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Fixed Bed Adsorption Column Studies for the Removal of Aqueous Phenol from Activated Carbon Prepared from Sugarcane Bagasse

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Abstract

Fixed bed adsorption has become a frequently used industrial application in wastewater treatment processes. Various low cost adsorbents have been studied for their applicability in treatment of different types of effluents. In this study, the potential of activated carbon derived from sugarcane bagasse was studied for the removal of aqueous phenol in a fixed column. Sugarcane bagasse was thermally activated under 600 ^{0}C in absence of air. A series of batch experiments were performed in order to identify the appropriate adsorption isotherm. Both Langmuir and Freundlich equilibrium isotherms were analyzed according to the experiment data and related parameters were estimated. Results revealed that the Langmuir isotherm provides the best fit with experimental data. Fixed bed experiments were performed and, breakthrough curves were drawn by varying activated carbon bed height. Accordingly the ideal breakthrough curves (IBC) were prepared and bed capacity (BC), length of the unused bed (LUB), the time required for full bed exhaustion at infinite rapid adsorption T_S and the breakthrough times T_b were calculated for each scenarios.

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Keywords : Adsorption, Isother; Fixed bed Column; Phenol; Sugarcane bagasse

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1. Introduction

Phenol has been categorized as a hazardous material by dint of the damage that can do when it gets in to the body of living beings. Though it is not listed as a carcinogenic substance phenol can make severe damage to the living organs [1]. Literature reveals that the overexposure of phenol affects on the central nervous system. In such situations the results are catastrophic as the damage is irreversible.

Phenol is an organic compound commonly used in various industrial applications [2]. It is a raw material used in many industries such as cleaning agent manufacturing, pesticides in agricultural industry and construction of automobiles and appliances [3, 4, 5]. Accordingly there is a possibility to discharge phenol contaminated water in to the natural water bodies without treatment. This makes an immense devastation to the entire ecosystem. In order to minimize the hazard causes by phenol, the US Environmental Protection Agency (EPA) has limited the permissible discharge level of phenol to less than 1mg/L [6].

In industry, the wastewater is generated in large volumes. Hence a convenient method to handle such load is required. Different techniques can be used to remove phenol from aqueous solutions [7] such as oxidation [8], precipitation, ion exchange, solvent extraction [9] and adsorption [10]. Adsorption has been recognized as an effective process in most of the industrial water and wastewater treatment [11].Batch adsorption processes may not be a convenient method for the industrial scale to deal with high flow rates.

Adsorption in a fixed bed column can be used continuously under high effluent flow rates and it has been used in many pollution control processes such as removal of ions by an ion-exchange bed or removal of toxic organic compounds by carbon adsorption [12].

Investigations have been conducted to test various adsorbents for organic material removal from aqueous solutions. Studies have shown that activated carbon prepared from Tectona grandis saw dust [13], ratten saw dust [2], coconut shell [14], Rice husk and Rice husk ash [15] can be used for adsorbing organic materials.

In this study the activated carbon prepared from sugar cane bagasse has been tested for removal of aqueous solutions.

2. Materials and Methods

2.1 Materials

Phenol detached crystals with an assay of 98% min and Non-volatile residue <0.05% supplied by SURECHEM Products LTD, England was used to prepare all synthetic phenol solutions. It was kept in a bottle cooler in order to prevent any contaminations and assure the material quality.

2.2 Instrumentation

All the phenol concentrations were measured using UVvisible spectrophotometer (UV-1800, SHIMADZU) at 269 nm wavelength. The pH of the solutions were measured by a pH meter model HI98103 HANNA and an electronic balance supplied by OHAUS corp. USA, was used for weighing. In fixed bed experiments, a peristaltic pump (Model: BT100-1J Longerpump) was used to feed the phenol solution in to the bed.

2.3 Adsorbate Preparation

Adsorbate was prepared by dissolving required amount of phenol in distilled water. The solutions with the concentrations of 50, 100, 150 mg/L were used for the batch experiments and concentration of 20 mg/L solution was used for the column experiments. The pH was measured and maintained in the range of 6-7. Our previous study on batch experiments of phenol removal using activated carbon prepared from sugarcane bagasse showed that the effective removal could be achieve under solution pH in the range of 6-7 [16]. Hence all the experiments were conducted at this solution pH range.

