

EQUILIBRIUM AND KINETIC STUDIES ON ADSORPTION OF ANILINE BLUE FROM AQUEOUS SOLUTION ONTO RICE HUSK CARBON

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ABSTRACT

Equilibrium and kinetic studies on the adsorption of Aniline Blue dye from aqueous solution onto activated rice husk carbon have been reported. The rice husk carbon has been characterized for its specific surface area, XRD and TEM analysis. The effects of dye initial concentration, adsorbent-adsorbate contact time and temperature on the percent adsorption of the dye on the adsorbent have been investigated. Kinetics of adsorption of Aniline blue onto the adsorbent in aqueous solution was monitored, spectro-photometrically. At the given dye initial concentration, % adsorption of dye increases with increase in temperature as well as the contact period. However, at the given temperature, % adsorption of the dye decreases with the increase in dye initial concentration. The observed data was analyzed in the light of Langmuir and Freundlich adsorption isotherms. Dye adsorption rate constant (k_{ad}) follows the first order kinetics. Activation energy (E_a) of adsorption, intra-particle diffusion rate constant and thermodynamic parameters of adsorption of the dye on the rice-husk carbon have been evaluated and interpreted.

Keywords: Adsorption, Kinetic, Aniline blue, Adsorption, Thermodynamic, Activation energy

INTRODUCTION

Wastewater contaminated with various dyes discharged from tanneries, distilleries, textile, paper and pulp mills, electroplating and food processing industries is one of the serious cause of water pollution in the environment. The colored effluents from the above sources, on mixing with surface and ground water system, also contaminate the drinking water. Color being a visible pollutant, the water contaminated with dyes is not only unfit for drinking purpose but is also not suitable for agriculture due to its inhibitory action on photosynthetic process in plants. Disposal of rice husk solid accumulated in and around rice processing units is a big challenge for solid waste management. Using rice husk for the synthesis of carbon may not only provide a solution for the disposal of the solid waste but will also provide a low cost adsorbent for the effective removal of water pollutants such as organic dyes. *Aniline Blue Dye* is widely used in dye industries and its presence in the industrial discharge water also contributes to environmental pollution.

Adsorption method may be one of environment friendly, economic and efficient techniques with considerable potential for the removal of dyes from contaminated water, Grabowska & Gryglewicz 2007¹. Adsorbents that have earlier been used for dye removal from contaminated water include: wood powder, Ozacar & Sengil 2005², fly ash, Acemioglu 2004³, coconut husk (coir pith), Tan et al 2008⁴, lignin, Cotoruelo et al 2009⁵, pomegranate peel, Amin 2009⁶, banana stalks, Salman and Hameed 2010⁷, rice husk ash, Lakshmi et al 2009⁸, sugar beet, Demiral and Gündüzoğlu 2010⁹, cotton stalk, Deng et al 2010¹⁰.

There has been a wide use of activated carbon as adsorbent for the removal of dyes and biologically resistant organic pollutants from the polluted water, Arivoli et al 2008¹¹. The studies on the adsorption of dyes on adsorbent surfaces in aqueous systems may not only provide valuable information regarding the nature of intermolecular interaction involved at solid-liquid interface but it may also help in designing the technique for effective removal of color from the contaminated water

MATERIALS AND METHODS

Materials

Rice husk carbon

Rice husk was thoroughly washed with distilled water and dried at 80 °C for 24 hours. The dried material was mixed with equal volume

of concentrated H₂SO₄ at room temperature. After 24 hours excess of the acid was removed by washing the solid residue, repeatedly with distilled water till the residue was free from the acid and then dried the product at room temperature. The carbon thus prepared was kept in hot air oven at 120 °C for 10 hours and then transferred to a muffle furnace kept at 500 °C for an hour.

The activated carbon thus obtained was ground to yield a fine powder and fractionated into different mesh sizes. The carbon thus prepared was analyzed for its physico-chemical parameters.

Aniline Blue

Aniline Blue (MERCK) (molecular formula: C₃₇H₃₉S₃O₉N₆; Molecular mass: 807.0) is an anionic sulphonate triphenyl methane dye derivative.

Methods

XRD Spectra

XRD spectra of activated rice husk carbon was obtained at SAIF Punjab University Chandigarh, India, using X-Ray diffractometer (Model: XRDML) (X-Ray wave length: 1.5406 Å, 2θ range: 5-70°, step size: 2θ=0.0170°, step time: 30.368 second)

TEM Analysis

Transmission Electron Microscopic (TEM) analysis of activated rice husk carbon adsorbent was carried out at SAIF Punjab University, Chandigarh, India. TEM picture was obtained in imaging mode using HV=80 KV and at magnification 3x10⁵.

