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Removal of Dyes from Aqueous Solution using Low Cost Activated Carbons Derived from *Moringa Oleifera* Fruit Shell Waste

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Abstract

The purpose of this study is to suggest an efficient process, which does not require a big investment for the removal of dye from wastewater. Activated carbon developed from agricultural waste material were characterized and utilized for the removal of dye from water. Systematic studies on dyes adsorption equilibrium and kinetics by low cost activated carbons were carried out. Adsorption studies were carried out at different temperatures, particle size, pH and adsorbent doses. Both Langmuir and Freundlich models fitted the adsorption data quite reasonably. The results indicate that the Langmuir adsorption isotherm model fits the data better as compared to the Freundlich adsorption isotherm model. Plausible mechanism was established for dye adsorption on developed adsorbent. Further, the data are better correlated with linear regression form of each model. The kinetics studies were conducted to delineate the effect of temperature, initial adsorbate concentration and particle size of the adsorbent. The adsorption of dye follows the pseudo second order rate kinetics. On the basis of these studies, various parameters such as effective diffusion coefficient, activation energy and entropy of activation were evaluated to establish the mechanisms. It is concluded that the adsorption occurs through a particle diffusion mechanism at temperature 30 ^{0}C to 60 ^{0}C.

Keywords: *Acid Blue 92; Activated carbon; Adsorption; Isotherm; Kinetics; Moringa Oleifera fruit shell waste.*

1. INTRODUCTION

Many industries use dyes and pigments – such as those involving textiles, dying and paper-making discharge large amounts of colorful dye materials in their wastewater. The textile industry, which is one of the largest water consumers in the world, produces waste water composed of various recalcitrant agents such as dye, sizing agents and dyeing aids, that should be of concern in releasing into the environment. The dye precursors and degradation products are proven carcinogenic and mutagenic in nature (Kalyuzhnyi *et al*.2001). It is estimated that 10-20% of dye produced is lost into wastewater during textile dyeing process (Graca *et al.* 2001). The largest class of dyes used at present is referred to as acid dyes, which are anionic compounds mainly used for dyeing nitrogen containing fabrics like wool, polyamine and silk (Wijetunga *et al.* 2007).

Various methods have been used for the treatment of dye-containing wastewater including biological treatment, adsorption, chemical oxidation, coagulation and reverse osmosis (Wang *et al.* 2006; Gupta *et al.* 2004). Adsorption using activated carbon is one of the efficient procedures for treatment of waste water. Cellulosic and Lignocellulose wastes have long

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been recognized as starting materials for the preparation of activated carbon (Dean *et al.* 1972, Mukherjee, 1986). Commercial activated carbons are expensive and their use requires elaborate regeneration and reactivation procedure (Karthikeyan *et al.* 2007). Several low cost carbon and non conventional adsorbents have been used. Adsorbents used include fly-ash (Nagarnaik *et al.* 2003; Kelleheri *et al.* 2002), Wollastonite (Swamy *et al.* 1998; Sharma, 2001; Saravanan *et al.* 2002) Saw dust and rice husk with coir pith carbon (Namasivayam *et al.* 2000), Pomegranate Peel (Murugan *et al.* 2003), *Feronia Limonia(L)* Single Wood (Karthikeyan and Sivakumar, 2012) etc.

The moringa tree is grown mainly in semi-arid, tropical and subtropical areas corresponding in the United States USDA hardiness zones. It grows best in dry sandy soil, it tolerates poor soil, including coastal areas. It is a fast-growing, drought resistant tree. India is the largest producer of moringa, with an annual production of 1.1 to 1.3 million tones of tender fruits. Andhra Pradesh leads both in area and production followed by Karnataka and Tamilnadu. Mature seeds of the fruit yield 38-40% edible oil called ben oil. *Moreinga oleifera* seed oil finds extensive medicinal application but the disposal of fruit shell is a challenging task because it cannot be degraded easily. The objective of the present work is to report the results of the feasibility study of utilizing *Moringa olifera* fruit shell waste as an adsorbent for the removal of Acid Blue 92 in aqueous solution.