2.4 Preparation of activated carbon

Fine bagasse pith collected from a leading local sugar manufacturing factory in Sri Lanka was used for the experiments. Bagasse was washed with tap water in order to remove any mud and other impurities. Then the material was washed with distilled water for three times and dried in an oven under the temperature of 70^0C for 24h. Preparation of activated carbon was done by heating a bagasse sample at 600^0C for 1 hour in a muffle furnace in the absence of air. The prepared activated carbon (AC) sample was put into distilled water and material was recovered by filtering. Recovered AC was dried again under the temperature of 70^0C for 24 hours and finally sieved to separate dust carbon particles as well as large particles. AC particles between 1-2 mm in size were used for all the experiments.

2.5 Batch adsorption and isotherm studies

Batch experiments were conducted in order to find the suitable adsorption isotherm by varying the adsorbent weight from 0-10g/L for the phenol samples of 100mL with concentration of 100 mg/L. The samples were kept in a bottle shaker under 200 rpm for 4h to reach equilibrium. All batch experiments were carried out under the temperature of (30±2 ^{0}C).

The amount of phenol adsorbed on activated carbon at equilibrium q_{eq} (mg/g), was calculated.

$$q_{eq} = \frac{\left(C_0 - C_{eq}\right)V}{W} \tag{1}$$

Where C_0 and C_{eq} (mg/L) are the liquid – phase concentrations of phenol at initial and equilibrium stages, respectively. V (L) is the volume of the solution, and W (g) is the mass of the dry adsorbent used.

Among the several adsorption isotherms which have been developed considering various adsorption theorems Langmuir and Freundlich isotherms are commonly used to identify the most suitable adsorption mechanism. Accordingly Langmuir and Freundlich adsorption models used to fit corresponding equilibrium data and related model parameters were estimated.

2.5.1 Langmuir model

Langmuir model is based on several assumptions and adsorption is limited to monolayer adsorption. There the energy of adsorption is assumed to be same all over the surface, no interactions between adjacent molecules on the surface and molecules adsorb at fixed sites and do not migrate over the surface and given by the equation 2 [17].

$$q_{eq} = \frac{Q^0 K C_{eq}}{1 + K C_{eq}} \tag{2}$$

Where C_{eq} is the equilibrium concentration (mg/L), q_{eq} is the amount of adsorbed at equilibrium (mgg^{-1}) and Q^0 and K are Langmuir parameters related to maximum adsorption capacity and bonding energy of adsorption respectively.

2.5.2 Freundlich model

Freundlich model given by the equation 3 describes the equilibrium on heterogeneous surfaces and does not limited to monolayer adsorption [4].

$$q_{eq} = K_F C_{eq}^{1/n} \tag{3}$$

Where K_F and n are Freundlich parameters indicating the adsorption capacity (mg/g)(L/mg)$^{1/n}$ and intensity of the adsorption.

2.6 Column experiments

Column experiments were conducted using a glass tube of 3 cm diameter and 55 cm height. A schematic of the experimental setup used for column study is shown in Fig.1. The experiments were conducted by varying the weight of Activated carbon using initial solution concentration of 20mg/L. The height of the activated carbon bed was measured before the tests in order to monitor the variation cause by bed height. Distilled water was passed through the column in order to remove impurities from the adsorbent. Then the phenol solution was fed to the column by a peristaltic pump. The treated phenol samples were immediately collected from the exit at time intervals and measured for the remaining phenol to indentify the bed exhausting time. Experiments were continued until the column reached a concentration of 15 to 17 mg/L. All experiments were carried out under room temperature (30±2^{0}C).

