pseudo second order model at 200 ppm initial concentration (V = 250 mL; m=0.5 g; temp = 25^{o}C).

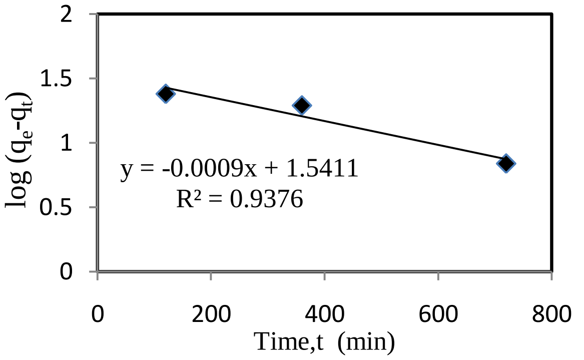

Figure 5: Kinetics of phenol adsorption according to the pseudo first order model at 200 ppm initial concentration (V = 250 mL; m=0.5 g; temp = 25^{o}C).

The analysis of the R^2 values shown in Table 2 suggest that the experimental data fit the pseudo second-order model with R^2 value equal to 0.983 than that of the pseudo first-order with R^2 value 0.9376. The $q_e$values calculated from pseudo second order kinetics relatively close to experimental values of q_e. For this reason, pseudo second order model better predicts the adsorption kinetics than the pseudo first-order model. Such a finding is also good agreement with previous studies

Table 2: First order and second order parameters for 200ppm concentrations

C_0 (mg/ L)	q_e(exp) (mg/g)	Pseudo first order		Pseudo secondorder	
		K_1x10^3 (1/min)	q_e (mg/g)	K_2 x10^3 (min mg/g)	q_e (mg/g)
200	48.2	2.02	34.7	0.069	56.1

3.3 Adsorption Isotherms

The isotherm present in Figure 6 is in consistent with Type-I according to B.D.D.T classification. Type-I isotherm are typical of adsorbents with a predominantly microporous structure, as the majority of micropore filling will occur at relatively low pressure. So according to this theory phenol rings adsorb parallel to the surface and no strong competition exist between the adsorbate and the solvent to occupy the adsorption sites.

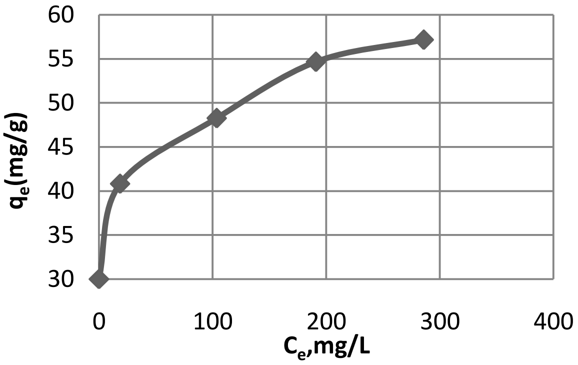

Figure 6: Adsorption isotherms of phenol onto activated carbon (V=250 mL; m=0.5g; C_o = 100-400 mg/L).

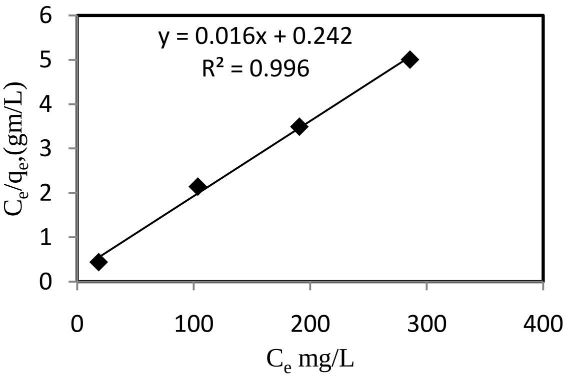

Figure 7: Langmuir adsorption isotherms of phenol (V=250mL; m = 0.5 g; C_o = 100-400 mg/L).

Table 3.Langmuir and Freundlich isotherm constants.

Langmuir			Freundlich		
q_o(mg/g)	b (L/mg)	R^2	K_F	1/n	R^2
59.17	0.06	0.9964	29.94	0.125	0.876

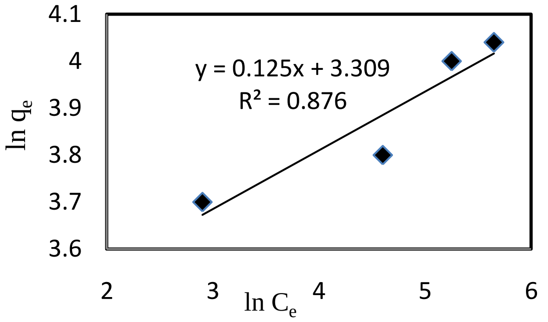

Figure 8: Freundlich adsorption isotherms of phenol (V=250 mL; m = 0.5 g; C_o = 100-400 mg/L)

The constant parameters of Langmuir and Freundlich isotherm equations are given in Table 2. As the value of R^2 was found 0.9964 shows the applicability of Langmuir isotherm model for phenol adsorption. Q_o is the maximum adsorption capacity which was found 59.17 mg/g. From the literature, the adsorption capacity of AC is generally ranging from 73 to 120mg/g [11]. So the result is close to the theoretical value. This is because the BET surface area and pore volume of prepared activated carbon are less than its required value. The Langmuir and Freundlich isotherm model adequately describe the adsorption phenomenon of phenol though Freundlich isotherm is less applicable comparing to Langmuir and from the Langmuir parameter a model isotherm is generated.

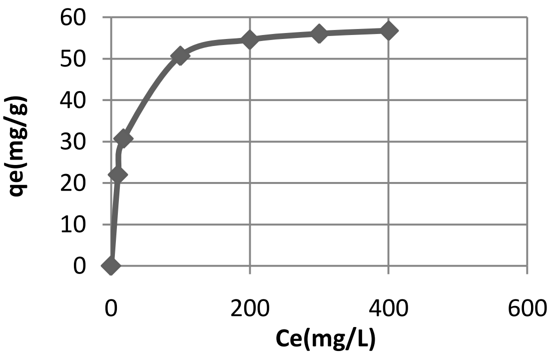

Figure 9: Adsorption isotherms of phenol onto activated carbon (V=250 mL; m=0.5g; C_o = 100-400 mg/L

4. Conclusion

Activated carbon was successfully prepared from coconut shell by carbonization process in absence of air with tubular furnace. The experimental setup for preparing activated carbon was also developed in this research work. In this research work, physical activation method was applied for preparation of activated carbon from coconut shell. Various surface characteristics (pore volume, surface area) and surfacechemistry (acidic and basic functional group) were analyzed by BET theory and Boehm titration respectively. Adsorption isotherm was generated at various equilibrium concentrations. From this study, it was found that phenol adsorption mechanism follow Pseudo second order kinetic model. The equilibrium data was analyzed using Langmuir and Freundlich adsorption model to describe the adsorption isotherm and estimate the adsorption isotherm parameters.

5. Acknowledgement

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