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Adsorption of Acid Blue 74 Onto a New Low-Cost, Non-Conventional Adsorbent: Sorption Equilibrium and Kinetic Studies

KEYWORDS: Adsorption isotherms, Acid Blue 74, Kinetic, models, Activated carbon

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ABSTRACT *Liquid phase adsorption of acid dye Acid Blue 74 on a mesoporous activated carbon obtained from cotton boll pod has been investigated and the maximum adsorptive capacity was determined. BET surface area of the activated carbon was determined as 781.42m2.g-1 and SEM observations showed the amorphous nature of the carbon. Langmuir, Freundlich, Halsey, Dubinin–Radushkevich (D–R), Tempkin and Harkins–Jura isotherms were used to analyze the equilibrium data at different temperatures. The time dependent kinetic studies have been done under the limelight of pseudo first and second order mechanism to predict the rate constants. The rates of adsorption were confirmed to pseudo-second-order kinetics with good correlation. The results indicate that the cotton boll pod activated carbon could be used to effectively adsorb Acid Blue 74 from aqueous solutions and is also economically viable.*

1. Introduction

Dye contamination exists in aqueous waste streams of many industries, such as textiles, paper, plastics, leather, food, cosmetics, etc. which use dyes or pigments to color their final products. Dyes along with other auxiliary chemicals are recognized as the highest relative mammalian toxic and continued usage causes environmental pollution. Hence, the removal of dyes from aqueous solutions is extremely important. The methods of color removal from industrial effluents include biological treatment, coagulation, flocculation, adsorption, oxidation and hyper filtration[1]. Among the treatment options, adsorption is a highly effective, proven and economical method to remove dyes from aqueous solutions. Activated carbons, with their high surface area, porous structure and chemical nature of their surface, are potential adsorbents for the removal of different dyes from industrial wastewaters[2].

The high cost of the commercial activated carbon, coupled with the problems associated with efficiency, selectivity and regeneration, has necessitated the search for alternate adsorbents. Therefore, there is a need to produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale[3].

Cotton boll pod, an undesirable agriculture mass residue, is a byproduct of the cotton harvest. It is one of the most important agricultural residues which is available in large quantities at no cost and can form a good basis for the development of adsorbent materials[4] The goal of this study was to investigate the dye removal efficiencies of the activated carbon produced from cotton boll pod. The adsorption of dyes onto activated carbon was studied in batch equilibrium conditions. The kinetic and equilibrium data on batch adsorption studies were carried out to understand the adsorption process. The influences of various parameters such as temperature, dye structure and adsorbent surface area on the adsorption process were also determined statistically.

2. Materials and methods

2.1 Preparation of adsorbent

Cotton boll pods, agro-waste was collected from nearby cotton fields as solid wastes. The collected materials were then washed with distilled water several times to remove all the dirt particles. The washed materials were cut into small pieces (1-3 cm) and dried in a hot air oven at 70°C for 24 h. Activated carbon was prepared by impregnating of the precursor with Zinc chloride 60(50 vol.%) followed by carbonization at 850°C for 1 h in a purpose made tubular muffle furnace. A constant nitrogen (purity 99.99 %) flow of 150 mL/min was maintained throughout the process of carbonization. Chemical activation was preferred over physical activation owing to the lower temperatures[5] and shorter time needed for activating material. The cooled activated mass was subjected to thorough washing with distilled water, so as to get rid of extra catalyst. The activated carbon was dried in a hot air oven at 110°C, ground and sieved to obtain the desired particle size (180-250 microns) and stored in desiccators for further use.

2.2 Adsorbate preparation:

In this study a commercially available textile dyestuff namely acid blue 74 is used as adsorbate. The dye is widely used in textile industries. The selected dyestuff is a dye contaminant in the discharged effluents commonly used in dye houses.

Stock solution of dye was prepared by dissolving 1gm of dye in 1000ml of double distilled water to give the concentration of 1000mg/L. The stock solutions were diluted with known initial concentrations say 20, 40, 60 and 80mg/L in accurate proportions.