2. MATERIALS & METHODS

2.1 Preparation of adsorbent

Moringa Oleifera fruit shell waste is collected and it was dried and cut into small pieces, the pieces were then impregnated in potassium carbonate solution of known concentration for 24 hours. Then the resultant mass was washed with excess quantity of water and dried at 110 °C for 1 hour. Carbonization of the sample was carried out at 650 °C 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 °C and then finely grined.

2.2 Chemical and reagents

A stock solution of 1000 mg/L of Acid Blue 92 was prepared by dissolving 1 g of dye in 1000 mL of double distilled water and used for further studies by diluting as concentrations required. The properties of dye Acid Blue 92 is represented in Table 1. The working solutions were obtained by diluting the dye stock solution to the required concentrations. The pH of solutions was adjusted with 0.1 M concentrations of HCl and NaOH, using a pH-meter.

Table 1. Properties of Acid Blue 92

Parameters	Value
C. I. Name	Acid Blue 92
C. I. Number	13390
Ionization	Anionic
Molecular Formula	$C_{26}H_{16}N_3Na_3O_{10}S_3$
Molecular Weight	695.58

2.3 Batch adsorption experiments

The batch adsorption studies were performed at 30 °C. 100 mg of adsorbent was mixed with known initial concentration (20, 30, 40 mg/L respectively) of Acid Blue 92 solution and agitated, the adsorbent and the adsorbate were separated by filtration and the filtrate was analyzed for residual dye concentration spectrophotometrically (using Elico make Bio-UV Spectrophotometer, Model BL-192).

3. 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.

3.1 Pseudo First Order Kinetic Model

A simple kinetic analysis of adsorption, the pseudo first order kinetics and its integrated form, is given by (Lagergren, 1898).

$$\log(q_e - q_t) = \frac{\log(q_e) - k_1}{2.303} \times t \qquad (1)$$

where k_1 is the pseudo first order rate constant that is calculated from the slope of the plot of log (q_e-q_t) vs time Fig. 1. 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.

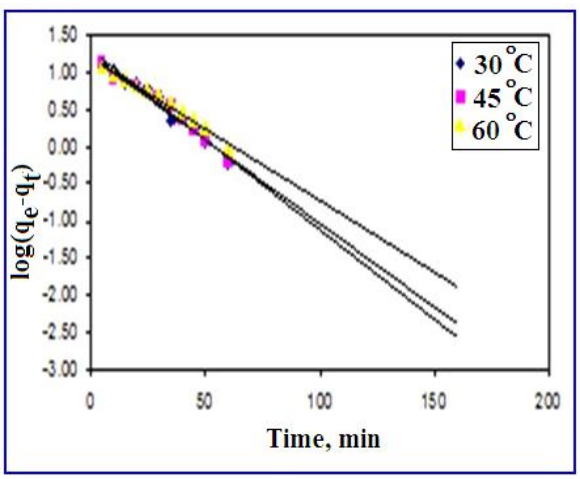

Fig. 1: Pseudo first order plot

3.2 Elovich Model

The Elovich or Roginsky – Zeldovich equation is generally expressed as follows (Low *et al.* 1999),

$$\frac{dq_t}{dt} = \alpha \, exp(-\beta q_t) \qquad (2)$$

where, α and β are the initial dye adsorption rate (mg/g) and desorption constant (g/mg) respectively.

To simplify the Elovich equation, Chien and Clayton (Chien *et al.* 1980) assumed αβ >> 1 and on applying the boundary conditions q_t=0 at t=0 and q_t=q_t at t=t, the above equation becomes,

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (3)$$

Thus the constants α and β can be obtained from the slope and intercept of linear plot of q_t versus ln t Fig. 2. The above equation will be used to test the applicability of the Elovich equation to the kinetics of chosen adsorbent adsorbate system.

