International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.12 pp 269-279, 2015

Batch Adsorption of Phenol by improved Activated *Acacia nilotica* branches char: Equilibrium, Kinetic and Thermodynamic studies

Bhajan Dass*, Pushpa Jha

[1]Department of Chemical Engineering, SLIET, Longowal-148106, Punjab, India

Abstract: Improved activated char of acacia nilotica branches (CANBI) was prepared by reforming in thermo-chemical treatment on powdered acacia nilotica branches. This process enhanced its overall surface area, percentage fixed carbon content, iodine number and methylene blue adsorption. SEM analysis on this adsorbent explained its highest BET surface area of $403m^2/g$ compared to that of other two adsorbents. Experimentally adsorption capacity of this char is established to be 250 mg/g which is much higher than other two adsorbents. Study of phenol sorption was done to optimize carbon dosage, pH of adsorbate-adsorbent system, contact time, initial phenol concentration and rpm of shaker. Adsorption equilibrium model of Langmuir, Freundlich, Temkin and Dubinin Radushkevich fitted well for phenol concentration range of 0 to *975* mg/l and all models established, high affinity of phenol towards CANBI. Kinetic data represented pseudo second order kinetics better. Thermodynamic study confirmed the phisibilty of adsorption process. Regeneration of CANBI was also successfully tested by various acidic and basic eluents. CANBI has been proved to be cheaper and renewable adsorbent.
Key Words: Acacia nilotica branches, Activated carbon, Adsorption, Equilibrium, Kinetics and Thermodynamics.

Introduction

Phenol is one of the most toxic chemical found in the effluents of various chemical and coke-oven industries. As this chemical is highly soluble in water, its presence is very hazardous for aquatic life. Among various methods available for removal of this chemical, adsorption on various types of biomass are well reported[1-3]. For last many years much investigation has been done for economical materials such as fly ash, peat, soil, rice-husk, saw dust, baggase, rice-straw, tendu leaf etc for their use as adsorbents[4-9]. Among various biomass, activated powdered branches of acacia nilotica (activated PBAN) is the most recent reporting[10]. Though this biomass seems very promising as an adsorbent in terms of its affinity towards phenol, it was investigated from litterature[11] that there was scope for its improvement by upgrading the thermo-chemical treatment so as to bring its properties near to that of commercial grade carbon to make it more economical. The improved adsorbent (CANBI) has best fixed carbon content, phenol number, iodine number, methylene blue value, BET surface area and particle size for using it for adsorption of phenol.

SEM analysis performed on PBAN, activated PBAN and CANBI, established that CANBI is morphologically the most improved adsorbent.

Based on CANBI emerging as the most improved adsorbent, it became focus of study. Effects of various parameters like adsorbent dosage, pH, contact time, agitation speed, initial phenol concentration on sorption was studied and the results obtained were used for further analysis of equilibrium, kinetic and thermodynamic studies. Adsorption equilibrium model of Langmuir, Freundlich, Temkin and Dubinin Radushkevich were tested for their fit into experimental data and it was found that they all fitted quite well within phenol concentration range of 0 to 975mg/l. Kinetic data represented pseudo second order kinetics better. All the analysis performed indicated that CANBI has favourable and better affinity for phenol. Also regeneration test for one step was conducted with 1M NaOH, KOH, HCl, H_2SO_4 and HNO_3. For all these chemicals regeneration of adsorbent was more than 90%. Present elaborative study on CANBI is to establish it as more promising adsorbent for phenol commercially.

Experimental

Preparation of Improved Char of Acacia Nilotica Branches (CANBI)

The powder of acacia nilotica branches, preparation of which is explained in earlier[10] section was taken to activate it. The powder was soaked in 30 % H_3PO_4 for 4 hrs with agitation at temperature of 35˚C. The resultant slurry was filtered and washed thoroughly to bring its pH to 7. The sample was oven dried and kept for charring at 600˚C in the muffle furnace for 3hrs. The dried sample was digested with 10 % NaOH solution for 4hrs at 70ºC. The residue was filtered out, washed thoroughly and dried. The dried sample was passed through 250 mesh screen. Obtained sample was stored for further studies.

Characterization of CANBI

Activated carbon obtained as above was subjected to various ways of characterization by adopting the standard procedures[12-15]. The adsorption characteristics were studied in terms of phenol number (the amount of powdered carbon required for 90% removal of phenol), iodine number and methylene blue number of the adsorbent. The surface area of the activated carbon was carried by nitrogen adsorption method (Quantachrome BET surface area analyser**).** The properties of adsorbents under study are shown in Table 1.