2.3 Batch adsorption Equilibrium studies

Test solution of desired concentration of dye was prepared from fresh stock solution. Adsorption experiments were carried out by adding a fixed amount of sorbent (0.50 g) into a number of 100mL stoppered glass Erlenmeyer flasks containing a definite volume (50mL in each flask) of different initial concentrations (10–200 mg/L) of dye solution at pH 5.5 and at three different temperatures of 30°C, 45°C and 60°C. The flasks were placed in a thermostatic water-bath shaker and agitated at 150rpm for 200 min to ensure equilibrium was reached. At time t = 0 and at equilibrium, the dye concentrations were measured using a double beam UV–vis spectrophotometer (Milton Roy, Spectronic 21D). Prior to the adsorption measurement, a calibration curve was obtained by using the standard AB74 solution with known concentrations. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

Amount adsorbed (q_e) = [($C_0 - C_e$) V]/M ..... (1)

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of dry sorbent used.

Volume : 3 | Issue : 7 | July 2013 | ISSN - 2249-555X

3. Results and discussion

3.1. Properties of activated carbon

Important properties of the prepared activated carbon which affect their adsorption characteristics were determined [5]. The results show that the prepared ACBPC possesses surface area S_{BET} 781.42 m^2/g, total pore volume V_{total} as 0.03135 cm^3/g in which micro pore volume V_{mic} as 0.031352 cm^3/g, meso pore volume V_{meso} as 0.031352 cm^3/g and BJH pore radius of 26.602A° **.** It is clear from the results that the cotton ball pod activated carbon has higher meso porosity and larger BET surface area.

3.2 Adsorption isotherm models

Isotherm studies explain most of the surface properties and affinity of the adsorbent for a particular adsorbate during adsorption which is critical in optimizing the usage of adsorbent[6]. To understand the mechanism of AB74 adsorption onto ACBPC single solute systems, the results obtained were tested with linear forms of 5 different two parameters isotherm equations namely Langmuir, Freundlich[7] Tempkin[8], Halsey[9], Harkins–Jura[10] , isotherm and D-R isotherm models[11], respectively. The model equations are shown below (Equations 2-7):

$$q_e = Q_m K_L C_e / (1 + K_L C_e) \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

$$q_e = \beta \ln K_T C_e \quad (4)$$

$$q_e = \exp[(\ln K_H - \ln C_e)/n] \quad (5)$$

$$q_e = [A_{HJ}/(B_{HJ} + \log C_e)]^{1/2} \quad (6)$$

$$q_e = q_{DR} \exp(-K_{DR}\beta^2) \quad (7)$$

where is q_e the adsorption capacity in equilibrium (mg g^{-1}), C_e is the sorbate equilibrium concentration (mg L^{-1}), K_L (L mg^{-1}) is the Langmuir constant associated to energy of adsorption and Q_m denotes the theoretical monolayer adsorption capacity (mg g^{-1}). $K_F$is the Freundlich constant (mg g^{-1})(L $mg^{-1})^{1/n}$ while 1/n represents dimensionless heterogeneity factor. β is the Tempkin constant related to heat of adsorption (kJ mol^{-1}). K_T is the equilibrium binding constant (L mol^{-1}) corresponding to the maximum binding energy, AHJ and BHJ are Harkins–Jura isotherm parameter and constant, K_H and n are the Halsey isotherm constant and exponent, q_{DR} is the D-R isotherm constant (mg g^{-1}), ε represents the Polanyi potential constant (kJ^2 $kmol^{-2}$) is given as $RT \ln(1+1/C_e)$, R is the universal gas constant, T is the absolute temperature (K) and K_{DR} (mol^2 kJ^{-2}) indicates the activation energy, E (kJ mol^{-1}) of adsorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution, where $E = 1/\sqrt{2K_{DR}}$. Prior to equilibrium data plotting, all model equations were linearized accordingly.

From the studies, "L (or Langmuir) shape" isotherms were obtained which means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent sites.

The fitness of each isotherm equation to the experimental data obtained was evaluated using linear coefficient of determinations, R^2 as an error function and the values are presented in table 1. The highest values of R^2 were obtained when the experimental data were fitted into Langmuir isotherm equation.