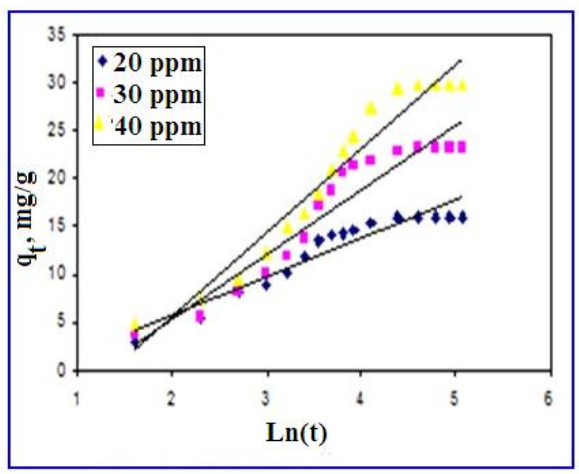

Fig. 2: Elovich plot

3.3 Pseudo Second Order Kinetic Model

To describe dye adsorption the modified pseudo second order kinetic equation is expressed as (Ho *et al.* 2000).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}(t) \qquad (4)$$

where, k_2 is the pseudo second order rate constant. A plot of t/q_t vs t Fig. 3 enables calculation of the rate constant k_2 which in turn is used to calculate the initial sorption rate h as follows

$$h = k_2 q_e^2 \qquad (5)$$

The q_e values calculated from the pseudo-second order model system are in good agreement with the experimental q_e values.

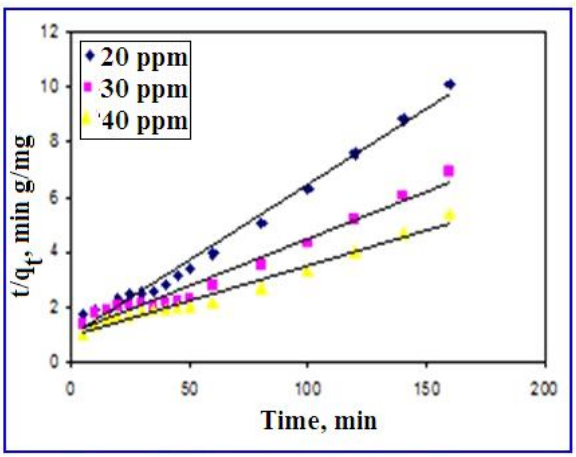

Fig. 3: Pseudo second order plot

4. ISOTHERM STUDIES

4.1 Langmuir Isotherm

The Langmuir adsorption isotherm is based on the assumption (Langmuir, 1918) that an adsorbent adsorbs the dye at specific homogeneous sites and once that site is occupied, no further adsorption takes place at that site. Theoretically, the adsorbent has a finite capacity to absorb the adsorbate and hence there is a limit beyond which no further adsorptions can occur (Wang *et al.* 2003). The monolayer capacity can be represented by the expression

$$q_e = \frac{Q_0 k_L C_e}{1 + k_L C_e} \qquad (6)$$

The linear form of the above equation is represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 k_L} + \frac{C_e}{Q_0} \qquad (7)$$

where k_L is related to the free energy of adsorption (L/mg) and q_0 is the maximum adsorption capacity. The values of Q_0 and k_L were calculated from the slope and intercept of the linear plot C_e/q_e versus C_e Fig. 4. The equilibrium concentration and hence the amount of dye adsorbed were calculated by varying the dye concentration between 20 mg/L and 40 mg/L with a fixed adsorbent dose and all other experimental conditions kept constant. The isotherm constants for the Langmuir isotherm under study were calculated from the linear form of the model and the correlation coefficients are given in Table 3. An essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant called the equilibrium parameter (Bulut *et al.* 2006).

$$R_L = \frac{1}{1 + K_L C_o} \qquad (8)$$

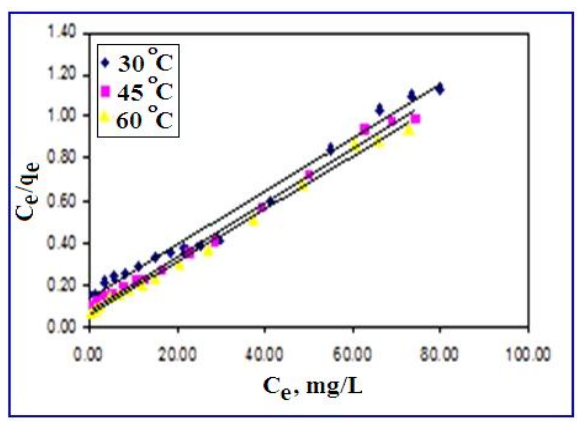

Fig. 4: Langmuir plot

Table 2. Kinetic Model Values for the adsorption of Acid Blue 92 on to *Moringa Oleifera fruit shell waste* Activated Carbon