Batch Experiment

For adsorption study batch experiments were done (for initial phenol concentration of 1g/l) as per already published work by present authors[10]. To optimize carbon dosage, pH of adsorbate-adsorbent system, contact time, initial phenol concentration and rpm of shaker, the adsorbent was equilibrated with phenol solutions for 24 hours at 225 rpm. The adsorption data of CANBI were fitted in various mathematical models like Langmuir, Freundlich, Temkin and D-R isotherms. Study of effect of time on adsorption, imparted kinetic study. Here data were fitted in kinetic models of pseudo-first order and pseudo-second order. To test the phisibility of adsorption, thermodynamic parameters, ΔS, ΔH, and ΔG were determined. The obtained carbon (CANBI) was also subjected to desorption tests with 1 M of NaOH, KOH, HCl, H_2SO_4 and HNO_3 at 25˚ C for 7hrs at rpm of 225 with carbon dosage of 1.5.

Table 1: Properties of Adsorbents

Properties	ANB [10]	Activated PBAN[10]	CANBI (Present Study)
Ash Content on dry basis (%)	2.73	1.6	1.3
Fixed Carbon on dry basis (%)	23.80	71.5	85.0
Volatile Matter on dry basis (%)	73.46	27	13.7
pH of slurry	6.3 (0.25%)	6.3 (1.75%)	7.1(1.5%)
Phenol Number (g)	-	1.4	1.0
Iodine Number ($mg.g^{-1}$)	493	680	866
Surface Area ($m^2.g^{-1}$)	54	298	403
Particle Size (μm)	78.463	56.727	47.01
Methylene Blue Adsorption (mg/g)	45	90	150

Results and Discussions

Characterization of Adsorbent

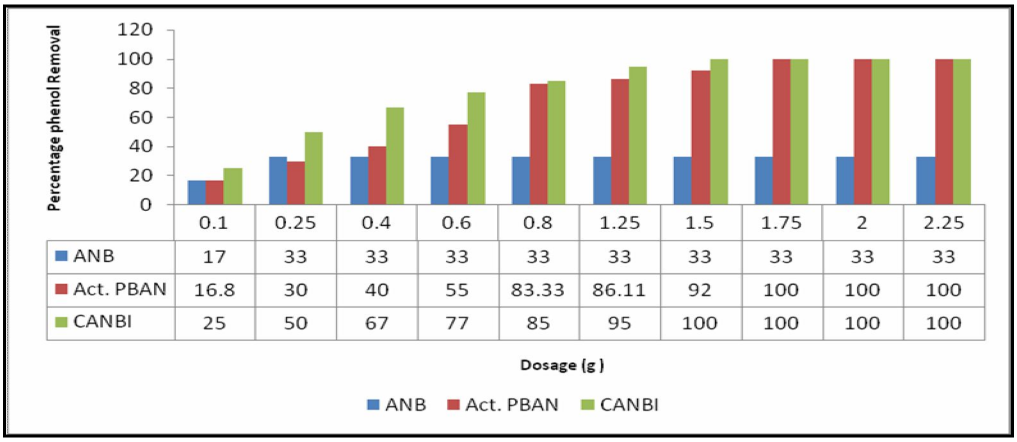


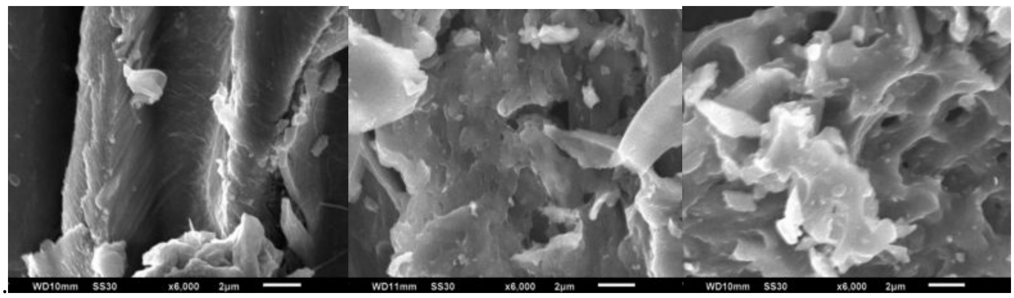
Fig.1 Comparison of Percentage Phenol Removal from various forms of Adsorbents

Table1 clearly shows that CANBI is much better adsorbent than ANB and activated PBAN due to its increased percentage of Fixed Carbon (F.C.) compared to activated PBAN and decreased percentages of Volatile Matter (V.M.) and Ash on dry basis. CANBI has better iodine number, B.E.T. surface area, particle size and methylene blue adsorption values compared to that of ANB and activated PBAN indicating that CANBI is best adsorbent for further study. Phenol Number (i.e., adsorption of 90 % phenol) takes place at lower amount of CANBI making it more economical than PBAN and activated PBAN which is also evident from Fig.1.

