



Sorption dynamics and equilibrium uptake of reactive red 2 using activated carbon prepared from agricultural waste

Karthikeyan S^{1,*} and Sumithra C²

¹Department of Chemistry, Chikkanna Government Arts College, Tirupur, India.

²Department of Chemistry, Tejaa Shakthi Institute of Technology for Women, Coimbatore, India.

ARTICLE INFO

Article history:

Received: 15 May 2012;

Received in revised form:

16 August 2012;

Accepted: 1 September 2012;

Keywords

Activated *Moringa Oleifera* fruit shell waste,

Carbon adsorption,

Reactive Red 2,

Kinetics,

Isotherm.

ABSTRACT

The feasibility of activated carbon prepared from *Moringa Oleifera* fruit shell waste to remove Reactive Red 2 from aqueous solutions was investigated through batch mode contact time process. The effects of various experimental parameters, such as initial concentration, pH, adsorbent dosage and temperature were investigated in a batch-adsorption technique. The optimum conditions for removal of the basic dye were found to be pH 6.5. The equilibrium data were best represented by the Langmuir isotherm model, with maximum mono layer adsorption capacity. The kinetic data were fitted to pseudo first order, pseudo second order and intra particle diffusion models and it was found to follow closely the pseudo first order kinetic model.

© 2012 Elixir All rights reserved.

Introduction

Textile effluents are known toxicants, which inflict acute disorders in aquatic organisms. Uptake of textile effluents through food chain in aquatic organisms may cause various physiological disorders like hyper tension, spordiac fever, renal damage, cramps etc¹. Reactive Red 2 is one such effluent which causes various disorders when present in aqueous solution. Hence the treatment of waste water containing Reactive Red 2 is a challenging problem. Adsorption using activated carbon is one of the efficient procedures for treatment of waste water². Cellulosic and Lignocellulose wastes have long been recognized as starting materials for the preparation of activated carbon^{3,4}. Commercial activated carbons are expensive and their use requires elaborate regeneration and reactivation procedure⁵. Several low cost carbon and non conventional adsorbents have been used. Adsorbents used include fly-ash^{6,7}, Wollastonite^{8,9,10}, Saw dust and rice husk with coir pith carbon¹¹, Pomegranate Peel¹² 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 produce 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.

Moringa 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 oleifera* fruit shell waste as an adsorbent for the removal Reactive Red 2 in aqueous solution.

Materials and Methods

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 waste and dries at 110 °C for 1 hours carbonization of the sample was carried out at 650 °C in a temperature programmable furnace under N₂ atmosphere at the end of carbonization, the material in the furnace was let to cool down to ambient temperature under the same N₂ flow rate¹² the carbon sample thus obtained was washed with pure distilled water and dried in the oven at 120 °C and then finely grinded. The grinded powder was sieved in the size large from 180-250 μm. A stock solution of 1000 mg/L of Reactive Red 2 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 Reactive Red 2 is represented in Table 1. The batch adsorption studies were performed at 30 °C. 100 mg of adsorbent was mixed with known initial concentration (20, 40, 60 mg/L respectively) of Reactive Red 2 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).

Kinetics 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 by¹³

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303(t) \tag{1}$$

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 from the slope and intercept of the plot, $q_{e(pred)}$ can be calculated.

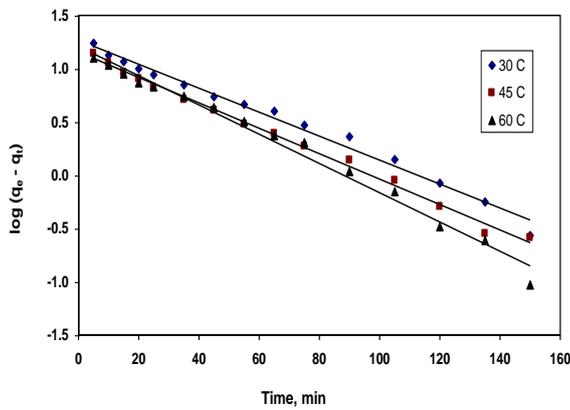


Fig. 1 : Pseudo First Order Plot

Elovich Model

The Elovich or Roginsky – Zeldovich equation is generally expressed as follows¹⁴,

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

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 Clayton¹⁵ assumed $\alpha\beta \gg 1$, and on applying the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, the above equation becomes,

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

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.