Conc.	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^{-4} g mg^{-1} min^{-1}	h mg. $g^{-1}min^{-1}$	r^2
20 ppm	5.87	0.970	2.09	0.2446	0.901	18.31	30.64	1.027	0.988
30 ppm	5.16	0.956	2.034	0.1486	0.9058	28.90	11.73	0.9797	0.9696
40 ppm	4.17	0.953	2.264	0.1144	0.9477	38.76	6.53	0.9810	0.9763

Table 3. Parameters of Langmuir and Freundlich Adsorption Isotherms

Temp. °C	Langmuir Isotherm			Freundlich Isotherm		
	b , L/mg	Q_o, mg/g	r^2	1/n	n	k_f mg, g^{-1}
30	0.0998	78.12	0.9839	0.4985	2.006	10.104
45	0.1664	78.74	0.9935	0.4305	2.323	14.548
60	0.2111	80	0.9958	0.3995	2.503	17.18

Table 4. D_p and D_f values for the chosen adsorbent – adsorbate system

S.No.	Dye	Temp. °C	$t_{1/2}$, s	D_p x 10^{-13}, cm^2s^{-1}	D_f x 10^{-11}, cm^2s^{-1}
1.	Acid Blue 92	30	945	12.88	0.1323
		45	855.55	40.52	0.229
		60	708.35	96.81	0.3753

Table 5. Values of energy of activation E_a, entropy of activation $\Delta S^{\#}$, and pre-exponential constant for the present study

S.No.	Parameter	Value
1.	D_i, cm^2 S^{-1}	
	30 °C	6.4932x10^{-7}
	45 °C	7.1144x10^{-7}
	60 °C	7.453x10^{-7}
	E_a, KJ mol^{-1}	-3.794
	ΔS^{-1}, $JK^{-1}mol^{-1}$	-181.45
	Do, cm^2s^{-1}	1.435x10^{-11}

Table 6. Thermodynamic parameters for the adsorption of Acid Blue 92 on to *Moringa Oleifera* fruit shell waste Activated Carbon

Temp.	ΔG, KJ $mole^{-1}$	ΔS, J $mole^{-1}$	ΔH, KJ $mole^{-1}$
303 K	-1.433		
318 K	-6.802	89.05	21.72
333 K	-7.826		

The value of R_L indicates the type of isotherm to be favourable ($0 < R_L < 1$), linear (R_L=1), unfavorable ($R_L > 1$) or irreversible R_L =0, where K_L is the Langmuir constant and C_0 is the highest initial dye concentration (mg/L).

4.2 Freundlich Isotherm

Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is commonly given by (Freundlich, 1926).

$$q_e = k_f C_e^{1/n} \tag{9}$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), k_f and n are Freundlich constants indicating the relative adsorption capacity and sorption intensity of the adsorbents (mg/g). A linear form of the Freundlich expression can be obtained by taking logarithms of the nonlinear form and can be written as

$$\log q_e = \frac{1}{n} \log C_e + \log k_f \tag{10}$$

The Freundlich constant k_f and n can be calculated from the slope and intercept of the linear plot with log q_e versus log C_e Fig.5.

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 (Stephen Inbaraj *et al.* 2002).

$$k_c = C_{Ae} / C_e \tag{11}$$

$$\Delta G = -RT \ln K_c \tag{12}$$

$$\log K_c = \frac{\Delta S}{2.303\,R} - \frac{\Delta H}{2.303\,RT} \tag{13}$$

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.