2.2.4. Specific Surface Area of Carbon

Surface area per gm of the activated rice husk carbon was obtained using Sears method, Sears 1956¹². 1.5 g of carbon sample was mixed with 100 ml of water and 30 g NaCl. The mixture was stirred for five minutes. To this 0.1 N HCl was added to make final volume 150 ml and final pH = 4.0. It was then titrated against 0.1N NaOH.

The volume (V ml) of 0.1N NaOH required to raise the pH from 4.0 to 9.0 was noted. The specific area (i.e. area per gm) was obtained using the formula:

$$A = 32.V - 25 \text{ -----} (2.2.4.1)$$

Where A = Surface area of carbon per gm (in m²/gm); V = volume of 0.1N NaOH required to raise the pH from 4.0 to 9.0.

2.2.5 Kinetics of Adsorption:

A known amount (0.5 or 1.0 g) of the adsorbent (rice husk carbon) was thoroughly mixed with 100 ml of dye solution in a conical flask. The reaction flask, kept in a water-thermostat, was maintained at the desired constant temperature ($\pm 0.1^\circ\text{C}$). Concentration of Aniline blue dye solution, free of suspended carbon, at a regular interval of time was determined using a UV-Visible digital spectrophotometer (SIC Model 301).

RESULTS AND DISCUSSION

The characteristic parameters of the rice husk carbon are presented in Table-1.

XRD Spectra

XRD spectra of activated rice husk carbon (Fig. 3.1) show a single hump ranging from $2\theta = 16^\circ$ to 29° indicating amorphous disordered structure. It indicates that the X-Ray diffraction is mainly due to amorphous silica particles. As the atomic scattering factor of

Carbon is very small, intervening carbon atoms seems to contribute little with respect to scattering from silica.

TEM analysis

Transmission Electron Microscopic (TEM) analysis of activated rice husk carbon is presented in Fig. 3.2. The observed TEM image suggests the presence of aggregates of carbon nanoparticles of 15-25 nm.

Table 1: Characteristic parameters of activated rice husk carbon

| Property | Value |
|---|-------------|
| Particle size(mm) | 0.14 - 0.19 |
| Density(g/cc) | 0.492 |
| Water soluble matter (%) | 0.17 |
| pH (dispersed in water) | 6.4 |
| Moisture content (%) | 0.26 |
| Specific surface area (m ² /g) | 610 |

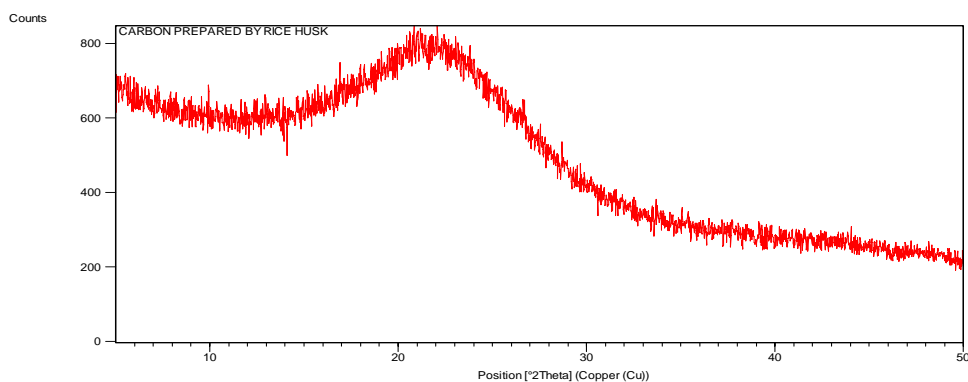


Fig. 3.1: XRD spectra of activated rice husk carbon

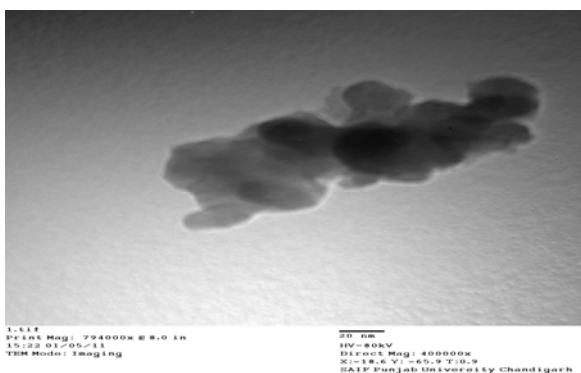


Fig. 3.2: Transmission Electron Microscopic (TEM) image of activated rice husk carbon adsorbent

Specific Surface Area of Carbon

Surface area per gm of the activated rice husk carbon adsorbent described above in section 2.2.4. was found to be 610 m²/g.