Table- 1: Results of isotherm plots for the adsorption of AB74 onto ACBPC

Model	Constant	Temperature, K		
		303	318	333
Langmuir	Q_m(mg g^{-1})	92.8673	93.1695	96.8184
	K_L*10^{-3}(L mg^{-1})	0.0989	0.1104	0.1224
	R^2	0.9919	0.9974	0.9967
Freundlich	n	2.0958	2.3373	2.3550
	K_F(mg g^{-1})(L $mg^{-1})^{1/n}$	12.8729	14.8463	16.1274
	R^2	0.9608	0.9364	0.9428
Tempkin	β(kJ mol^{-1})	16.4907	17.2781	17.6853
	K_T(L mg^{-1})	1.5996	1.6524	1.9115
	R^2	0.9715	0.9806	0.9702
DU-RA	K_{DR}X10^{-4}(mol^2 kJ^{-2})	9.7261E-06	8.4177E-06	5.6318E-06
	Q_m(mg g^{-1})	57.3043	59.1092	60.0763
	R^2	0.6985	0.6905	0.6404
Harkin-Jura	E	0.0015	0.0014	0.0012
	A	289.0864	298.7391	312.0314
	b	1.6233	1.5941	1.5524
	R^2	0.5256	0.5254	0.5520
Halsy	N	2.0958	2.3373	2.3550
	K_h(mg g^{-1})	211.6833	547.6033	697.8842
	R^2	0.9608	0.9364	0.9428

According to Table 1, a linear regression coefficient of Langmuir isotherm indicates a strong correlation between the experimental data and the model. However, the data seem to be less in agreement with other models where the R^2 values were less than 0.99level.

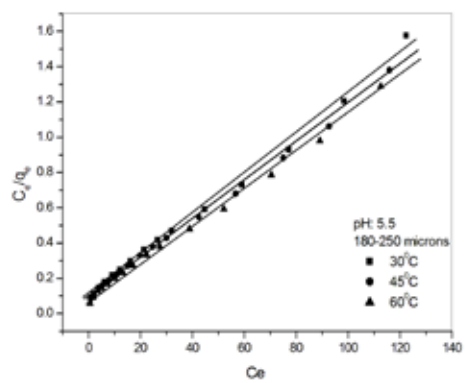

Fig.1. Langmuir adsorption model for AB74 onto ACBPC

The sorption result of AB74 onto ACBPC by the Langmuir isotherm equations is a pointer to: (i) the monolayer coverage of the sorbate on a sorbent surface at constant temperature, (ii) homogeneity of the surface of the ACBPC. The values of maximum adsorption capacity 92 to 96 mg/g determined using Langmuir model was almost nearer to the experimental adsorbed amount (≈89 mg/g), which shows the higher fitness to this model. From table 1, higher value of b representing the affinity of sorbate to sorbent (L/mg) parameter of the Langmuir model shows higher affinity of sorbate to sorbent. R_L values between 0.0 and 1.0 at different concentrations indicate favorable adsorption of AB74 onto ACBPC. However, the Freundlich isotherm model, based on multilayer adsorption, described the data fairly well (R^2 = 0.93–0.96). The Freundlich adsorption constants (K_F) obtained from the linear plot were fall between 12.87 and 16.12mg/g. From table 1, the Freundlich coefficient (*n*), values ranging from 1 to 10, (2.09 –2.33), supports the favorable adsorption of AB74 onto the adsorbent.

Volume : 3 | Issue : 7 | July 2013 | ISSN - 2249-555X

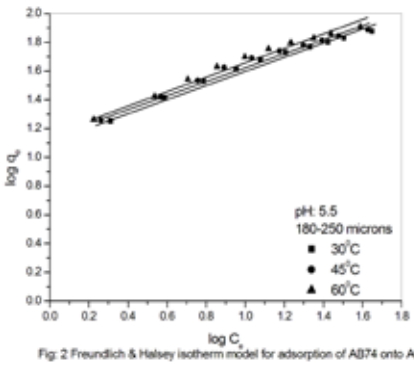

Fig: 2 Freundlich & Halsey isotherm model for adsorption of AB74 onto ACBPC

Tempkin(Fig. 3), linear plotting at 303, 318 and 333 K results β values indicative of the heat of adsorption onto ACBPC is 16.4907, 17.2781, and 17.6853 kJ/mol respectively and was positive which indicates that the adsorption reaction is endothermic. The Tempkin model shows a strong conformation to experimental data judging on satisfactorily values shows the strong interaction between acid blue 74 molecules and the adsorbent surface.

