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REMOVAL OF ACID BLUE 92 FROM AQUEOUS SOLUTION USING *MORINGA OLEIFERA* FRUIT SHELL WASTE: OPTIMIZATION AND KINETIC STUDIES

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ABSTRACT
A carbonaceous adsorbent prepared from an indigenous *Moringa oleifera* fruit shell waste by carbonate treatment process was tested for its efficiency in removing Acid Blue 92 (AB 92). Adsorption of AB 92 on the *Moringa oleifera* fruit shell waste showed the highest value around pH 4.0 and followed the pseudo second order kinetic model. The adsorption equilibrium was represented with Langmuir and Freundlich isotherms. To identify whether the ongoing process is particle diffusion or film diffusion, the treatment given by Boyd and Reichenberg was employed. Thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) were studied, and the adsorption process of AB 92 was found to be endothermic and spontaneous.
Keywords: *Moringa oleifera* fruit shell waste, Activated Carbon, Acid Blue 92, Kinetics, Isotherm, Particle diffusion, Film diffusion.

INTRODUCTION

Synthetic dyes have been excreted in the wastewater from different industries, particularly from paper, textile, plastic, rubber, drug and cosmetic food industries which used dyes to color their products. It is reported that over 1, 00,000 commercially available dyes exist and the global annual production of synthetic dyes is more than 7x 10^5 metric tones[1]. These dyes are discharged into the water bodies after usage in large quantities by all the above industries. AB 92 is one such effluent which causes various disorders when present in aqueous solution. Hence the treatment of waste water containing AB 92 is a challenging problem.

Adsorption using activated carbon is one of the efficient procedures for the treatment of wastewater[2]. Several low cost carbon and non-conventional adsorbents were used as activated carbons for this process. The adsorbents were prepared by Olive Stones[3], *Pongamia pinnata*[4], Cashew nut sheath[5], *Jatropha curcas*[6,7], Rice hulls[8], *Feronia limonia*[9], *Balsamodendron caudatum*[10],eucalyptus bark[11] etc. In the present work the low cost, high value activated carbon prepared using *Moringa oleifera* fruit shell waste was used for the adsorption of Acid Blue 92. Three simplified kinetic models including pseudo first order, pseudo second order and Elovich equations were used to describe the adsorption process.

EXPERIMENTAL

Preparation of activated carbon

Moringa oleifera fruit shell waste is collected and it was dried and cut into small pieces, the pieces were then impregnated in a potassium carbonate solution of known concentration for 24 hours. Then the resultant mass was washed with excess quantity of water and dried at 110 ^oC for 1 hour. Carbonization of the sample was carried out at 650 ^oC in a temperature programmable furnace under N_2 atmosphere. At the end of carbonization, the material in the furnace was left to cool down to ambient temperature under the

same N_2 flow rate. The carbon sample thus obtained was washed with pure distilled water and dried in the oven at 120 ^oC and then finely grinned.

Kinetic Models

In order to investigate the mechanism of sorption and potential controlling steps such as mass transport, several kinetic models were tested including the pseudo first order kinetic model, the Elovich model and the pseudo second order kinetic model for a batch contact time process, where the rate of sorption of dye on to the given adsorbent is proportional to the amount of dye sorbed from the solution phase.

Pseudo First Order Kinetic Model

A simple kinetic analysis of adsorption, the pseudo first order kinetics and its integrated form, is given by Lagergren[12]-

$$\log (q_e-q_t) = \log q_e - k_1/2.303 \quad (1)$$

Where k_1 is the pseudo first order rate constant. A plot of $\log (q_e-q_t)$ vs time enables calculation of the rate constant k_1 and q_e from the slope and intercept of the plot.

Elovich Model

The Elovich or Roginsky – Zeldovich equation[13] is generally expressed as follows-

$$dq_t / dt = \alpha\exp(-\beta q_t) \quad (2)$$

On integrating this equation for the boundary conditions,

$$q_t = (1/ \beta)\ln (\alpha\beta) + (1/ \beta)\ln t \quad (3)$$

Where, α and β are the initial dye adsorption rate (mg/g) and desorption constant (g/mg) respectively are obtained from the slope and intercept of linear plot of q_t vs ln t.