Effects of dye initial concentration, contact time and Temperature on Dye adsorption:

Values of % dye adsorbed as a function of time and temperature, using 10 mg/dm³ initial Aniline blue dye concentration are given in

Table-2 Plots of percent adsorption of dye as a function of dye initial concentration at different temperatures are given in Figs. 3.3-3.5. It is evident that at the specified initial dye concentration, its % adsorption increases with increase in temperature as well as with the increase in the adsorbate-adsorbent contact period and the equilibrium was established after 120 minutes.

The plots are single and continuous leading to saturation, suggesting monolayer coverage of the dye on the adsorbent surface.

At the given temperature, the percentage adsorption of aniline blue decreases with the increase in dye initial concentration. It may be because at higher initial concentration of the adsorbate (dye), the number of available active sites per adsorbate molecule at the adsorbent surface become fewer, resulting in a decrease in the adsorption of dye, Gopal & Elango 2007¹³. However, net amount of the dye adsorbed per unit mass of the adsorbent, increases with the increase in the dye initial concentration.

Table 2: Values of % Aniline Blue dye adsorbed as a function of time at varying temperature (Dye initial concentration: 10 mg/dm³; Adsorbent: 1.0 g/100ml; mesh No.: 60

| Time(min) | 298.15K | 308.15K | 318.15K |
|-----------|---------|---------|---------|
| 15 | 39.5 | 50.0 | 62.5 |
| 30 | 45.8 | 56.3 | 68.7 |
| 45 | 53.1 | 62.5 | 75.0 |
| 60 | 62.5 | 68.7 | 81.3 |
| 75 | 68.7 | 75.2 | 87.5 |
| 90 | 75.1 | 81.3 | 93.7 |
| 105 | 81.3 | 87.5 | 96.8 |
| 120 | 81.5 | 87.7 | 96.4 |

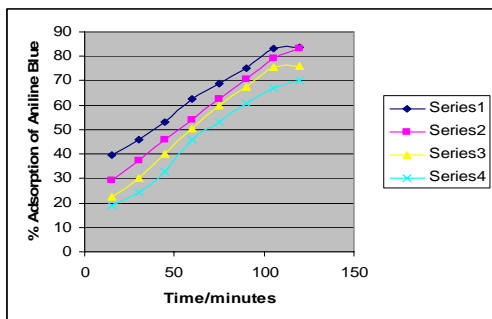


Fig. 3.3: Plot of % Aniline Blue dye adsorbed as function of time using various initial dye concentrations (Series-1: 10 mg/ dm³; Series-2: 30 mg/ dm³; Series-3: 50 mg/dm³;Series- 4: 75 mg/ dm³) at 298.15K. Adsorbent: 1.0 g/100ml; mesh No.: 60

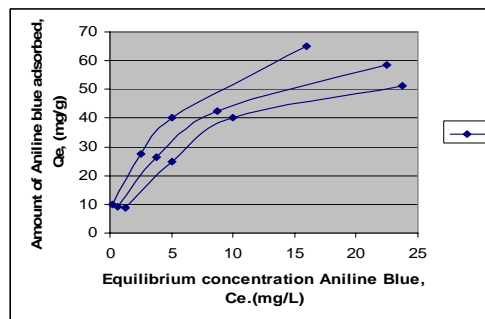


Fig.3.6: Plot of amount of dye adsorbed at equilibrium, Q_e , (mg/g) as a function of equilibrium concentration C_e / (mg/L) of Aniline Blue at different temperatures (lowest curve: 298.15K; middle curve: 308.15K; top curve: 318.15K). Adsorbent: 1.0 g/100ml; mesh No.: 60

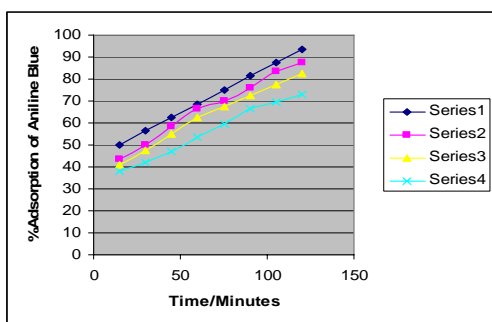


Fig. 3.4: Plots of % Aniline Blue dye adsorbed as a function of time using various initial dye concentrations (C_0) (Series-1: 10 mg/ dm³; Series-2: 30 mg/ dm³; Series-3: 50 mg/ dm³; Series-4: 75 mg/ dm³) at 308.15K. Adsorbent: 1.0 g/100ml; mesh No.: 60