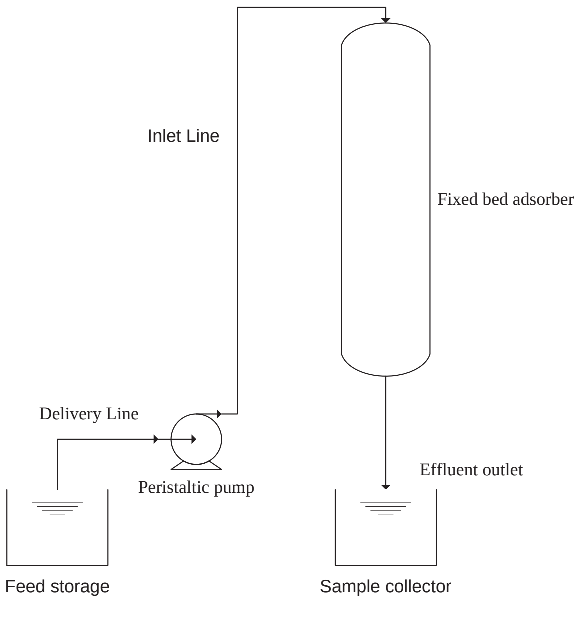

Fig . 1. Experimental setup for fixed bed operation.

3. Results and Discussion

3.1 Isotherm study

In isotherm studies, the parameters involved in both Langmuir and Freundlich isotherm were estimated according to the batch experiment results. The estimated parameters are listed in Table 1. The correlation coefficient R^2 reveals that the Langmuir isotherm provides the best fit to the experimental data. Having estimated the relevant parameters, the experimental and calculated adsorption isotherms of Langmuir and Freundlich isotherms were plotted and shown in Fig .2.

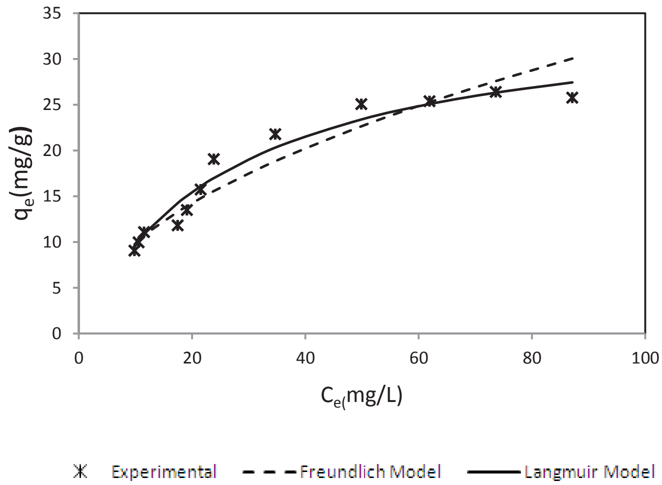

Fig. 2. Different isotherm models for adsorption of phenol on activated carbon

The variation of solution phenol concentration with time was observed under the initial phenol concentrations of 50,100,150 mg/L. Due to the high initial concentrations at the beginning high rate of phenol uptake observed and with the time it gradually decreased and came to an equilibrium condition between solution phenol and adsorbed phenol. Under that equilibrium, the rate of adsorption is equal to the rate of desorption of phenol in the solution. Fig.3. presents the variation of phenol concentration with time under different initial solution phenol concentrations.

Table 1. Estimated parameters for adsorption isotherms

Isotherms	Parameters
Langmuir	
Q^0(mg/g)	35.71
K(L/mg)	0.038
R^2	0.970
Freundlich	
K_F(mg/g)(L/mg)$^{1/n}$	3.11
n	1.97
R^2	0.929

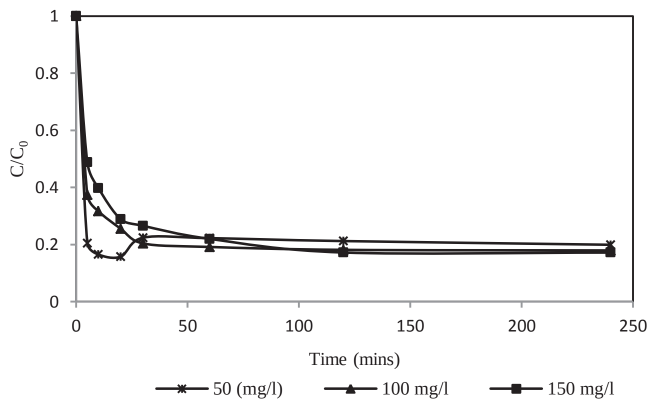

Fig. 3. Variation of phenol concentration with time under different initial solution phenol concentrations

3.2 Column test results

The objective of the column test is to quantify the parameters which are required to design industrial scale fixed bed adsorption columns. The experimental results were analyzed and breakthrough curves (Fig.4) were drawn for both bed weight of 5g and 10g under 20 mg/L initial concentration. The corresponding bed height for each bed was 16 and 32 cm respectively. Both tests were conducted under uniform flow rate of 33.3 mL/min corresponds to the rotational speed of the pump of 40 rpm. Practically the concentration of the solution leaving the column changes very slowly when it is near to solution initial concentration. Thus it is assumed that the bed exhaustion is achieved at almost infinite time.