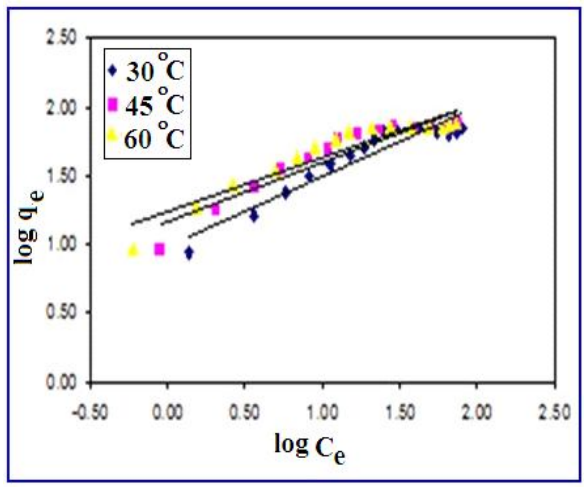

Fig. 5: Freundlich plot

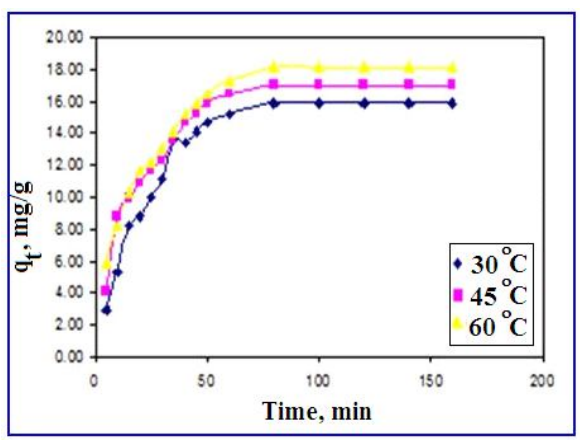

Fig. 6: Effect of temperature on adsorption

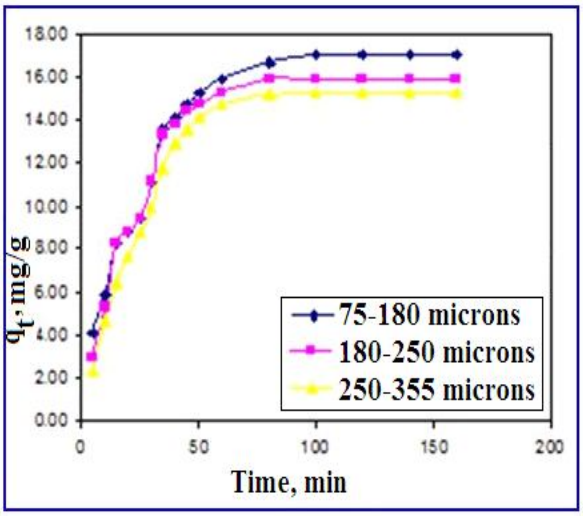

Fig. 7: Effect of particle size on adsorption

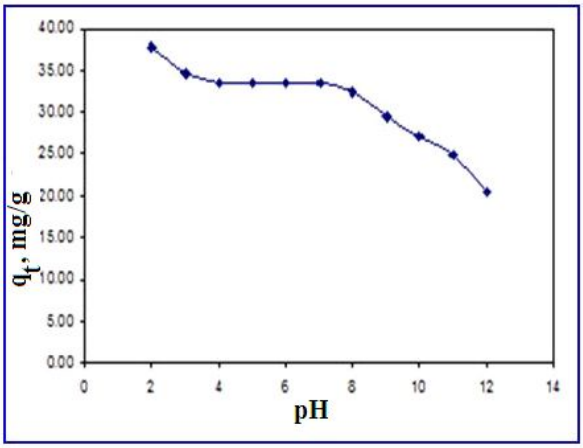

Fig. 8: Effect of pH on adsorption

6. RESULTS & DISCUSSION

6.1 The effect of temperature on adsorption

Temperature influences the Acid Blue 92 adsorption properties of dried *Morienga Oleifera* fruit shell waste. The temperature effect on the bio sorption capacity of dried *Morienga Oleifera* fruit shell waste was examined at 30, 45 and 60 °C using initial dye concentration of 20mg/L at pH 2 and is shown in Fig.6. The adsorption capacities of the activated *Morienga Oleifera* fruitshell waste increases with increasing temperatures from 30 to 60 °C, which indicates that the adsorption process is endothermic. The optimum temperature for dye adsorption of the dried *Morienga Oleifera* fruit shell waste within the temperature range studied was found to be 30 °C.