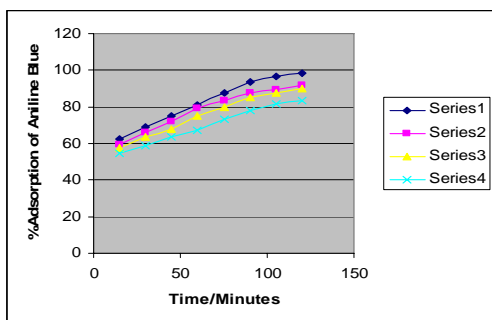


Fig. 3.5: Plots of % Aniline Blue dye adsorbed as a function of time using various initial dye concentrations (C_0): Series-1: 10 mg/ dm³; Series-2: 30 mg/ dm³; Series-3: 50 mg/ dm³;Series-4: 75 mg/ dm³) at 318.15K. Adsorbent: 1.0 g/100ml; mesh No.: 60

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is represented by the equation, Langmuir 1918¹⁴.

$$C_e/Q_e = 1/(Q_0b) + C_e/Q_0 \text{ -----(3.6.1)}$$

Where, C_e is the equilibrium concentration (mg/L) of adsorbate (Aniline Blue) in the bulk; Q_e is the amount of adsorbate(mg/g) adsorbed at equilibrium. Q_0 and 'b' are Langmuir constants related to *adsorption efficiency* and *energy of adsorption*, respectively. The observed linear plots of C_e / Q_e as a function of C_e for Aniline Blue Dye (Fig.3.7) at different temperatures suggest the applicability of the Langmuir isotherms. The values of Q_0 and 'b' are obtained from the slope and intercept of the plot, respectively, and these are presented in table-3. The observed Q_0 value, an index of adsorption efficiency of the adsorbate (dye) on the adsorbent, is positive. The positive values of parameter 'b', that increases with increase of temperature, indicates the endothermic nature of the adsorption process, suggesting the absence of any chemical interaction in the adsorbate-adsorbent system.

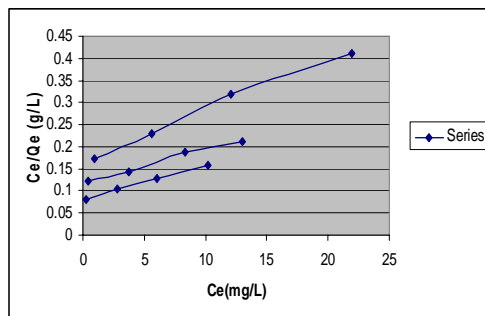


Fig. 3.7: Plot of C_e/Q_e (g/L) as a function of C_e (mg/L) at different temperatures for Aniline Blue (Top Curve: 298.15K; Middle Curve: 08.15K; Lower Curve: 318.15K. Adsorbent: 1.0 g/100ml; mesh No.: 60

Table 3: Parameters of Langmuir and Freundlich adsorption Isotherms for Aniline Blue dye on Rice Husk Carbon Langmuir Parameters Freundlich Parameters

| Temprature (K) | Q_0 (mg/g) | b (dm ³ /g) | K_f | N |
|----------------|--------------|--------------------------|--------|-------|
| 298.15 | 50.18 | 0.119 | 6.310 | 1.463 |
| 308.15 | 60.42 | 0.184 | 12.590 | 2.000 |
| 318.15 | 71.17 | 0.281 | 22.391 | 2.217 |

Freundlich Adsorption Isotherm

Freundlich adsorption isotherm is given by the relation, Freundlich 1906¹⁵.

Adsorption Isotherms

Plots of Aniline Blue(dye) adsorbed at equilibrium, Q_e , versus equilibrium dye concentration, C_e , (mg/L) are presented in Fig.3.6. Adsorption isotherms show leveling trend at higher adsorbate concentrations suggests Langmuir type adsorption and flat position of the adsorbate molecules at the adsorbent surface. It also infers monolayer coverage, Grabowska & Gryglewicz 2007¹ of adsorbent surface with the adsorbate molecules. The observed data was further analyzed using the linear form of Langmuir and Freundlich isotherms.

$$\log Q_e = \log K_f + 1/n \log C_e \text{ -----(3.6.2.1)}$$

where Q_e and C_e have their usual meanings and the constants ' K_f ' and ' n ' are measures of adsorption capacity and intensity of adsorption, respectively. Plots of $\log Q_e$ as a function of $\log C_e$ at the studied temperatures are linear (Fig.3.8.) suggesting that the adsorption of the aniline blue dye on the adsorbent (rice husk carbon) follows the Freundlich isotherm. The parameters ' K_f ' and ' n ' were obtained from the intercept and slope, respectively, of $\log Q_e$ versus $\log C_e$ linear plots and these are also recorded in Table-3. The value of ' K_f ', a measure of adsorption capacity of the adsorbate on the adsorbent surface, increases with increasing temperature. This may be attributed to the enhanced rate of transfer of dye molecules from bulk to the adsorbent surface at higher temperature. Also, higher temperature may produce a swelling effect within the internal structure of the adsorbent enabling more number of dye molecules to penetrate further, Dogan & Alkan 2003¹⁶. The values of ' n ', a measure of intensity of adsorption, also increases with the rise of temperature. The observed values of ' n ', greater than unity, suggests the feasibility of the process of adsorption in present adsorbate-adsorbent systems.