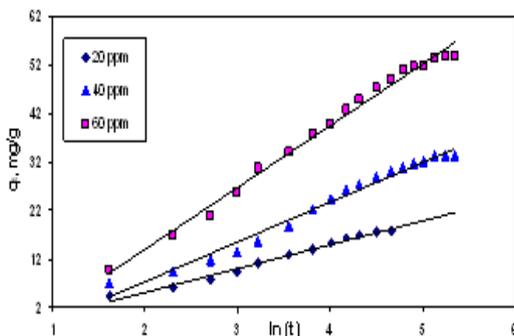


Fig. 2 : Elovich Plot

Pseudo Second Order Kinetic Model

To describe dye adsorption, the modified pseudo second order kinetic equation is expressed as¹⁶

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

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

$$h = k_2 q_e^2 \tag{5}$$

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

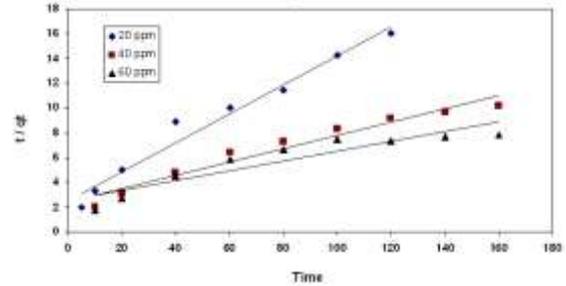


Fig. 3 : Pseudo Second Order Plot

Isotherm Studies

Langmuir Isotherm

The Langmuir adsorption isotherm is based on the assumption¹⁷ 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 occur¹⁸. The monolayer capacity can be represented by the expression:

$$q_e = Q_0 k_L C_e / (1 + k_L C_e) \tag{6}$$

The linear form of the above equation is represented as:

$$C_e / q_e = 1 / Q_0 k_L + C_e / Q_0 \tag{7}$$

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 (Fig. 4). The equilibrium concentration and hence the amount of dye adsorbed were calculated by varying the dye concentration between 20mg/L and 60mg/L with a fixed adsorbent dose and all other experimental conditions kept constant.

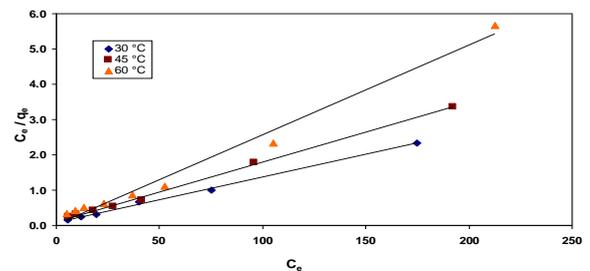


Fig. 4: Langmuir Plot

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 parameter¹⁹.

$$R_L = 1 / (1 + K_L \times C_0) \tag{8}$$

The value of R_L indicates the type of isotherm to be favourable ($0 < R_L < 1$), linear ($R_L=1$), unfavourable ($R_L > 1$) or

irreversible $R_L = 0$, where K_L is the Langmuir constant and C_0 is the highest initial dye concentration (mg/L).

Freundlich Isotherm

Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is commonly given by²⁰

$$q_e = k_f C_e^{1/n} \quad (9)$$

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

$$\log q_e = 1/n \log C_e + \log k_f \quad (10)$$

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)

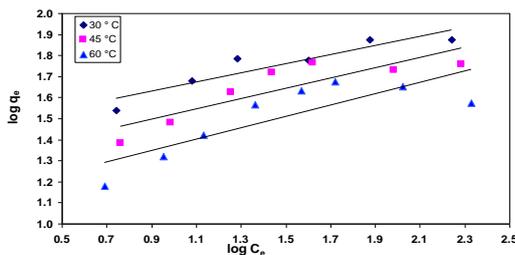


Fig. 5 : Freundlich Plot

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 relations²¹,

$$K_c = C_{Ae} / C_e \quad (11)$$

$$\Delta G^0 = - RT \ln K_c \quad (12)$$

$$\log K_c = \Delta S / 2.303R - \Delta H / 2.303RT \quad (13)$$

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.