6.2 The effect of particle size on adsorption

The effect of particle size of the adsorbent on the Acid Blue 92 adsorption capacity of the activated carbon was investigated in the range of 75–355 micrometer and the results were indicated in Fig. 7. As seen in figure, the equilibrium dye adsorption changed significantly by the particle size.

6.3 The effect of pH on adsorption

The effect of pH for the adsorption of Acid Blue 92 on to activated carbon over a pH range of 2 to 12 is represented in Fig. 8. The uptake of Acid Blue 92 decreased from 37.84 to 20.54 mg g^{-1} when the solution pH was increased from 2 to 12. The maximum uptake of Acid Blue 92 by activated carbon was obtained at pH 2.The interaction between the sorbate and sorbent is affected by pKa of dye as well as the isoelectric point (pH_{PZC}) of the adsorbent. When the solution pH is above the pKa of dye (pKa for AB 92 is 3.2), the adsorption decreases due to the electrostatic repulsion between dissociated adsorbate and adsorbent surface. Below the isoelectric point (pH_{PZC} = 9.8) the electrostatic repulsion between the adsorbed molecules is minimum, resulting in a maximum adsorption. At pH below 9.8 the surface of the adsorbent may acquire a positive charge leading to an increased anionic dye adsorption due to electrostatic attraction. The complete dissociation of the dye molecule takes at its pKa value (3.2) and hence the maximum adsorption takes place at pH 2. At pH above the pH_{PZC} the adsorbent surface acquires 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.

6.4 The effect of carbon dosage on adsorption

The carbon dosage was varied in the range of 0.05 to 0.15g and the adsorption of Acid Blue 92 for a dye concentration of 20mg/L was studied. The percentage dye removal increased from 86.36% to 95.45 % for an adsorbent dosage of 0.05 to 0.15 g. This is due to the increased surface area and availability of more adsorption sites. When the adsorbent in the solute concentration is high then the adsorption is more onto the adsorbent surface and hence there is a decrease in the solute concentration in the solution. This is due to the adsorption of a fixed amount of dye on a fixed mass of the adsorbent.

6.5 Kinetic Modeling

6.5.1 Pseudo First Order Equation

Fig. 1 shows a plot of Pseudo First Order Equation for the results of adsorption of Acid Blue 92 from 20 mg/L to 40 mg/L between log (q_e - q_t) agitation time over whole sorption period and the results are presented in the Table 2. The pseudo first order constant ranged from $5.87x10^{-2}$ to $4.17x10^{-2}$.The calculated q_e values obtained for pseudo first order model is in good agreement with the experimental q_e values. The correlation coefficients (r^2) found to range from 0.970 to 0.953 for the pseudo first order kinetic models, which are relatively low. Even though q_e cal. and q_e exp. values are closer, the r^2 values suggest that the adsorption data fitted poor to pseudo first order kinetics.

6.5.2 Elovich Model

The results of the sorption of Acid Blue 92 on to *Morienga Oleifera* fruit shell waste has been represented in the form of Elovich Equation in Fig. 2 at various Initial dye concentrations(Viz 20 mg/L, 30 mg/L, 40 mg/L). From the plot a linear relationship between the amount of Acid Blue 92 adsorbed q_t and ln(t) was established. These plots showed different distinct linear regions within individual sets of data. In these cases, it was thus necessary to perform multiple regressions on different ranges of the data. The kinetics could not be approximated using Elovich model.

6.5.3 Pseudo Second Order Model

A plot of t/q_t and t should give a linear relationship if the adsorption follows second order. q_e and k_2 values can be calculated from the slope and intercept of the plot . The data for the adsorption of Acid Blue 92 on to activated carbon applied to pseudo second order kinetic model as shown in Fig. 3 and the results are presented in Table 2. From the results it is clear that the equilibrium sorption capacity q_e, increases and the sorption rate constant, k_2, decreases with an increase in the initial dye concentration. Based on the r^2 values the adsorption of Acid Blue 92 on to the activated carbon follows pseudo second order kinetics.