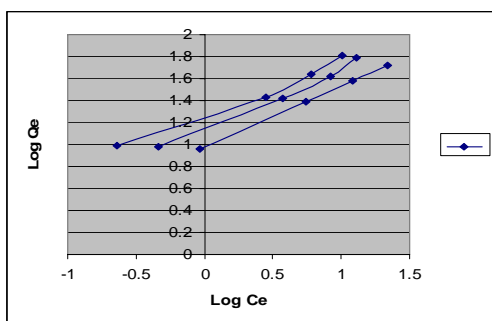


Fig. 3.8: Plot of $\log Q_e$ as a function of $\log C_e$ for Aniline Blue dye (bottom curve : 298.15K; middle curve: 308.15K; Top Curve: 318.15K) dsorbent: 1.0 g/100ml; mesh No.: 60.

3.7. Kinetics of adsorption:

The rate constant (k_{ad}) of adsorption, was determined using the following first order kinetic equation-

$$\log (C_0/C_t) = (k_{ad}/2.303).t \text{ -----(3.7.1)}$$

Where, C_0 is the dye initial concentration and C_t is its concentration of dye at time 't'. The rate constant, k_{ad} value was obtained from the slope of the linear plot of $\log (C_0/C_t)$ as a function of time t (minutes) (Fig.3.9). Adsorption rate constant, k_{ad} at varying dye initial concentrations and temperatures for the studied dye systems are given in table-4. At the given temperature, the adsorption rate constant (k_{ad}) decreases with the increase in initial dye concentration. This may be because at higher dye initial concentration, the number of available binding sites, at the adsorbent surface, per adsorbate molecule, decreases. However, at a constant initial dye concentration, k_{ad} value increases on increasing the temperature for the dye systems. This may be due to enhanced intra-particle diffusion as well as larger pore size at the adsorbent surface at higher temperatures.

Table 4: Values of adsorption rate constant ($k_{ad} \times 10^2$) at varying initial dye concentration (C_0) and temperature (K) for Aniline Blue.

| Temperatu re (K) | $C_0=10$ mgd m^{-3} | $C_0=30$ mgd m^{-3} | $C_0=50$ mgd m^{-3} | $C_0=75$ mgd m^{-3} |
|------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| 298.15 | 1.149 | 0.7215 | 0.6375 | 0.6246 |
| 308.15 | 1.380 | 1.0442 | 0.8645 | 0.8178 |
| 318.15 | 1.494 | 1.1899 | 1.0345 | 0.9650 |

Adsorption rate constant ($k_{ad} \times 10^2$)

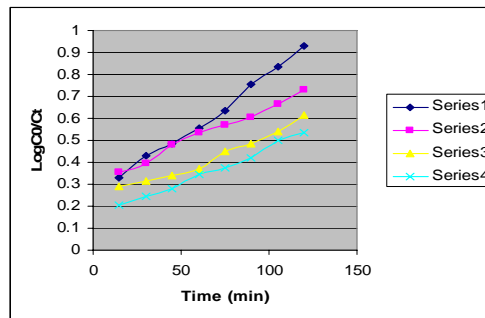


Fig.3.9: Plots of $\log (C_0/C_t)$ as a function of time of contact, t, (minutes) at 298.15K for Aniline Blue dye (Dye initial concentrations: Series-1: 10 mg/L; Series-2: 30 mg/L; Series-3: 50 mg/L; Series-4: 75 mg/L.); Adsorbent: 1.0 g/100ml; mesh No.: 60.

3.8. Activation energy (E_a) of adsorption

Activation energy (E_a) of adsorption as a function of dye initial concentration (C_0) were obtained from the observed adsorption rate constants (k_{ad}) values at different temperatures using Arrhenius equation-

$$k_{ad} = A. e^{(-E_a/RT)} \text{ -----(3.8.1)}$$

$$\text{or } \log k_{ad} = - E_a / (2.303RT) + \log A \text{ -----(3.8)}$$

Where, A = Arrhenius factor; R = Gas constant (8.314 J/K/Mol); T = Temp. in Kelvin.