Results and Discussion

Effect of pH on Reactive Red 2 removal

The pH is an important controlling parameter in the adsorption process and thus the role of hydrogen ion concentration was studied for the adsorption of Reactive Red 2 at different pH, covering a range of 4 to 8 at 30 °C. Batch experiments were conducted. The initial concentration of the Reactive Red 2 solution used was 0.1 mg/50 ml with 100 mg of the adsorbent. The Removal of Reactive Red 2 was found to be maximum at a pH of around 7 to 8. At lower pH the large numbers of H^+ ions neutralizes the negatively charged coal surface or convert a neutral group to be positively charged.

Effect of initial concentration of Reactive red 2 solutions

The initial concentration of Reactive Red 2 solution was varied (10 ppm to 80 ppm) and batch adsorption experiments were carried out with 100mg of the adsorbent at 30 °C and at pH 7. An decrease in percentage removal of Reactive Red 2 from 92 to 24 % was observed with 100mg of the adsorbent (Fig. 6), when the initial concentration of the Reactive Red 2 solution was varied from 10 mg/L to 80 mg/L. The higher uptake of Reactive Red 2 at low concentration may be attributed to the availability of more active centers on the surface of the

adsorbent for lesser number of adsorbate species. It is also observed that the actual amount of dye adsorbed increase with increases in initial dye concentration (C_0) is due to increase in the interactions between the adsorbent and adsorbate, therefore an increase in the amount of dye adsorbed for unit weight of adsorbent.

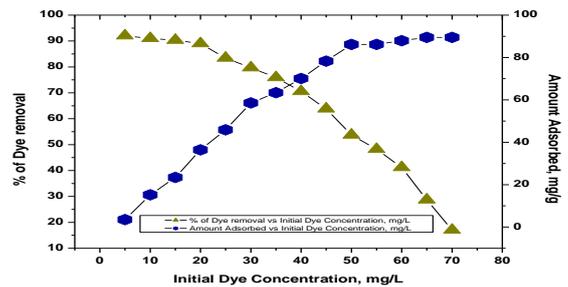


Fig. 6 : Effect of Initial Concentration of Reactive Red Solution

Effect of temperature of Reactive red 2 solutions

Temperature influences the Reactive Red 2 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 7. The adsorption capacities of the activated *Morienga Oleifera fruit shell waste* increases with decreasing temperatures from 60 to 30 °C, which indicates that the adsorption process is exothermic. 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.

Effect of Adsorbent Dosage

The amount of dye adsorbed (mg/g) and the percentage dye removal with increase in adsorbent dosage is shown in Fig. 7. The carbon dosage was varied in the range of 0.02 to 0.12g and the adsorption of Reactive Red 2 for a dye concentration of 80mg/L was studied.

The percentage dye removal increased from 38.16% to 98.99 % for an adsorbent dosage of 0.02 to 0.12 g. This is due to the increased surface area and availability of more adsorption sites. An adsorbent dosage of 0.12 g was required to attain 98.99 % dye removal. When the adsorbent and the solute concentration are low then the adsorption rate is low. On the other hand, when the adsorbent to 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. At high adsorbent to solute concentration, the adsorption is high on the adsorbent surface and hence the solute concentration in the solution decreases. This is due to the adsorption of a fixed amount of dye on a fixed mass of the adsorbent.