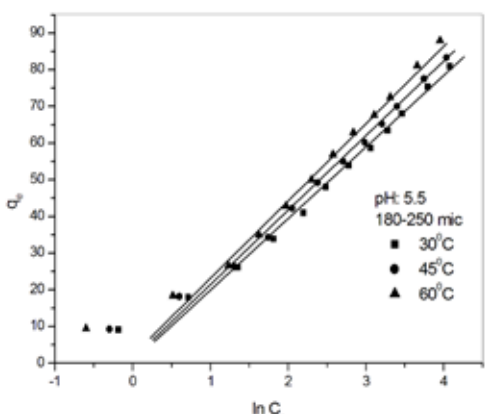

Fig:3 Tempkin adsorption model for AB74 onto ACBPC

As can be seen in Table 1, the values of linear regression coefficient for Harkins-Jura model (Fig. 4), were in the order of 0.5 which are very high in comparison with other models. Similarly Hasley could not describe the sorption of AB74 onto ACBPC acceptably, because this model also assumes a multilayer behavior for the sorption of a sorbent onto adsorbent. This reveals that Harkins-Jura and Hasley model could not describe the experimental isotherm data in clarity and hinders the possibility of explaining the adsorption of AB74 onto ACBPC solemnly by assumption of multilayer adsorption phenomena.

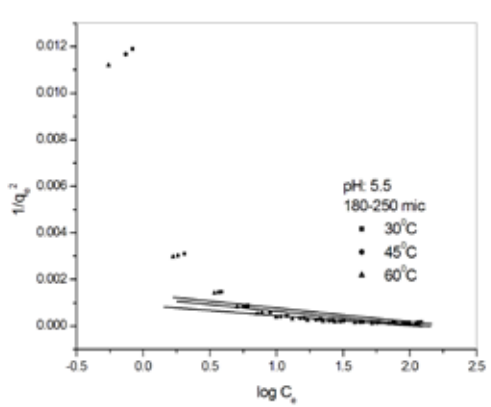

Fig:4 Harkin-jura adsorption model for AB74 onto ACBPC

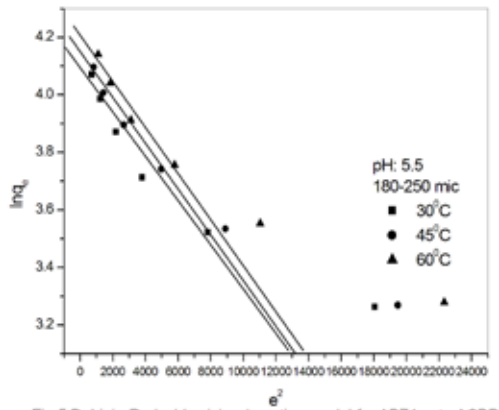

Fig:5 Dubinin-Radushkevich adsorption model for AB74 onto ACBPC

As shown in Table 1, Dubinin-Radushkevich model, provides better agreement with experimental data in comparison with Tempkin, Freundlich , Halsey and Harkins-Jura models. From the Dubinin-Radushkevich model linear plot (Fig. 5), the values of K_{DR} less than unity implies that ACBPC consists of fine meso pores and the observed surface heterogeneity may be arisen from the pore structure as well as adsorbate-adsorbent interaction. However, the model is not able to describe the experimental data properly because of the poor linear Correlation.

The comparison of Dubinin-Radushkevich and Langmuir models maximum monolayer capacity show that Langmuir models reveals a better agreement with experimental data than Dubinin- Radushkevich. Langmuir parameter (q_m) was 92.86 mg/g which is more close to experimental capacity in comparison with corresponding Dubinin- Radushkevich parameter (q_{DR}) which is almost one and a half times of the experimental capacity. Consequently, Langmuir better explained the acid blue 74 sorption on ACBPC experimental data than Dubinin-Radushkevich model.

These findings are very important to indicate that ACBPC might have major homogenous and minor heterogeneous surface energy distributions which include the possibility of single and multilayer adsorption.

3.3 kinetic adsorption models

Kinetic models are useful for the design and optimization of effluent treatment models which describes the rate of adsorption and this rate controls the equilibrium time. Pseudo first order and pseudo second order kinetic models were analyzed for the mechanism of AB74 adsorption by ACBPC.

3.3.1 Pseudo first order model:

The adsorption data fitted to the simple pseudo-first-order equation as suggested by Lagergren[12], and further cited by Ho et al[13], and Ho[6], that describes the process of adsorption is

$$dq_t/dt = k_1(q_e - q_t) \quad \text{----------} \quad (8)$$

The integrated linear form of the model is

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303\ t \quad \text{----------} \quad (9)$$

where q_e is amount of dye adsorbed at equilibrium(mg/g), q_t is amount of dye adsorbed at time t(mg/g), k_1 is rate constant for first order adsorption (min^{-1}). A plot of $\log(q_e - q_t)$ versus time gives a linear line from which the values of k_1 and q_e can be determined from the slope and intercept respectively.