Fig.1 also indicates that percentage phenol removal is highest for CANBI at all dosages of adsorbent ranging from 0.1(g) to 1.5(g) indicating CANBI is the most improved adsorbent.

Scanning Electron Microscopy Analysis

The surface morphologies of PBAN, Activated PBAN and CANBI were investigated using 'JEOL JSM-6610LV'. By comparing SEM micrographs of these adsorbents in Fig.2(a), (b) and (c), it was found that CANBI has the most porous and rough morphology, clearly justifying its highest BET surface area of 403 m^2/g (as shown in Table 1)



(a) (b) (c)

Fig.2: SEM micrographs of (a) PBAN (b) Activated PBAN (c) CANBI

Effects of various Parameters on Adsorption Study on CANBI

As CANBI has emerged as most improved adsorbent, the focus was on study of various parameters on the process of adsorption, for further studies.

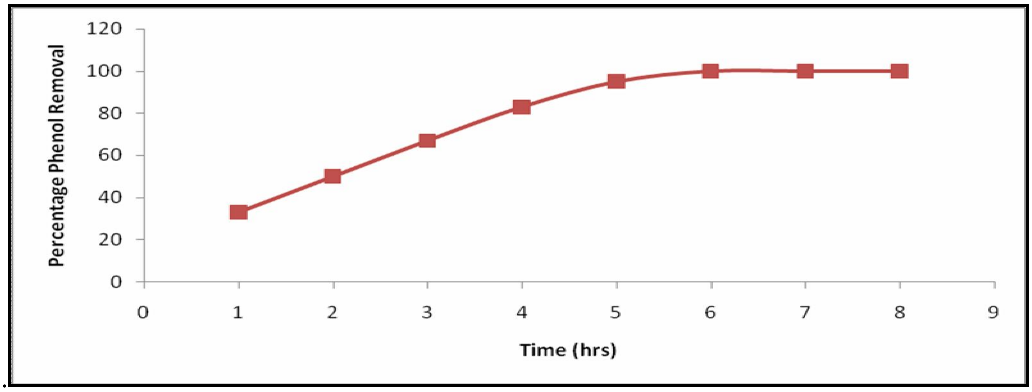


Fig.3: Effect of Contact Time on adsorption of CANBI

Effect of Carbon Dosage

Fig.1 shows the percentage of phenol removal with adsorbent dosage from the aqueous solution at pH of 7.1(found to be optimum). The solution was equilibrated for 24 hours. To remove the entire amount of phenol (with initial phenol concentration of 1g / litre), the minimum amount of CANBI dosage required was determined to be 1.5g.

Effect of Contact Time

Effect of contact time on the removal of phenol by CANBI is shown in Fig.3.The optimum pH was taken at 7.1 for fixed amount of adsorbent as 1.5g. The study reveals that 6 hour as equilibrium time for adsorption of phenol by CANBI.

Effect of Initial Phenol Concentration

Percentage phenol removal by CANBI was studied for initial phenol concentration in the range of 250 mg/l to1000 mg/l with contact time for 6hrs (equilibrium time) at pH of solution at 7.1. It was found that percentage phenol removal was constant at the value of 100%.

Effect of agitation speed

The agitation speed was studied between 50 to 250 rpm for CANBI (as shown in Fig.4). When contact time of 6hrs was kept at pH 7.1 and temperature 25°C, the percentage phenol removal increased to 100 % at 200 rpm from that of 50 % at 50 rpm. Percentage removal of phenol remained constant at 100 % till 250 rpm.