Pseudo Second Order Kinetic Model

To describe the dye adsorption, the modified pseudo second order kinetic equation[14] is expressed as-

$$t / q_t = (1 / k_2 q^2_e) + (1 / q_t (t)) \quad (4)$$

Where, k_2 is the pseudo second order rate constant. A plot of t/q_t vs t enables calculation of the rate constant k_2 which in turn is used to calculate the initial sorption rate h as follows-

$$h = k_2 q^2_e \quad (5)$$

Adsorption Thermodynamics

Any chemical system tends to attain a state of equilibrium from one of non-equilibrium. The thermodynamic parameters, which characterize the equilibrium of the system, are the Gibbs free energy change ΔG, the enthalpy change ΔH and the entropy change ΔS. These parameters were determined using the following relations[15]-

$$K_c = C_{Ae} / C_e \quad (6)$$

$$\Delta G = -RT\ln K_c \quad (7)$$

$$\log K_c = (\Delta S / 2.303R) - (\Delta H / 2.303RT) \quad (8)$$

Where K_c is the equilibrium constant, C_{Ae} is the solid phase concentration at equilibrium, C_e is the residual concentration at equilibrium, R is the gas constant in J/mole and T is the temperature in Kelvin.

RESULTS AND DISCUSSION

Optimum pH for adsorption

The effect of pH for the adsorption of AB 92 on to activated carbon over a pH range of 2 to 11 is represented in Fig. 1. The uptake of AB 92 decreased when the solution pH was increased from 2 to 11. The uptake of AB 92 by activated carbon was increased from pH 2 to 4 and then decreased. The interaction between the sorbate and sorbent is affected by pKa of dye as well as the isoelectric point (pH_{PZC}) of the adsorbent[16]. The pKa value of AB 92 is 3.2. Below the isoelectric point (pH_{PZC} = 8.2), the electrostatic repulsion between the adsorbed molecules is minimized, resulting in a maximum adsorption. At pH below 8.2, the surface of the adsorbent may acquire a positive charge leading to an increased anionic dye adsorption due to electrostatic attraction. At pH above the pH_{PZC} the adsorbent surface acquires a negative charge, which repels the negative anionic dye molecules. On increasing the pH, the added NaOH increases the ionic strength, which also makes more competition for adsorption sites, hence, the adsorption decreases.

Effect of initial concentration on kinetic rate constants and rate parameters

The batch adsorption studies were performed at 30 °C and at pH 4.0. 50 mg of adsorbent was mixed with known initial concentration (20, 30, 40 mg/L) of AB 92 solution and agitated. The rate constants and rate parameters at different initial dye concentrations are presented in Table- 1 showed that the rate constants decreased with better increase in initial dye concentration. An analysis of the data reveals that the influence of the initial concentration of AB 92 has very little influence on the pseudo second order rate constant. It also reveals that the influence of the initial concentration of AB 92 on the Elovich and Pseudo first order rate constant is neither appreciable nor very little (Fig. 2a, 2b, 2c).

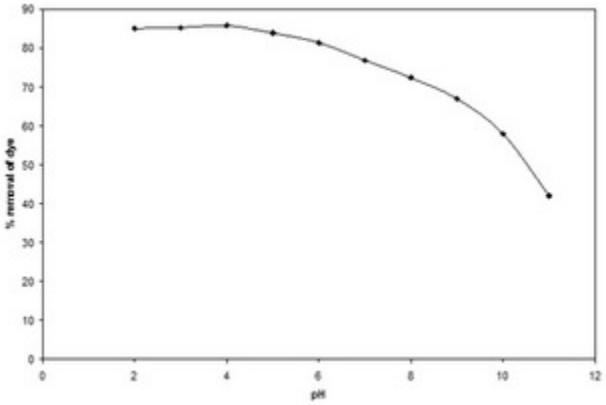
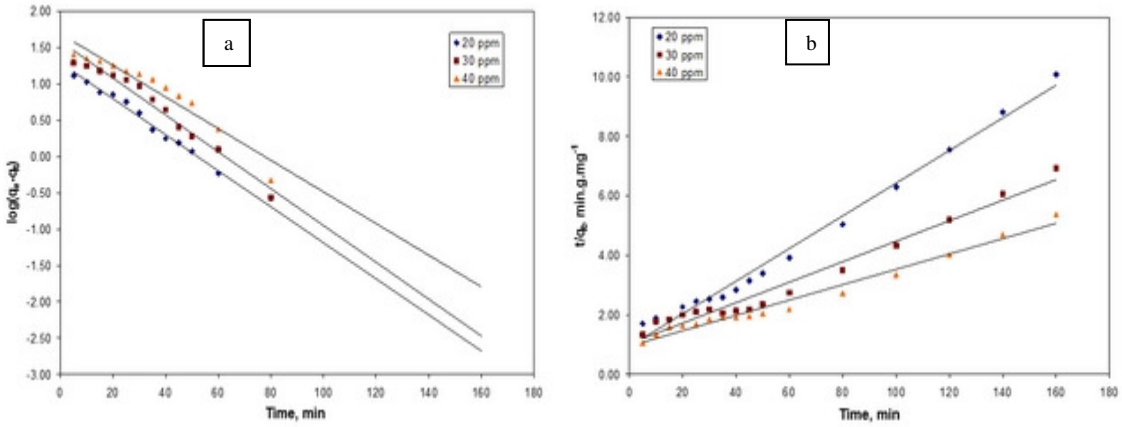