Activation energy (E_a) of adsorption were obtained from the slope of the linear plot between $\log k_{ad}$ and $1/T$ (Fig.3.10). The values of activation energy (E_a) as a function of dye initial concentration (C_0) are given in table-5. The magnitude of E_a increases with the increase of dye initial concentration. It may be due to the involvement of stronger solute-solute as well as solute-solvent interactions at higher solute (dye) concentrations which obstructs closer approach of adsorbate (dye) molecules to the adsorbent surface. Further, the values of activation energy are low, suggesting that adsorption process may be controlled by intra-particle diffusion, Sismanoglu & Pura 2001¹⁷.

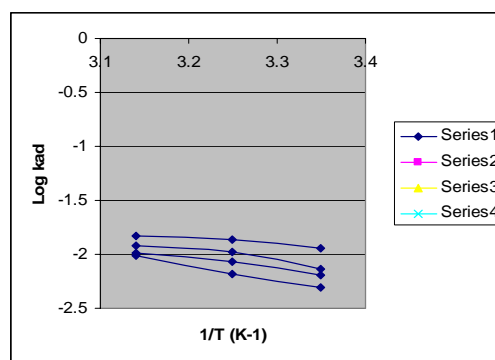


Fig. 3.10: Plots of $\log k_{ad}$ as a function of $1/T$ for Aniline Blue (from top to bottom: $C_0= 10,30, 50, 75$ mg/L); Adsorbent: 1.0 g/100ml; mesh No.: 60.

Table 5: Values of Energy of Activation (E_a/K)mole⁻¹ of adsorption at varying Aniline Blue initial concentration for the studied dye systems

| C_0 (mg/L)→ | 10 | 30 | 50 | 75 |
|----------------------------|-------|-------|-------|-------|
| E_a/K mole ⁻¹ | 10.32 | 15.27 | 17.26 | 19.14 |

Intra-particle diffusion

Possibility of intra-particle diffusion was explored by using the relation:

$$Q_t = k_{dif} \cdot (t)^{0.5} + C \quad \text{----- (3.9.1)}$$

Where, Q_t ($\text{mol} \cdot \text{g}^{-1}$) is the amount of dye adsorbed at time 't'. Intra-particle diffusion rate constant k_{dif} ($\text{mol} \cdot \text{min}^{-0.5} \cdot \text{g}^{-1}$) is obtained from the slope of plot between Q_t and $(t)^{0.5}$. The magnitude of the intercept C, is a measure of the thickness of adsorbed layer. Larger the intercept greater is the boundary layer effect, Kannan & Sundaram 2001¹⁸. The values of Q_t versus $(t)^{0.5}$ at 298.15K at different Aniline Blue initial concentration are presented in Fig.3.11. The values of intra-particle diffusion rate constant, k_{dif} , and intercept C, as a function of dye initial concentration (C_0) and temperature for the studied dye systems are given in table-6. It is found that at the given temperature diffusion rate constant k_{dif} , as well as intercept C, increases with the increase of dye initial concentration. The increase in diffusion rate constant at higher dye initial concentration may be attributed to larger adsorbent (dye) concentration gradient between the surface and the bulk solution.

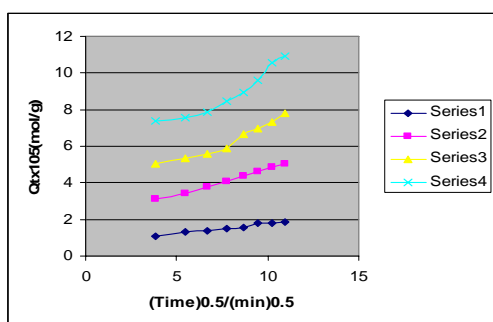


Fig.3.11 Amount of Aniline Blue dye adsorbed (Q_t) $\times 10^5$ ($\text{mol} \cdot \text{g}^{-1}$) as a function of $t^{0.5}/(\text{min})^{0.5}$ at 298.15K :- Dye initial concentration of dye, C_0 , are:- series-1: 10 mg/dm^3 ; series-2: 30 mg/dm^3 ; Series-3: 50 mg/dm^3 ; Series-4: 75 mg/dm^3 Adsorbent: 1.0 g/100ml; mesh No.: 60.