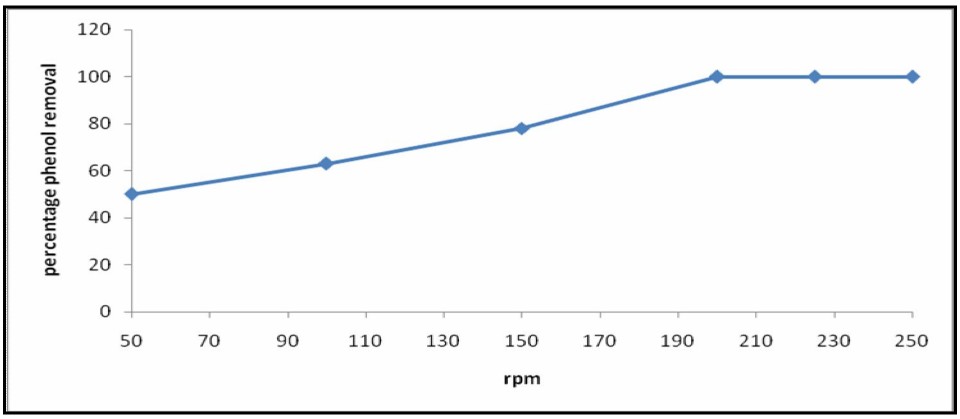


Fig.4: Study of Effect of agitation speed on percentage phenol removal

Adsorption Isotherms

Adsorption isotherm were studied experimentally as explained in Experimental Section under Batch Experiments, by taking 100 ml of phenol solution with 1g/l concentration for 24 hours, at 25°C with agitation speed of 225 rpm. Maximum adsorption capacity of this adsorbent is 250 mg/g as indicated in Fig.5. This capacity is much higher than that of PBAN and activated PBAN (already studied and published by the authors) as confirmed from Table 2. This indicates values of maximum adsorption capacity of various biomass based adsorbents and it is interesting fact that CANBI is having better adsorption capacity than most of the reported values.

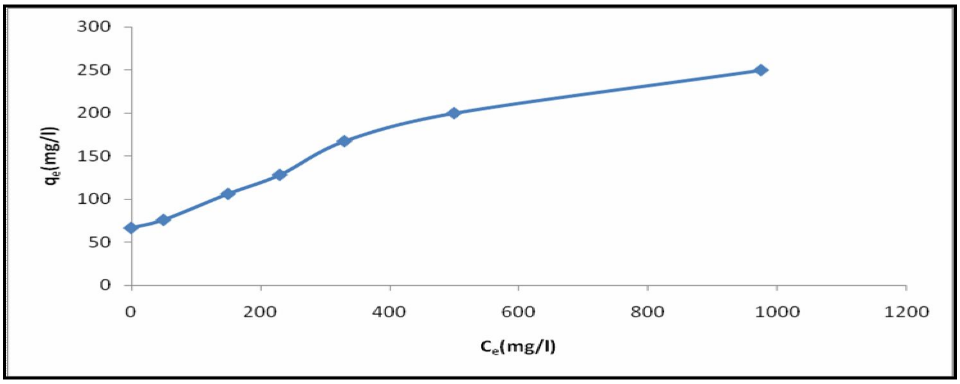


Fig.5: Adsorption Isotherm of CANBI

Table 2—Adsorption capacities of various biomass for phenol removal from aqueous solutions

Adsorbent	**Adsorption Capacity (mg/g)**
Plum Kernel[16]	257.80
Sheensham sawdust[17]	337.49
Date stones[18]	43.27
Pecan shells[19]	167.00
Coconut shell[20]	191.00
Bagasse fly ash[21]	16.90
Bagasse[22]	308.00
Rice-Husk[23]	150.00
Millet straw[24]	80.36
Sorghum straw[24]	82.34
PBAN[10]	132.00
Activated PBAN[10]	167.00
Hazelnut bagasse[25]	81.18
Bamboo charcoal[26]	24.96
Rubber seed coat[27]	56.00
Avocado kernel seeds[28]	87.50
Jute fibers[29]	180.00
Sugarcane baggasse[30]	27.00
Beet pulp[31]	90.00
CANBI (Present Work)	**250.00**

Adsorption isotherm data (as shown in Fig.5) were also analysed by fitting into Langmuir, Freundlich, Temkin and Dubinin Radushkevich mathematical models[32,33]. Adsorption kinetics were also analysed by fitting into pseudo-first and pseudo-second order kinetic models.

Langmuir Isotherm[13]

This isotherm is based on the assumption that adsorption process takes place on a homogeneous surface with monolayer of adsorbate.

The linear form of Langmuir isotherm is given as:

$1/q_e = \left(\frac{1}{Q0bCe}\right) + \left(\frac{1}{Q0}\right)$ …(1)

Where, q_e represents the amount of adsorbate, adsorbed per unit mass of adsorbent, C_e represents equilibrium concentration (mg/l) of supernatant solution, Q_0 monolayer adsorption capacity (mg/g) of adsorbent, and b surface energy (g/l) corresponding to the process of adsorption. Values of b and Q_0 are found from slope and intercept of plot of $1/q_e$ vs $1/C_e$.

The Langmuir adsorption isotherm gives separation factor R_L which indicates the nature of adsorption process (shown in Table 2) and expressed by following equation [34]**:**

$R_L = 1/ (1+b\ C_i)$ …(2)

Table 3 shows adsorption data fitted quite well for concentration range of 230 mg/l to 975 mg/l in Langmuir isotherm model with $R^2>0.95$. As per values of intercept and slope, value of R_L is 0.4 which lies between 0 and 1, confirming that the adsorption process to be favourable. Here b value comes out to be 0.0015g/l which represents low surface energy, indicating stronger bonds between phenol and adsorbent[35]**.** Fairly low to moderate b values have been reported in many of sorbent-phenol systems[6, 7, 15].