Fig.- 1: Influence of pH on Acid Blue 92 Adsorption



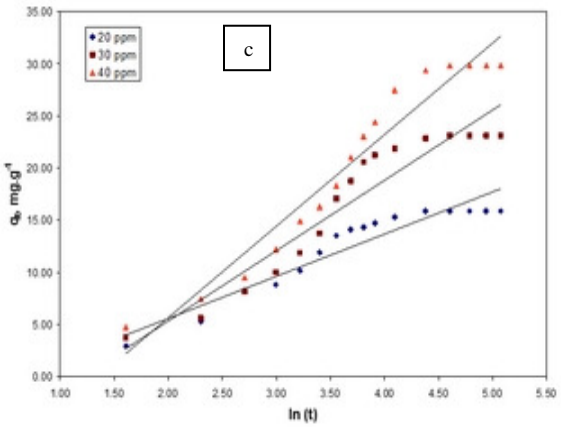


Fig.-2(a), (b), (c): Pseudo first order plot, Pseudo second order plot, Elovich plot for Initial Concentration variation

Effect of Temperature on kinetic rate constants and rate parameters

The temperature effect on the biosorption capacity of dried *Moringa oleifera* fruit shell waste was examined at 30, 45 and 60 °C using initial dye concentration of 20 mg/L at pH 4 and is shown in Fig. 3a, 3b, 3c. From the slope of the linear trace, the rate constants were calculated and the results are presented in the Table- 2. The data obtained separately for each of the kinetic models from the slopes of plots show a better compliance with the pseudo second order equation, the R^2 values for the linear plots being greater than 0.985 showed that the kinetic data fitted best with pseudo second order kinetic equation.