7. ISOTHERMIC MODELLING

The Langmuir adsorption isotherm obtained in 160 minutes of agitation time is shown in the Fig. 4. The values of R_L<1, obtained in this study indicates the applicability of Langmuir adsorption isotherm. The values of absorption intensity 1/n<<1 reveals the applicability of the Freundlich adsorption isotherm. The values of 1/n and k_f are given in the Table 3. The study of temperature effects on the Freundlich parameters reveals a decreasing trend in the adsorption capacity with increase in temperature. However, the variation in the adsorption intensity is negligible. These data are useful for practical design purposes.

8. MECHANISM FOR SORPTION OF ACID BLUE 92 ON TO *MORINGA OLEIFERA* FRUIT SHELL WASTE

Because of the high correlation coefficients obtained using pseudo first order, pseudo second order

and Elovich kinetic models, it was impossible to conclude which adsorption mechanism actually occurred and was responsible for the ability of adsorbent to review other sources of information in an attempt to identify the specific adsorption mechanism.

In adsorption process of dye ion on the solid surface, the dye species migrate towards the surface of the adsorbent. This type of migration proceeds till the concentration of the adsorbate species adsorbed on to the surface of the adsorbent. Once equilibrium is attained the migration of the solute species from the solution stops. Under this situation, it is possible to measure the magnitude of the distribution of the solute species between the liquid and solid phases. The magnitude of this kind of distribution is a measure of the efficiency of the chosen adsorbent in the adsorbate species.

When a powdered solid adsorbent material is made in contact with a solution containing dyes, the dyes first migrate from the bulk solution to the surface of the liquid film. This surface exerts a diffusion barrier. This barrier may be very significant or less significant. The involvement of a significant quantum of diffusion barrier indicates the dominant role taken up by the film diffusion in the adsorption process. Furthermore, the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusions.

The external diffusion controls the migration of the solute species from the solution to the boundary layer of the liquid phase. However the internal diffusion controls the transfer of the solute species from the external surface of the adsorbent to the internal surface of the pores of the adsorbent material (Gupta *et al.* 2005).

It is now well established, that during the adsorption of dye over a porous adsorbent, the following three consecutive steps have taken place (Gupta *et al.* 2003).

(i) transport of the ingoing adsorbate ions to external surface of the adsorbent (film diffusion),

(ii) 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

iii) adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent.

Out of these three processes, the third process is considered to be very fast and is not the rate limiting step in the uptake of organic compounds (Crank, 1956). The remaining two steps impart the following three possibilities:

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 H≈ 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.

In the batch mode contact time adsorption experiment, rapid stirring is maintained. This induces Acid Blue 92 from the solution to the pores of the asorbent material and this step may control the rate of the adsorption process (Weber *et al.* 1963).

According to Michelson *et al.* (1975) for the adsorption of dyes on the carbon surface, for film diffusion to be rate-determining step, the value of the film diffusion coefficient. D_{fo}, should be in the range 10^{-6} – 10^{-8} cm^2/ sec. If pore diffusion were to the rate limiting step, the pore diffusion coefficient, D_p should be in the range 10^{-11}- 10^{-13} cm^2/ sec. In order to find out the nature of the process responsible for adsorption on to activated *Moringa Oleifera* fruit shell waste, attempts were made to calculate the diffusion co-efficient of the process.

Assuming spherical geometry of the sorbents (Bhattacharya *et al*. 1984), the overall rate constant of the process can be correlated to the pore diffusion coefficient in accordance with the expression,

$$t_{1/2} = 0.03 \frac{r_0^2}{D_p} \text{ or}$$

to the film diffusion coefficient in accordance with

$$t_{1/2} = 0.23 \frac{r_o^{\partial}}{D_f} \times \frac{\overline{C}}{C} \quad (14)$$

where r_o is radius of the sorbent (cm), D_p and D_f are pore diffusion coefficient (cm^2/sec) and film diffusion coefficient (cm^2/sec) respectively, $\frac{\bar{c}}{c}$ is equilibrium loading of the adsorbent , ∂ is the film thickness (cm) and $t_{1/2}$ is the time for half change (sec) .