Freuendlich Isotherm[13]

The linear form of Freundlich equation can be expressed by

$\ln q_e = \ln k + 1/n \ln C_e$ …(3)

Where, k [(mg/g). $(l/g)^{1/n}$] and n are the measures of adsorption capacity and intensity of adsorption. Qe is the amount of phenol adsorbed per unit mass of adsorbent and C_e is the equilibrium concentration in mg/l.

Plot of ln q_e vs ln Ce gives values of k and n from slope and intercept. Adsorption of phenol on activated carbon obeys Freundlich isotherm for almost entire concentration range as indicated by very high R^2 values (>0.95) in Table 3. Here values of k and n calculated from slope and intercept are shown in Table 3 indicating very good affinity for phenol towards CANBI in the entire concentration range. Also value of n comes out to be 2.38 indicating it is satisfying the condition of heterogeneity[36] i.e., 1<n<10 as well as 0<1/n<1.

Temkin Isotherm[10]

Temkin isotherm is represented by:

$q_e = B \ln A + B \ln C_e$ …(4)

Where A (l/g) and B (dimensionless) = RT/b_1 are Temkin constants which is found from slope and intercept of the plot q_e versus ln C_e. Here b_1 ($Jmol^{-1}$) is constant which gives heat of sorption. Values of Temkin constants are given in Table 3.

The values of R^2, A and b_1 showed that model highly favoured the adsorption of phenol on CANBI in the concentration range of 150 mg/l to 975 mg/l of phenol.

Dubinin Radushkevich Isotherm

Dubinin Radushkevich model[37] was applied to determine characteristic porosity of the biomass and apparent energy of adsorption

Linearized form of Dubinin Radushkevich equation is:

$\ln q_e = \ln q_m - \beta \varepsilon^2$ …(5)

Here β ($mmol^2J^{-2}$) is D-R constant; ε (Jmmol-1) is Polanyi potential and

$\varepsilon = RT \ln (1+1/C_e)$ …(6)

Here R (8.314 J mol^{-1} K^{-1}) is universal gas constant, T (K) is temperature. β is related with free energy of adsorption per mole of adsorbate as it migrates to the surface of biomass from infinite distance in the solution. Plot of ln q_e versus ε^2 for phenol concentration range of 230 mg/l to 975 mg/l gives values of q_m and β from slope and intercept values (shown in Table 3).

Porosity parameter value β for CANBI towards phenol was less than unity indicating sorption of phenol was significant. Value of q_m = 249 mg/g supports the experimental value. R^2 value > 0.97 indicated that this model fitted experimental adsorption data under study.

Table 3—Comparison of Adsorption Isotherm Constants

Equilibrium Isotherm	Equilibrium Constants	CANBI	Activated PBAN[10]
Langmuir	Q_0 (mg/g)	500	250
	b (g/l)	0.0015	4
	R^2	0.965	0.998
	R_L	0.4	0.00025
Freundlich	**k** [(mg/g). $(l/g)^{1/n}$]	13.93	23.48
	n	2.38	4.46
	R^2	0.980	0.994
Temkin constants	A (l/g)	0.024	0.16
	b_1($Jmol^{-1}$)	31.20	113.65
	R^2	0.991	0.994
Dubinin Radushkevich	β ($mmol^2 J^{-2}$)	0.007	0.063
	q_m (mg/g)	249	282
	R^2	0.979	0.942

Adsorption Kinetics

For measuring adsorption efficiency, kinetics of adsorption is required to be analysed. This study gives solute uptake rate. The dosage of 1.5 g of CANBI was taken in phenol solution (1g/l) of 100 ml. The adsorbent was separately exposed to phenol solution for different times till equilibrium was achieved. The amount of phenol adsorbed was estimated between 60 minutes to 360 minutes.

Pseudo-First-Order Kinetics

Lagergren model was used to study the pseudo first order kinetics [38-39] integrated form of which is given as:

$$\log (q_e-q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \ldots(7)$$

Where q_e (mg/g) and q_t (mg/g) refers to the amounts of phenol adsorbed on CANBI at equilibrium and time, t (min) respectively. Here k_1 (min^{-1}) refers to rate constant.

Thus the rate constant (k_1) can be obtained from the slope of plots of log (q_e-q_t) vs t. Value of R^2>0.9 confirming the fitting of data in Lagergren model. Pseudo first order kinetic constants as per calculations (shown in Table 4) are q_e = 108.39 mg/g and k_1= 0.0092min^{-1}.