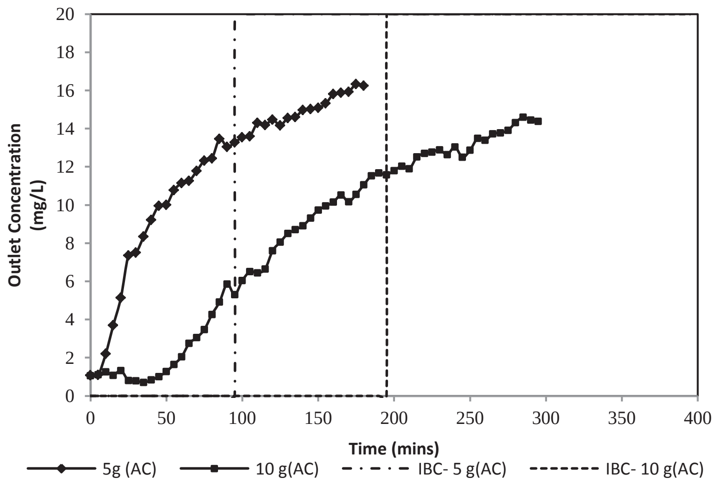

Fig.4. Breakthrough curves for adsorption of phenol onto activated carbon. Flow rate – 33.3 mL/min (40 rpm).

The area above the breakthrough curve represents the bed capacity (BC) and is given by [18].

$$\mathrm{BC} = G\int_0^T (C_0 - C)dt \tag{4}$$

Where G is the solution rate in L/min, C_0 and C are the inlet phenol concentration and outlet phenol concentration in mg/L at time t, respectively, and T is the actual time required for full bed exhaustion. Under infinitely rapid mass transfer rate between solution and adsorbent, the breakthrough curve would be a vertical line (step change) at T_s, which is the time required for full bed exhaustion under ideal conditions.

Table 2. Results on adsorption of phenol in fixed bed column 33.3 mL/min (40 rpm) flow rate and 20 mg/L initial concentration

Adsorbent (weight in g)	T_s (min)	T_b at C/C_0=0.2(min)	LUB (cm)	Amount adsorbed at T_b		Amount adsorbed at full bed exhaustion	
				Total (mg)	mg/g	Total (mg)	mg/g
5	95	15	13.47	9.5	1.9	60.11	12.02
10	195	80	18.87	50.62	5.06	123.38	12.34

Ideal breakthrough curves (IBC) have been drawn in Fig.4. for the adsorbent dosages of 5g and 10g respectively. In industrial practice, a bed is operated until an effluent reaches an arbitrary chosen low concentration value which is known as the breakpoint concentration and it is the maximum allowable concentration that the effluent can reach. At this breakpoint the bed is not fully used for the effluent uptake. Thus a term called LUB is defined for the equivalent length of unused bed.

$$\mathrm{LUB} = \frac{Z}{T_s}\left(T_s - T_b\right) \tag{5}$$

The bed capacity (BC) is then given by

$$\mathrm{BC} = \mathrm{G}\left(\mathrm{C}_0 - C^*\right)T_s \tag{6}$$

Where Z is the bed height, C^* the concentration of the solution in equilibrium with the fresh adsorbent or concentration of the solution leaving the bed initially, T_s the time required for full bed exhaustion at infinite rapid adsorption and T_b is the breakthrough time.

Having reviewed the experimental data, the parameters of BC, LUB, T_s, T_b were calculated and tabulated in Table2. C^* indicate the equilibrium concentration of effluent with fresh adsorbent and that is 1mg/L for both bed heights.