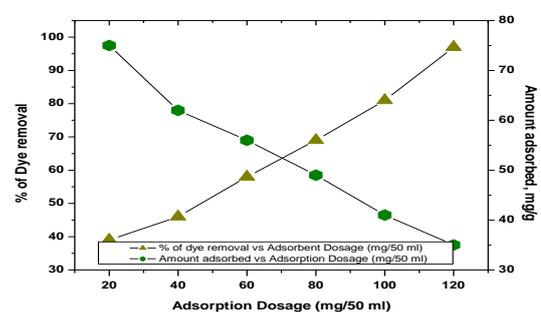


Fig. 7 : Effect of Adsorption dosage of Reactive Red Solution

Kinetic Modeling

Pseudo First Order Equation

Fig. 1 shows a plot of Pseudo First Order Equation for the results of adsorption of Reactive Red 2 from 20 mg/L to 60 mg/L between $\ln(q_e - q_t)$ and agitation time over whole sorption period with high correlation coefficient (>0.98) for all the lines (table 2). It is clear that the pseudo first order equation may be used to describe the kinetics of sorption of Reactive Red 2 on to *Morienga Oleifera* fruit shell waste. Although the Pseudo First Order Equation does not provide any mechanistic evidence, it has been proved suitable for highly heterogeneous systems of which the adsorption of Reactive Red 2 on *Morienga Oleifera* fruit shell waste is undoubtedly such a case.

Elovich Model

The results of the sorption of Reactive Red 2 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, 40 mg/L, 60 mg/L). From the plot a linear relationship between the amount of Reactive Red 2 adsorbed, qt 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.

Pseudo Second Order Model

The same data are shown as pseudo second order equations in Fig. 3. These plots show the data fits had good correlation coefficients (>0.987) when the pseudo second order equation was employed. It was possible to ascertain from them whether the rate determining process is a chemical reaction. Thus, increasing the initial dye concentration from 20 mg/L to 60 mg/L the Reactive Red 2 sorbed at any contact time increases. This is obvious for higher initial concentration values, as a more efficient utilization of the sorptive capacities of the sorbent would be expected due to greater sorption driving force.

The corresponding linear plots of the values of q_e , k_2 and h against C_0 were regressed to obtain the expressions for these values in terms of the initial Reactive Red 2 concentration, C_0 , with high correlation coefficients (> 0.992). Hence, it was further considered that q_e , k_2 and h could be expressed as functions of C_0 as follows

$$q_e = \frac{C_0}{1.010C_0 - 20.85} \quad (14)$$

$$k_2 = \frac{109.4C_0 - 1.616 \times 10^4}{C_0} \quad (15)$$

$$h = \frac{0.6113C_0 - 11.19}{C_0} \quad (16)$$

Substituting the values of q_e , k_2 and h from equations (14) and (16) into equations (4), the rate law for a pseudo-second order reaction and the relationship of qt , C_0 and t can be represented as:

$$qt = \frac{C_0 t}{(0.6113C_0 - 11.19) + (1.010C_0 - 20.85)t} \quad (17)$$

Equation (17) represents the generalized productive model for Reactive Red 2 adsorption at any contact time and initial concentration within the specified concentration range. It indicates that the amount of Reactive Red 2 at any contact time increased with increasing the initial dye concentration. This is obvious for higher initial concentration values, as a more efficient utilization of the sportive capacities of the sorbent would be expected due to greater sorption driving force. This

equation can then be used to derive the amount of Reactive Red 2 sorbed at any given initial dye concentration and reaction time.

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 $1/n \ll 1$ 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.

Mechanism for sorption of Reactive Red 2 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 material²².

It is now well established, that during the adsorption of dye over a porous adsorbent, the following three consecutive steps have taken place²³

- (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 compounds²⁴. 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 \approx 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 experiments, rapid stirring is maintained. This induces Reactive Red 2 from the solution to the pores of the adsorbent material and this step may control the rate of the adsorption process²⁵.