Pseudo-Second-Order Kinetics

Adsorption data were also studied for second order kinetics[38]**.**The mathematical model after integration is given as given below:

$$t/q_t = 1/(k_2 q_e^{2}) + t/q_e \quad \ldots(8)$$

Where k_2 (g/mg.min) refers to the rate constant, q_e as phenol adsorbed per gram of adsorbent at equilibrium and q_t as phenol adsorbed per gram of adsorbent at any time t.

Eq.8 can also be expressed as below:

$t/q_t = 1/h + t/q_e$ …(9)

The plot of t/q_t vs t gives linear relationship with correlation coefficient R^2=0.95.Hence the data got fit to Pseudo-Second-Order Kinetics quite well. Values of kinetic constants are given in Table 4

Table 4: Comparison of Adsorption Kinetic Constants

Adsorption Kinetics	Kinetic Constants	CANBI	Activated PBAN[10]
Pseudo first order model	q_e (mg/g)	108.39	79.80
	k_1 (min^{-1})	0.0092	0.0046
	R^2	0.922	0.950
Pseudo second order model	q_e (mg/g)	125	-
	H (mg/g.min)	0.408	-
	R^2	0.953	0.711

Adsorption Thermodynamics

The batch experiments were performed by varying the temperature from 298 to 318 K with fixed initial concentration of 1g/l at pH 7.1 and adsorbent dosage of 1.5g/l of CANBI. The equilibrium sorption of phenol was better at higher temperatures and this could be attributed to increase in molecular diffusion or expansion of pores.

Thermodynamic parameters such as free energy (ΔG°), enthalpy(ΔH°) and entropy(ΔS°) change of biosorption can be evaluated from the following equations[40]:

$\Delta G^\circ = -RT\ln K_d$ …(10)

Where R is the gas constant (8.314 J $mol^{-1}K^{-1}$), T is the temperature (K) and K_d is the equilibrium constant. The value of K_d was calculated using Eq. 11.

$K_d = q_e / C_e$ …(11)

Where q_e and C_e are equillibrium concentrations of phenols and in the solutions respectively.

Also we know that

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ …(12)

From Equationss (10), (11) and (12)

$\ln K_d = (\Delta S^\circ/R) - (\Delta H^\circ/RT)$ …(13)

A plot between ln K_d versus 1/T is shown in Fig.6 for the adsorbent. The values of (ΔH°) and (ΔS°) can be calculated from slope and intercept respectively and value of (ΔG°) can be calculated from Eq.12 which is (-966.744J/mol). Negative value of ΔG° confirms the spontaneity of the process. Value of ΔH° is 74252.33 J/mol, indicating that the process be endothermic. Value of ΔS° is 252.413 J/mol which shows increased randomness at the solid-solution interface.

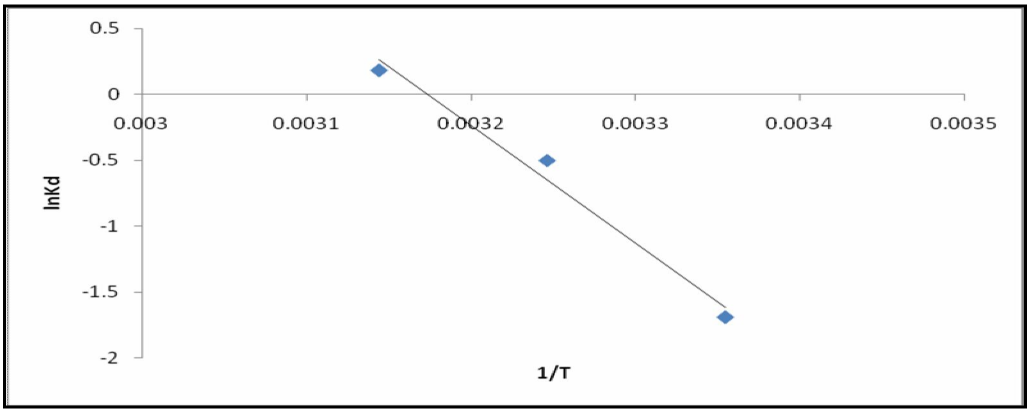


Fig 6: Plot of ln k_d vs 1/T

Regeneration of CANBI

Regeneration of adsorbent is an important aspect from economics point of view. Attempts were made to desorb phenol from CANBI with various acidic and basic eluents. This desorption process was performed using the batch process using 1.5g of spent adsorbent at pH of 7.1 and was shaken at 25°C and 225 rpm with 100 ml of 1M NaOH, KOH, HCl, H_2SO_4 and HNO_3 which was completed in 7 hrs duration. About 93, 83, 92, 90, 92 % of adsorbed phenol respectively was desorbed in a single step from initial concentration of 1g/l of phenol solution respectively. Although the achievement of arsenic and strong acidic elution have been reported in literature[41], the present work showed that effective regeneration was obtained with both strong acidic and basic solution.