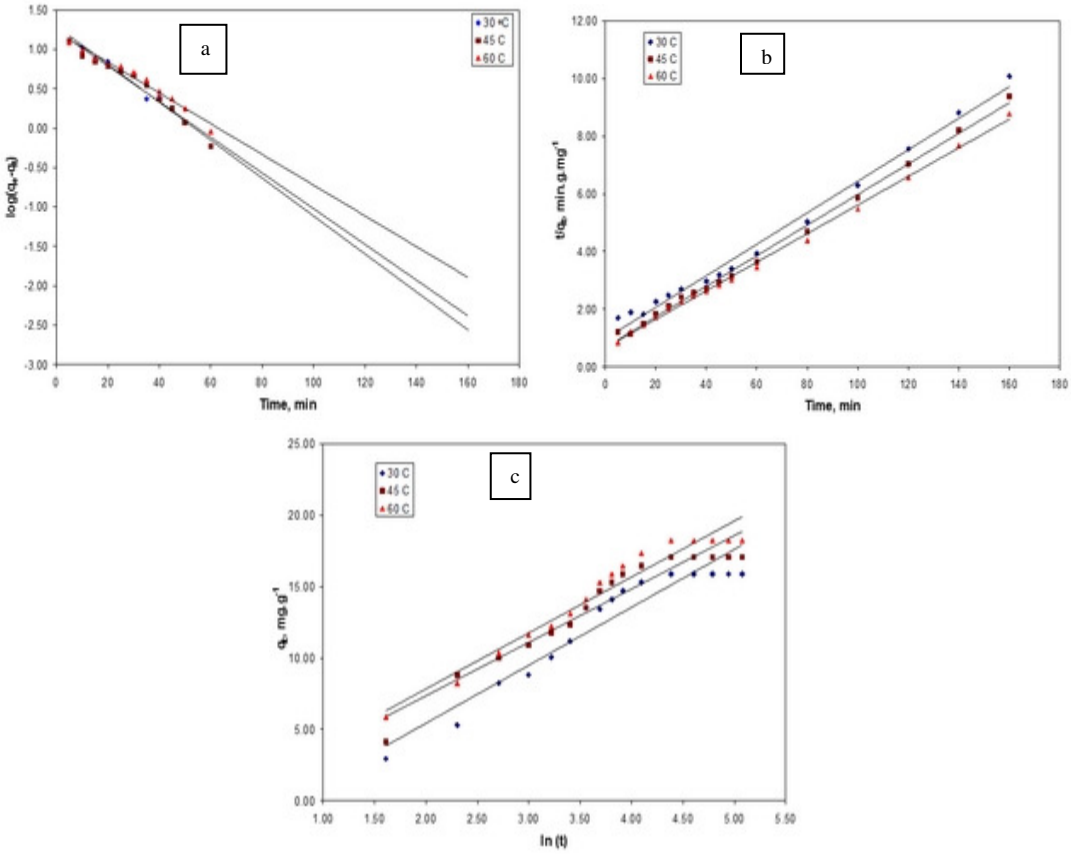


Fig.- 3(a), (b), (c): Pseudo first order plot, Pseudo second order plot, Elovich plot for Temperature variation

Mechanism for sorption of AB 92 on to *Moringa oleifera* fruit shell waste

The mathematical treatment as suggested by Boyd et al. and Reichenberg [17, 18] was used to identify whether the ongoing process is particle diffusion or film diffusion. These mathematical models also helped in determining the mechanism of the undergoing process. An established fact is that when a solid chemical substance adsorbs over the porous adsorbent, three types of diffusion processes takes place in following three consecutive steps[19]-

1. Transport of the ingoing adsorbate ions to external surface of the adsorbent (film diffusion),
2. Transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion) and
3. Adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent.

The third step is very fast and cannot be considered as a rate-determining step, while for the adsorption carrying out via remaining two steps, the following three possibilities exist.

Case 1: External transport > internal transport, where rate is governed by particle diffusion.

Case 2: External transport < internal transport, where the rate is governed by film diffusion.

Case 3: External transport = internal transport, which accounts for the transport of the adsorbate ions to the boundary and may not be possible within a significant rate, which later on gives rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

To investigate the actual process involved in the present adsorption, the quantitative treatment of the sorption dynamics was founded in accordance with the observation of Reichenberg[18], as described by the following equation-

$$F = 1 - \frac{6}{\pi^2}\sum_{N=1}^{\infty}\frac{1}{n^2}exp\left(\frac{-Dit\pi^2n^2}{r^2}\right) \quad (8)$$

$$F = 1 - \frac{6}{\pi^2}\sum_{N=1}^{\infty}\frac{1}{n^2}exp[-n^2\beta_t] \quad (9)$$

Where F is the fractional attainment of equilibrium at time t and is obtained by using following equation and n is the adsorption intensity of the adsorbate.

$$F = q_t / q_e \quad (10)$$

Where q_t and q_e are the amounts adsorbed at time t and at equilibrium respectively.

Table-1: Kinetic Model Values for the Effect of Initial concentration variation of Acid Blue 92 on to *Moringa oleifera* fruit shell waste Activated Carbon

Concentration	Pseudo First Order Values		Elovich Values			Pseudo Second Order Values			
	k_{Lager} x $10^{-2}min^{-1}$	r^2	α mg $g^{-1}min^{-1}$	β g^{-1}	r^2	q_e mg g^{-1}	k_2 x10^{-3} g $mg^{-1}min^{-1}$	h mg g^{-1} min^{-1}	r^2
20 ppm	0.0587	0.9705	2.09	0.2446	0.901	18.31	3.064	1.027	0.9875
30 ppm	0.0516	0.9561	2.034	0.1486	0.9058	28.90	1.173	0.9797	0.9696
40 ppm	0.0417	0.9539	2.264	0.1144	0.9477	38.76	0.653	0.9810	0.9763

On the basis of F values, the corresponding values of B_t were obtained from Reichenberg's Table[18] and the linearity test was carried out by plotting B_t with respect to time for the solutions at different time intervals and at 30°C, 45°C and 60°C. The linearity test of B_t versus time plot drawn for different temperatures is employed to distinguish between film diffusion and particle diffusion. From the slope of the straight line obtained from time versus B_t graph, the B value (time constant) was calculated. The

values of the effective diffusion coefficient (D_i) were calculated at different temperatures using the following equation-

$$B = \pi^2 D_i / r^2 \quad (11)$$

Table-2: Kinetic Model Values for the effect of Temperature on Acid Blue 92 adsorption on to *Moringa oleifera* fruit shell waste Activated Carbon