4. Conclusion

This study was carried out to investigate the use of fixed bed adsorption column to treat aqueous phenol using a low cost adsorbent. Hence activated carbon derived from sugarcane bagasse is a good adsorbent for the removal of aqueous phenol. According to the isotherm studies, results reveal that the Langmuir isotherm is the best model to illustrate the adsorption mechanism. There are many parameters involve in evaluation of performance of fixed bed column such as solution initial concentration, flow rate, amount of adsorbent used and particle size of the adsorbent. According to this study results show that the increases of adsorbent dose in column enhance the adsorbent capacity of the bed. Further Percentage of length of the unused bed to its original bed height decreases with the increases of amount of adsorbent used.

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References

[1] Knop, A.; and Pilato, L.A. 1985. Phenolic resins-chemistry. Application and performance.Springer-Veriag.

[2] Hameed, B.H.; and Rahman, A.A. 2008. Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material. J.Hazard.Mater.160:576-581.

[3] Gray, R.C.F., Hogerzeil, H.V., Pruss, A.M.; and Rushbrook, P. 1999. Guide line for safety disposal of unwanted pharmaceuticals and in emergencies, World health organization.

[4] Dursun, G.; Cicek, H.; and Dursun, A.Y.2005. Adsorption of phenol from aqueous solution by using carbonized beet pulp. J.Hazard.Mater B125: 175 – 182.

[5] Ozkaya, B. 2006. Adsorption and desorption of phenol on activated carbon and a comparison of isotherm model. J.Hazard.Mater B129: 158 – 163.

[6] Banat, F.A.; Al-Bashir, B.; Al-Asheh, S., and Hayajneh, O. 2000. Adsorption of phenol by bentonite. Environ.pollut.107:391-398.

[7] Lin, S.; and Juang, R. 2009. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbent. J.Envion.Manage. 90: 1336-1349.

[8] Cárdenas, A.S.; Gallardo-Velázquez, T.; Osorio-Revilla, G.; López-Cortéz, M.S.; and Gómez-Perea, B. 2005. Adsorption of Phenol and Dichlorophenols from Aqueous Solutions by Porous Clay Heterostructure (PCH). J. Mex. Chem. Soc 49(3): 287-291.

[9] Uddin, M. T.; Islam, M. S.; and Abedin, M. Z. 2007. Adsorption of phenol from aqueous solution by water hyacinth ash. ARPN Journal of Engineering and Applied Sciences. vol. 2, no. 2.

[10] Carmona, M.; Lucas, A.D.; Valverde, J.L.; Velasco, B.; and Rodr´ıguez, J.F. 2006. Combined adsorption and ion exchange equilibrium of phenol on Amberlite IRA-420. Chem. Eng. J. 117:155–160.

[11] Goshadrou, A.; and Mohed, A. 2010. Continuous fixed bed adsorption of C.I. acidblue 92by exfoliated graphite: An experimental and modeling study. Desalination. 269:170-176.

[12] Unuabonah, E.I.; Olu-Owolabi, B.I.; Fasuyi, E.I.; and Adebowale, K.O. 2010. Modeling of fixed-bed column studies for the adsorption of cadmium onto novel polymer-clay composite adsorbent. J.Hazard.Mater.179:415-423.

[13] Mohanty, K..; Das, D.; and Biswas, M.N. 2005. Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by $ZnCl_2$ activation, Chemical Engineering .J. vol.115: 121-131.

[14] Mohd Din, A.T.; Hameed, B.H.; and Ahmad, A.L. 2009. Batch adsorption of phenol onto physiochemical-activated coconut shell, J. Hazard. Mater 161: 1521-1529.

[15] Mahvi, A.H.; Maleki, A.; and Eslami, A. 2004. Potential of rice husk and rice husk ash for phenol removal in aqueous systems. American Journal of Applied Sciences 1(4):321-326.

[16] Karunarathne, H.D.S.S. and Amarasinghe, B.M.W.P.K. 2011. Sugar cane bagasse based activated carbon as an adsorbent for phenol removal from aqueous solutions. In proceedings of the international conference on chemical engineering. Dhaka, Bangladesh, 29-30 December.

[17] Coulson, J.M.; and Richardson, J.F.; Chemical engineering, vol.2, 5th ed., Butterworth-Heinemann, 2002

[18] Treybal, R.E.; Mass transfer operations, 3rd ed., McGraw-Hill Companies,1980.