Table 6: The values of Intra-particle diffusion constant (k_{dif}) and C for Aniline Blue dye as a function of initial dye concentration (C_0) at 298.15K; Adsorbent: 1.0 g/100ml; mesh No.: 60.

| T(K) | C_0 (mg/dm ³) | $k_{dif} \times 10^6$ ($\text{mol} \cdot \text{min}^{-0.5} \cdot \text{g}^{-1}$) | Intercept, C |
|--------|-----------------------------|--|--------------|
| 298.15 | 10 | 1.08 | 0.63 |
| 298.15 | 30 | 2.71 | 2.16 |
| 298.15 | 50 | 3.92 | 4.01 |
| 298.15 | 75 | 5.01 | 5.87 |

An increase in the intercept (C), a measure of thickness of the adsorbate layer, at higher dye initial concentration, is obvious as the amount of dye adsorbed then would be more. It is also seen that at the given dye initial concentration, on increasing the temperature the diffusion rate falls. It is because at higher temperature, due to

more thermal agitation, the concentration gradient of the adsorbate between adsorbent surface and the bulk vanishes resulting in the lowering of the diffusion rate. Further, the observed higher value of the intercept (an indicator of more adsorbate thickness at the adsorbent surface) at higher temperature, may be due to enhanced adsorption at higher temperature, described earlier.

Equilibrium constant and Thermodynamic Parameters of adsorption:

Equilibrium constant K_0 , for the adsorption of adsorbate (dye) at the adsorbent surface was calculated using the relation-

$$K_0 = C_{ad}/C_{sol} \quad \text{----- (3.10.1)}$$

Where C_{ad} and C_{sol} represent the concentrations of the adsorbate (dye) on the solid adsorbent and in solution phase, respectively. Gibbs free energy of adsorption (ΔG_0) values were obtained using the relation-

$$\Delta G_0 = -RT \cdot \ln K_0 \quad \text{----- (3.10.2)}$$

Where, $R = 8.314 \text{ JK}^{-1} \cdot \text{mol}^{-1}$ and $T =$ temperature in Kelvin. Entropy of adsorption (ΔS_0) was obtained from the relation-

$$\Delta S_0 = -d(\Delta G_0)/dT \quad \text{----- (3.10.3)}$$

Enthalpy of adsorption (ΔH_0) was obtained using Gibbs Helmholtz equation-

$$\Delta H_0 = \Delta G_0 + T \cdot \Delta S_0 \quad \text{----- (3.10.4)}$$

The values of equilibrium constant (K_0) and thermodynamic parameters (ΔG_0 , ΔH_0 and ΔS_0) thus obtained for Aniline blue dye systems are given in table-7. Equilibrium constant (K_0) value decreases at higher dye initial concentration but increases at higher temperature. The observed negative values of ΔG_0 for the studied adsorbate-adsorbent systems, indicates that adsorption process is spontaneous irrespective of initial dye concentrations as well as temperatures. At the given temperature, ΔG_0 values increase (becomes less negative) with the increase of initial dye concentration. This may be due to decrease in intra-particle diffusion rate at higher concentrations of the dye. However, at a fixed initial dye concentration, ΔG_0 decreases (becomes more negative) with the increase of temperature. It may be attributed to (a) the enhanced diffusion rate of the adsorbate molecules which facilitates their approach to the active sites at the adsorbent surface and (b) the larger pore-size of the adsorbent at higher temperature. The values of ΔH_0 are positive indicating endothermic nature of adsorption process suggesting that the uptake of the adsorbate (dye) by the adsorbent is through physisorption, Gopal & Elango 2007¹³. The observed positive ΔS_0 indicates the increase of disorder and randomness at the adsorbent-adsorbate interface. This may be due the displacement of larger number of water molecules by the adsorbate (dye) species from the adsorbent surface, resulting in a gain of more translational entropy than that lost by the adsorption of adsorbate (dye) molecules, Gopal & Elango 2007¹³. At the given concentration, equilibrium constant (K_0) and % adsorption of dye increase and ΔG_0 values decrease on raising the temperature. This may be attributed to the enlargement of pore size and more activation of the adsorbent surface at higher temperature, Gopal and Elango, 2007¹³.

Table 7: Equilibrium constants (K_0) and thermodynamic parameters (ΔG_0 , ΔH_0 and $T\Delta S_0$) for adsorption of dye (Aniline Blue) onto activated carbon. Adsorbent: 1.0 g/100ml; mesh No.: 60.

| Dye mg/l | K_0 (KJ/mol) | | | - ΔG_0 (KJ/mol) | | | ΔH_0 (KJ/mol) | | | $T\Delta S_0$ | | |
|----------|----------------|-------|-------|-------------------------|------|------|-----------------------|-------|-------|---------------|-------|-------|
| | 25°C | 35°C | 45°C | 25°C | 35°C | 45°C | 25°C | 35°C | 45°C | 25°C | 35°C | 45°C |
| 10 | 9.75 | 20.74 | 42.48 | 5.64 | 7.76 | 9.92 | 58.16 | 58.18 | 58.16 | 63.8 | 65.94 | 68.08 |
| 30 | 4.38 | 7.06 | 9.75 | 3.66 | 5.01 | 6.02 | 31.52 | 31.35 | 31.52 | 35.18 | 36.36 | 37.54 |
| 50 | 3.13 | 4.99 | 7.26 | 2.83 | 4.12 | 5.24 | 32.95 | 32.86 | 32.94 | 35.78 | 36.98 | 38.18 |
| 75 | 2.42 | 4.75 | 6.35 | 2.19 | 3.99 | 4.89 | 38.06 | 37.61 | 38.06 | 40.25 | 41.6 | 42.95 |