Volume : 3 | Issue : 7 | July 2013 | ISSN - 2249-555X

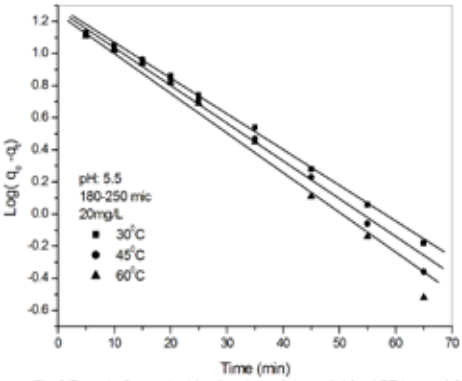

Fig:6 Pseudo first order kinetic adsorption model for AB74 onto ACBPC

In most of the cases, the first-order Lagergren equation is generally applicable over the initial 20–30 min of the sorption process and not applied satisfactorily throughout the complete range of contact time. It is evident from the figure 6, after a short initial contact time there was a considerable deviation in the plots of $\log(q_e - q_t)$ versus "time" from the theoretical data. The q_e values calculated from the plots are lower than the experimental one in Table 2. Therefore, it may be concluded that present adsorbent systems do not follow a first-order rate equation.

Table -2: Results of kinetic plots for the adsorption of AB74 onto ACBPC

Temperature	30°C	45°C	60°C
Pseudo-first order kinetics			
K_1 x 10^{-2}(1/min)	5.4720	6.064	7.1260
$q_e$exp(mg/g)	17.9574	18.1741	18.3220
$q_e$cal(mg/g)	20.7486	21.8766	25.7398
r^2	0.9899	0.9895	0.9667
Pseudo-second order kinetics			
K_2 x10^{-3}(g/mg min)	3.9222	4.4014	4.9129
$q_e$exp(mg/g)	17.9574	18.1741	18.3220
$q_e$cal (mg/g)	19.5357	19.7964	19.7985
h	1.4969	1.7249	1.9257
r^2	0.9964	0.9954	0.9972

3.3.2 Pseudo second order model:

The rate of adsorption for pseudo second order model[14] is

$$dq_t / dt = k_2(q_e - q_t)^2 \quad \text{---------- (10)}$$

The linearised form of the above model is

$$t / q_t = 1 / k_2 q_e^2 + t / q_e \quad \text{---------- (11)}$$

where q_e is amount of dye adsorbed at equilibrium(mg/g), q_t is amount of dye adsorbed at time t(mg/g), k_2 is rate constant for second order adsorption (g/mgmin^{-1}). A plot of t/q_t versus t should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot respectively.

From Table 2 the correlation coefficient R^2 for this linear plots are superior (in all cases > 0.9950), and its calculated equilibrium adsorption capacity $q_{e(cal)}$ is consistent with the experimental data. These suggest that the pseudo second-order adsorption mechanism is more operative and that the overall rate of the dye adsorption process appears to be predominantly controlled by the chemisorption process[14].

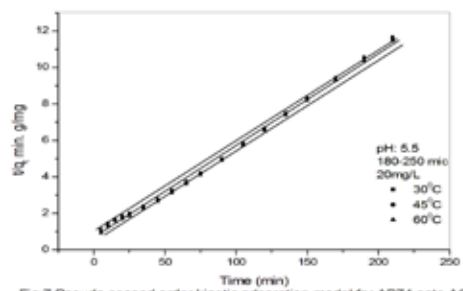

Fig:7 Pseudo second order kinetic adsorption model for AB74 onto ACBPC

According to the pseudo-second order model, the adsorption rate dq/dt is proportional to the second order of $(q_e - q_t)$. The adsorption capacities q_t of AB74 at 90min for almost all the temperature reached over 85% of the calculated equilibrium adsorption capacities $q_{e,cal}$ in Table 2. This is evident that the carbon in our experiments had very high equilibrium adsorption capacity q_e, the adsorption rates became very fast and the equilibrium times were short, indicating a high degree of affinity between the dyes and the carbon[15].

CONCLUSION

The dynamic data indicated that prepared meso porous activated carbon was suitable for AB74, primarily due to its high adsorption capacity and with the molecular size of the dye molecule. The contact time process could be adequately fitted by the pseudo second-order equation for the sorption system. The adsorption isotherms of dye could be described well by the Langmuir equation.

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