Concentration	Pseudo First Order Values		Elovich Values			Pseudo Second Order Values			
	k_{Lager} x 10^{-2}min^{-1}	r^2	α mg g^{-1}min^{-1}	β g^{-1}	r^2	q_e mg g^{-1}	k_2 x10^{-3} g mg^{-1}min^{-1}	h mg g^{-1} min^{-1}	r^2
30 ^oC	0.0587	0.9705	2.090	0.2446	0.901	18.81	3.064	1.027	0.9875
45 ^oC	0.0520	0.9663	3.673	0.2683	0.9272	18.87	4.16	1.48	0.9964
60 ^oC	0.043	0.9788	3.611	0.2505	0.988	20.32	3.436	1.42	0.9964

Here r is the radius of adsorbent particle. The D_i values are given in the Table- 3.

The plot of 1/T versus log D_i was found linear with negative slope indicating thereby the increase in the mobility of the ions. This is due the fact that with the rise in temperature the mobility of the ion increases, which consequently decreases the retarding force acting on the diffusing ions. The values of energy of activation E_a, entropy of activation $\Delta S^{\#}$ and pre exponential constant D_o were calculated using the following equations-

$$D_i = D_o exp\left[\frac{E_a}{RT}\right] \quad (12)$$

$$D_o = 2.72d^2\frac{kT}{h}exp\left[\frac{\Delta S^{\#}}{R}\right] \quad (13)$$

Where d is the average distance between the successive exchange sites and is taken as 5A^o R, h and k are the gas, plank and Boltzmann constants respectively. The values of E_a, D_o, $\Delta S^{\#}$ and other parameters are given in the Table- 3. The negative values of $\Delta S^{\#}$ reflect that no significant change occurs in the internal structure of choosing adsorbent using the adsorption process.

Table-3: Values of energy of activation E_a, entropy of activation $\Delta S^{\#}$, pre-exponential constant (D_o), Diffusion Coefficient (D_i) for the present study

S.No.	Parameter	Value
1.	D_i, cm^2 s^{-1}	
	30 ^oC	6.493x10^{-7}
	45 ^oC	7.1144x10^{-7}
	60 ^oC	7.454 x10^{-7}
2.	E_a, kJmol^{-1}	3.877
3.	D_o, cm^{2}s^{-1}	3.044x10^{-6}
4.	$\Delta S^{\#}$, J K^{-1}mole^{-1}	-79.463

Thermodynamic Parameters

ΔH and ΔS values were obtained from the slope and intercept of Van't Hoff plot (In $K_c$vs 1/T). A batch adsorption study was carried out with AB 92 solution at pH ≈4.0 and by varying the temperature (303K, 318K and 333K).The initial concentration of AB 92 solution used was maintained to be 20 mg/L with 50 mg of the absorbent. Table- 4 gives the value of ΔG, ΔS and ΔH for the adsorption of AB 92.The

negative values of free energy change (ΔG) indicate the feasibility and spontaneous nature of the adsorption of AB 92 species. The positive ΔH values of the process suggest the endothermic nature of the absorption of AB 92 onto activated *Moringa oleifera* fruit shell waste carbon. The positive value of ΔS is due to the increased randomness during the adsorption of AB 92.

Table-4: Thermodynamic parameters for the adsorption of Acid Blue 92 on to *Moringa oleifera* fruit shell waste Activated Carbon

Temperature	ΔG, kJ $mole^{-1}$	ΔS, J $mole^{-1}K^{-1}$	ΔH, kJ $mole^{-1}$
303 K	-1.433	89.05	21.72
318 K	-6.802		
333 K	-7.825		

CONCLUSION

In the present study, adsorption of AB 92 on *Moringa oleifera* fruit shell waste activated carbon has been investigated. The data obtained through this work supports that the *Moringa oleifera* fruit shell waste activated carbon is an effective low cost adsorbent for the removal of AB 92 from aqueous solution. The adsorption of AB 92 is dependent on the initial concentration and agitation time. Equilibrium of AB 92 adsorption reaches at 160 min. The pseudo first and second order equations provide a best fit description for the sorption of AB 92 on to *Moringa oleifera* fruit shell waste activated carbon, but the pseudo second order correlation coefficient has better correlation value than pseudo first order equation, pseudo second order equation is considered to be the most appropriate due to high correlation coefficient.

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