Since the carbon particles used were of size range (180-250 µm), the average diameter of the particle was taken as 0.0215x 10^{-4}cm. Using these values, the film diffusion coefficient and pore diffusion co-efficient were calculated.

Then considering the pseudo first order rate constant k_L for the adsorption of Acid Blue 92. The values of D_p and D_f were calculated under the given set of operating conditions and are presented in the Table 4.

The present study indicates the D_p in the order of 10^{-13} cm^2/sec and the D_f value in the order of 10^{-11} for the respective pseudo first order plots for each Acid blue 92 and hence the investigator concludes that the pore diffusion might be the rate determining step.

Since both external mass transfer and intraparticle diffusion constants varied with initial Acid Blue 92 concentration indicating the occurrence of both surface adsorption and intra particle diffusion the sorption data were further analyzed by the kinetic expression given by Boyd *et a1*. (1947).

$$F = 1 - \frac{6}{\pi^2} \sum_{N-1}^{\alpha} \frac{1}{n^2} exp\left(\frac{-Dit\pi^2 n^2}{r^2}\right) \quad (15)$$

$$F = 1 - \frac{6}{\pi^2} \sum_{N-1}^{\alpha} \frac{1}{n^2} exp[-n^2 \beta_t] \quad (16)$$

where F is the fractional attainment of equilibrium at time t and is obtained by using following equation, and n is the Freundlich constant of the adsorbate.

$$F = \frac{q_t}{q_e} \quad (17)$$

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

On the basis of F values, corresponding values of B_t were obtained from Reichenberg's table (Reichenberg, 1953) and the linearity test was carried out by plotting B_t with respect to time for both 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 concentrations is employed to distinguish between film diffusion and particle diffusion. From the slope of the straight line obtained from time versus B_t graph, B value (time constant) were calculated. The values of effective diffusion co efficient (D_i) were calculated at different temperatures using the following equation.

$$B = \frac{\pi^2 D_i}{r^2} \quad (18)$$

Here r is the radius of adsorbent particle. The D_i values are given in the Table 5. 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.

$$D_i = D_o exp\left[\frac{E_a}{RT}\right] \quad (19)$$

$$D_o = 2.72d^2\frac{kT}{h}exp\left[\frac{S^{\neq}}{R}\right] \quad (20)$$

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

9. THERMODYNAMICS PARAMETERS

ΔH and ΔS values were obtained from the slope and intercept of Vant Hoff plot (1/T vs In K_c). A batch adsorption study were carried out with Acid Blue 92 solution at pH ≈2.0 and by varying the temperature (303K, 318K and 333K). The initial concentration of Acid Blue 92 solution used was maintained to be 20 mg/L with 100 mg of the absorbent. Table 6 gives the value of ΔG, ΔS and ΔH for the adsorption of Acid Blue 92. The negative values of free energy change (ΔG) indicates the feasibility and spontaneous nature of the adsorption of Acid Blue 92 species. The positive ΔH values of the process suggest the endothermic nature of the absorption of Acid Blue 92 on to activated *Moringa Oleifera fruit shell waste* carbon. The positive value of ΔS is due to the increased randomness during the adsorption of Acid Blue 92.

10. CONCLUSION

In the present study adsorption of Acid Blue 92 on activated *Moringa Oleifera* fruit shell waste carbon has been investigated. The data obtained through this work supports that the *Moringa Oleifera* fruit shell waste carbon is an effective low cost adsorbent for the removal of Acid Blue 92 from aqueous solution. The adsorption of Acid Blue 92 is dependent on the initial concentration and agitation time. Equilibrium of Acid Blue 92 adsorption reaches at 80 min. The pseudo first and second order equations provide a best fit description for the sorption of Acid Blue 92 on to *Moringa Oleifera* fruit shell waste related to Elovich model, but the pseudo second order correlation coefficient has better correlation value than pseudo first order equation, pseudo second order equation is consider to be the most appropriate due to high correlation coefficient.

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