According to Michelson et al.²⁶ 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_f , should be in the range $10^{-6} - 10^{-8}$ cm²/sec. If pore diffusion were to be the rate limiting step, the pore diffusion coefficient, D_p , should be in the range $10^{-11} - 10^{-13}$ cm²/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 sorbents²⁷, the overall rate constant of the process can be correlated to the pore diffusion coefficient in accordance with the expression,

$t_{1/2} = 0.03 \frac{r_o^2}{D_p}$ or to the film diffusion coefficient in accordance with

$$t_{1/2} = 0.23 \frac{r_o \partial}{D_f} \times \frac{\bar{C}}{C} \quad (18)$$

where r_o is radius of the sorbent (cm), D_p and D_f are pore diffusion coefficient (cm²/sec) and film diffusion coefficient

(cm²/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 the size range (180-250 μ m), the average diameter of the particle was taken as 0.0215×10^{-4} cm. Using these values, the film diffusion co-efficient and pore diffusion co-efficient were calculated.

Then considering the pseudo first order rate constant k_L , for the adsorption of Reactive red 2, 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 values of D_p and D_f for all Reactive Red 2 in the present study are found to be in the order 10^{-10} to 10^{-11} and 10^{-9} to 10^{-10} cm/sec which indicates that pore diffusion has some amount of influence in the rate determining step.

Gupta et al²⁸, have reported a D_p value in the order of 10^{-10} cm/sec for the removal of Reactive Red 2 by a mixture of two adsorbents and these authors suggested that the adsorption process was governed by pore diffusion even though it could not be ascertained that pore diffusion was the only rate determining step.

Lakshman 2002²⁹ has stated that D_p value in the order of 10^{-10} cm/sec would confirm that the adsorption process was under the control of intraparticle diffusion. The author has also added that both film and intra particle diffusion have different degrees of influence on the rate determining step. The present study indicates the D_p in the order of 10^{-11} to 10^{-10} cm/sec and the D_f value in the order of 10^{-10} to 10^{-9} for the respective pseudo first order plots for each Reactive Red 2 and hence the investigator concludes that the mechanism of the removal of the Reactive Red 2 in the present study by *Moringa Oleifera fruit shell waste* is complex.

Since both external Mass transfer and intraparticle diffusion constants varied with initial Reactive Red 2 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 al³⁰,

$$F = 1 - \frac{6}{\pi^2} \sum_{N=1}^{\infty} \frac{1}{n^2} \exp \left[\frac{-Dit\pi^2 n^2}{r^2} \right] \quad (19)$$

$$F = 1 - \frac{6}{\pi^2} \sum_{N=1}^{\infty} \frac{1}{n^2} \exp \left[-n^2 \beta_t \right] \quad (20)$$

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.

$$F = \frac{q_t}{q_e}$$

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 table³¹ 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.

$$B = \pi^2 D_i / r^2 \quad (21)$$

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 ΔS^\ddagger and pre exponential constant D_o were calculated using the following equations.

$$D_i = D_o \exp[-E_a/RT] \quad (22)$$

$$D_o = (2.72d^2kT/h) \exp[\Delta S^\ddagger/R] \quad (23)$$

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

Thermodynamics Parameters

ΔH and ΔS values were obtained from the slope and intercept of Vant Hoff plot ($1/T$ vs $\ln K_c$). A batch adsorption study were carried out with Reactive Red 2 solution at $pH \approx 7.0$ and by varying the temperature (303K, 318K and 333K). The initial concentration of Reactive Red 2 solution used was maintained to be 20 mg/L with 100 mg of the adsorbent. Table 6 gives the value of ΔG , ΔS and ΔH for the adsorption of Reactive Red 2. The negative values of free energy change (ΔG) indicates the feasibility and spontaneous nature of the adsorption of Reactive Red 2 species. The negative ΔH values of the process suggest the exothermic nature of the absorption of Reactive Red 2 on to activated *Moringa Oleifera fruit shell*

waste carbon. The positive value of ΔS is due to the increased randomness during the adsorption of Reactive Red 2.

Conclusion

In the present study adsorption of Reactive Red 2 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 Reactive red 2 from aqueous solution. The adsorption of Reactive red 2 is dependent on the initial concentration and agitation time. Equilibrium of Reactive Red 2 adsorption reaches at 160 min.

The pseudo first and second order equations provide a best fit description for the sorption of Reactive Red 2 on to *Moringa Oleifera fruit shell waste* related to Elovich model, but the pseudo first order correlation coefficient has better correlation value than pseudo second order equation, pseudo first order equation is consider to be the most appropriate due to high correlation coefficient when compared to pseudo second order equation.