Effects of the size and the amount of the adsorbent on adsorption:

Effects of the size and the amount of the adsorbent (Aniline blue dye) on % adsorption at equilibrium, equilibrium constant and thermodynamic parameters of adsorption are given in table-8. At the given temperature, percent adsorption of dye increases and Gibb's free energy of adsorption (ΔG_0) decreases with the increase in the amount as well as the mesh number of the adsorbent particles. These observations may be explained in terms of the fact that on

increasing the amount as well as mesh number of the adsorbent, the number of available active binding sites per adsorbate (dye) molecule at the adsorbent surface are raised. The magnitudes of endothermic enthalpy and entropy of adsorption increase on increasing the amount as well as the adsorbent particle mesh number. It is obvious since at higher load of the adsorbent and with the finer size of adsorbent particles, the number of desorbing water molecules will be much higher compared to the number of adsorbing dye molecule leading to enhanced randomness as well as endothermicity in the system.

Table 8: Effects of temperature, particle size (Mesh No.) and amount of adsorbent on % adsorption and thermodynamic parameters for adsorption: (Initial concentration, C_0 of Aniline Blue: 1.0×10^{-4} M)

| Temp. (K) | Mesh No. of adsorbent | Amount of Adsorbent (g/100ml) | % adsorption | $-\Delta G_0$ (KJ/mol) | ΔH_0 /(KJ/mol) | ΔS_0 (KJ/mol) |
|-----------|-----------------------|-------------------------------|--------------|------------------------|------------------------|-----------------------|
| 298.15 | 30 | 0.50 | 78.80 | 5.56 | 16.05 | 21.61 |
| 298.15 | 60 | 0.50 | 80.93 | 6.45 | 18.45 | 24.90 |
| 298.15 | 30 | 1.00 | 85.42 | 7.04 | 25.91 | 32.95 |
| 298.15 | 60 | 1.00 | 92.97 | 8.45 | 24.35 | 32.80 |
| 308.15 | 30 | 0.50 | 81.75 | 6.33 | 16.01 | 22.34 |
| 308.15 | 60 | 0.50 | 88.45 | 7.08 | 18.65 | 25.73 |
| 308.15 | 30 | 1.00 | 90.77 | 7.57 | 26.48 | 34.05 |
| 308.15 | 60 | 1.00 | 93.66 | 8.76 | 25.14 | 33.90 |
| 318.15 | 30 | 0.50 | 90.22 | 7.01 | 16.05 | 23.06 |
| 318.15 | 60 | 0.50 | 91.46 | 8.12 | 18.45 | 26.57 |
| 318.15 | 30 | 1.00 | 93.76 | 9.25 | 26.91 | 36.16 |
| 318.15 | 60 | 1.00 | 95.87 | 10.65 | 24.35 | 35.00 |

CONCLUSION

The present work reports the kinetic and equilibrium studies on adsorption of Aniline Blue dye from aqueous solution onto activated rice husk carbon. The effect of parameters such as: contact time, dye initial concentration, temperature, adsorbent particle size and amount of adsorbent on % adsorption of Aniline Blue on the activated rice husk carbon has been investigated. At the specified dye initial concentration, percent adsorption increases with increase in temperature as well as with the increase in the adsorbate-adsorbent contact period. At the given temperature, the percentage adsorption of dye decreases with the increase in dye initial concentration. The observed data was analysed in the light of Langmuir and Freundlich adsorption isotherms. From the evaluated thermodynamic parameters of adsorption it is inferred that the adsorption of Aniline Blue dye at the rice husk carbon is endothermic and predominately controlled by entropy gain. The observed positive entropy of adsorption may be due to a net gain of more translational entropy due to the desorption of water molecules than that lost by the adsorption of dye molecules at the adsorbent surface. At the given temperature, percent adsorption of dye increases and Gibb's free energy of adsorption (ΔG_0) decreases with the increase in the amount as well as the mesh number of the adsorbent particles. These observations may be explained in terms of the fact that on increasing the amount and decreasing the particle size of adsorbent, the number of available active binding sites per adsorbate (dye) molecule at the adsorbent surface are raised, therefore, the adsorption becomes more feasible.

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