Conclusion

This study indicates that CANBI is quite an improved adsorbent based on various physical and chemical characteristics comparable to a good commercial adsorbent.SEM analysis confirmed its highest BET surface area of 250m^2/g. This fact has also been verified by its highest adsorption capacity of 250 mg/g compared to other adsorbents. Freundlich isotherm fitted quite well the experimental data for almost entire concentration range of phenol under study. Value of R_L deduced to be 0.4 indicating favorable adsorption of phenol. Adsorption isotherm data fitted quite well to various concentration ranges under study for Langmuir, Temkin and Dubinin-Radushkevich models indicating that phenol has very good affinity towards CANBI. Kinetics of adsorption was better explained by pseudo-second-order kinetics. Thermodynamic study on adsorption indicated that the process was phisible and endothermic in nature. CANBI proved to be regenerative by more than 90 % by various strong basic and acidic eluents. Hence CANBI has proved to be quite improved and cost effective adsorbent for removal of phenol.

Acknowledgement

The authors are grateful to Dr. S. S. Bhatnagar University Institute of Chemical Engineering & Technology, Punjab University, Chandigarh and IIT, Ropar for helping them to get BET surface area and SEM analysis done on the required samples.

References

1. Mostafa MR, Sarma SE, Yousef AM, Adsorption of Phenol by Activated Carbon. Indian J. Chem. ,1989 28A; 94-98.
2. El-Geundi : M.S., Adsorbents for Industrial Pollution Control., Assorp Sci Technol., 1997, 15;777-787.
3. Remenárová L, Pipiíška M, Florková E, Homik M, Rozložnik M, Augustin J: Zeolites from coal fly ash as efficient sorbents for cadmium ions, Clean Techn Environ Policy ,2014, 16;1551-1564.
4. Kummar S, Upadyay SN and Upadyay YD, Removal of phenols by adsorption on fly ash., J.Chem. Technol. Biotechnol, 1987, 37; 281-290.

5. Street M, Patrick JW and Parez MJ, Sorption of Phenol and p-chlorophenol from Water using Convention and Novel Activated Carbons, Water Sci. Res, 1995, 29(2); 467-572.
6. Banat FA, Al-Bashir B, Al-Asheh S and Hayajneh O, Adsorption of Phenol by Bentonite, Environmental Pollution, 2000, 107;391-398.
7. Rengaraj S, Seunny- hyeon M and Sivabalan R, Agricultural Solid Waste for the Removal of Organics, Adsorption of Phenol from Water and Wastewater by Palm Seed Coat Activated Carbon. Waste management ,2002, 22;543-548.
8. Nagda GK, Diwan, AM, Ghole, VS, Potential of tendu leaf refuse for phenol removal in aqueous systems, Applied Ecology and Environmental Research ,2007, 5(2) ;1-9.
9. Amin MM, Mustafa AI, Khalil MI, Rahman M, and Nahid I, Adsorption of phenol onto rice straw bio waste for water purification, Clean Techn Environ Policy ,2012, 14; 837-844.
10. Dass Bhajan & Jha Pushpa, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 2015, 4; 1361-1372.
11. Jha Pushpa, Biomass Characterization and Application of Biomass Char for Sorption of Phenol from Aqueous Solutions, PhD Thesis, Indian Institute of Technology, Delhi, 1996.
12. Iyer P V R, Rao T R, Grover P D, Biomass Thermo-Chemical Characterization, (Chemical Engineering Department, IIT Delhi), 2002, 45.
13. Srihari V, Das A, Applied Ecology and Environmental Research, 2009, 1;13
14. ASTM International, D4607-94, 2011.
15. Siggia S, Quantitative Organic Analysis via Functional Groups, (3rd edn, John Wiley & Sons, New Jersey), 1967, 54.
16. Juang R. S., Wu F-C., Tseng R-L, Mechanism of Adsorption of Dyes and Phenols from Water Using Activated Carbons Prepared from Plum Kernel, Journal of Colloid and Interface Science, 2000, 227; 437-444.
17. Mubarik S., Saeed A., Mehmood Z., Iqbal M., Phenol adsorption by charred sawdust of sheesham (Indian rosewood; Dalbergia sissoo) from single, binary and tertiary contaminated solution, Journal of Taiwan Institute of chemical Engineers, , 2012, 43 ; 926-933.
18. Dhidan S. K., Removal of Phenolic compounds from aqueous solutions by adsorption onto activated carbon prepared from date stones by chemical action with $FeCl_3$, Journal of Engineering, 2012, 18(1); 63-77.
19. Shawabkeh R. A., Abh-Namesh E. S. M., Absorption of phenol and Methylene Blue by Activated Carbon from Pecan Shell, Colloid Journal, 2007, 69; 355-359.
20. Mohd Din A. T., Hameed B. H., Ahmad A. L., Batch adsorption of phenol onto physiochemical-activated coconut shell", Journal of Harzardous Materials , 2009,161 ; 1522-1529.
21. Srivastava V. C., Swamy M. M., Mall I. D., Prasad B., Mishra I. M., Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics, Journal of Colloids and Surfaces A: Phsicochem. Eng. Aspects, , 2006, 272 ; 89-104
22. Juang R-S., Wu F-C., Tseng R-L., Characterization and use of activated carbons prepared from bagasse for liquid-phase adsorption, Journal of Colloids and Surfaces, 2002, 201; 191-199.
23. Jha P., Rice Husk as Adsorbent for Phenol Removal, International Journal of Science and Nature, 2011, 2(3) ; 593-596.
24. Lawal A. O., Lori J. A., Tuker D. T., Removal of Phenol from Water by Carbon Adsorbents Prepared by Pyrolysis of Sorghum and Millet Straws in Ortho Phosphoric Acid, Research journal of Egineering and Earth Sciences, 2011,3(4); 429-432.
25. Karabacakoglu B., Tümsek F., Demiral H., Demiral İ., Liquid phase adsorption of phenol by activated carbon derived from Hazelnut Bagasse, J. Int. Environmental Application & Science., (2008), 3(5); 373-380.
26. Yan MA., Naiyun GAO., Wenhai CHU., Cong LI ., Removal of phenol by powdered activated carbon adsorption, Front. Environ. Sci. Eng., (2013),7(2); 158-165
27. Rengaraj S., Moon S-H., Sivabalan R., Arabindoo B., Murugesan V., Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat, J. Hazardous Materials , 2002 , Vol. B89; 185-196.
28. Rodrigues L. A., Da Silva M. L. C. P., A-M M. O. A., Coutinho A. R., Thim G. P., Phenol removal from aqueous solution by activated carbon produced from avocado kernel seeds, Journal of Chemical Engineering, 2011, 174; 49-57.

29. Phan N. H., Rio S., Faur C., Coq L. L., Cloirec P. L., Nguyen T. H., Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications, Carbon, 2006, 44; 2569-2577.
30. Karunarathne H. D. S. S., Amarasinghe B. M. W. P. K. , Fixed bed adsorption column studies for the removal of aqueous phenol from activated carbon prepared from Sugarcane Bagasse, Energy Procedia., 2013,34; 83-90.
31. Duesun G., Çiçek H., Dursun A. Y., Adsorption of phenol from aqueous solution by using carbonized beet pulp, Journal of Harzardous Materials, 2005, B125; 175-182.
32. Mahvi, A.H., Maleki, A. and Eslami, A., Potential of Rice-Husk and Rice-Husk Ash for Phenol Removal in Aqueous Systems, American Journal of Applied Sciences ,2004, 1: 321-326.
33. Wang XS, Qin Y: Equilibrium sorption isotherm for of Cu^{2+} on rice bran. Process Biochem 2005, 40; 677-680.
34. Weber TW and Chakravorti RK: Pore and Solid diffusion model for fixed bed adsorbent. J.Am.Inst. Chem. Engg. ,1974, 2; 228-238.
35. Aksu Z and Yener J: A comparative adsorption/biosoption study of monochlorinated phenols onto various sorbent, Waste management, 2001, 21; 695-702.
36. Khalid N, Ahmad S and Toheed, A Potential of Rice-Husk for Antimony Removal, Applied Radiation and Isotopes, 2000, 52 ; 30-38.
37. Choudhary S, Saha PD, Bio sorption kinetics, thermodynamics and isosteric heat of sorption of Cu (II) *onto Tamrindus indica seed powder*, Colloids and Surfaces B: Bio interfaces , 2011, 88: 697-705.
38. Tseng RL, Wu FC and Juang RS, Liquid-phase adsorption of Dyes and Phenols using Pinewood Based Activated Carbons, Carbon , 2003, 41: 487-495.
39. Chiou MS and Li HY, Adsorption Behaviour of Reactive Dye in Aqueous Solutions on Chemical Cross Linked Chitosan Beads. Chemosphere ,2003, 50; 1095-1105.
40. Kilic M., A-V E., Pütün. A. E., Adsorption removal of phenol from aqueous solutions on activated Crbon prepared from tobacco residues: Equilibrium, kinetics and thermodynamics, Journal of Hazardous Materials, 2011, 189; 397-403.
41. Lorenzen L, Deventer JSJV, Landi W M, Factors affecting the mechanism of the adsorption of arsenic species on activated carbon, Miner Eng.,1995,8; 557-569.

*****