Langmuir and Freundlich adsorption isotherm correlate the equilibrium adsorption data. The adsorption of Reactive Red 2 on to activated *Moringa Oleifera fruit shell waste* carbon is an exothermic reaction based on enthalpy change values.

Acknowledge

We acknowledge the Principal and Head of the Department of Chemistry, Chikkanna Government Arts College, Tirupur for their kind co-operation and support to complete this work successfully.

References

- Karthikeyan S., Jambulingam M., Sivakumar P., Shekhar A.P. and Krithika J., Impact of Textile Effluent on Fresh Water Fish Mastacembelus Armatus (Cuv. & Val), *E-J. Chem.*, 13, 303 (2006).
- Jambulingam M., Renugadevi N., Karthikeyan S., Kiruthika J. and Pattabi S., Adsorption of Cr(VI) from Aqueous Solution Using a Low Cost Activated Carbon, *Indian J. Environ. Prot.*, 25, 458 (2005).
- Dean J. C., Bosqui F. L. and Lanovette K. M., Removing heavy metals from waste water, *Environ. Sci. Technol.*, 6, 518 (1972).
- Mukherjee A. F.,(ed) Environmental Pollution and Health Hazards: Causes and Control,(1986).
- Karthikeyan S., Jafar Ahamed A., Maiyalagan T. and Saravanan D., Removal and Recovery of Cr(VI) from waste water using an Agricultural waste material: *Moringa Oleifera* seed shell, *proc. of 3rd ICCE.*, (2007).
- Nagarnaik P.B., Bhole A.G. and Natarajan G.S., Adsorption of Arsenic on Fly ash, *Indian J. Environ. Health.* 45, 1 (2003).
- Kelleheri B.P., O' Callaghan M., Leahy M.J., O' Dwyer T.F. and Leahy J.J., The use of fly- ash from the combustion of poultry litter for the adsorption of Chromium (III) from aqueous solution, *J. Chem. Technol. Biotechnol.*, 77, 1212 (2002).
- Swamy M.M., Mall I.D., Prasad B. and Mishra I.M., Sorption characteristics of O – Cresol on Bagasse flyash activated carbon, *Indian J. Environ. Health*, 40, 67 (1998).
- Sharma Y.C., Adsorption of Cr(VI) on to Wollastenite, Effect of pH, *Indian J. of Chem.Tech.*, 8, 186 (2001).
- Saravanam R., Sundararajan T. and Sivamurthy Reddy S., Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from waste water. A Cooperative study, *Indian J. Environ. Health*, 44, 78 (2002).
- Namasivayam C. and Kadirvelu K., Agricultural by Product as Metal Adsorbent Sorption of Lead (II) From Aqueous

Solution on to Coir Pith Carbon, *Environ. Technol.*, 21, 1091, (2000).

- Murugan M. and Subramaniam E., Biosorbent Cupressus female cone in the Efficient treatment of effluent containing Cr(VI), *J. Sci. Indian Res.*, 62, 1071 (2003).
- Lagergren S., Zur Theorie Der Sogennten Adsorption Geloster Stoffe, *Hand linger.*, 24, 1 (1898)
- Low K. S., Lee C. K. and Ng A. Y., Column Study On The Adsorption of Cr(VI) Using Quaternised Rice Hulls, *Bioresour. Technol.*, 65, 205 (1999).
- Chien S.H. and Clayton W.R., Application of Elovich equation to the Kinetics of Phosphate Release and Sorption on Soils, *Soil Sci. Soc. Am. J.*, 44, 265 (1980).
- Ho Y. S. and Macy G., Study of the Sorption of Divalent Metal Ions to Peat, *Adsorpt. Sci. Technol.*, 18, 639 (2000).
- Langmuir I., The Adsorption of Gases on plain surfaces of Glass, Mica, Platinum, *J. Am. Chem. Soc.*, 40, 1361 (1918).
- Wang Y.C., Szeto Y.S., Cheung W.H. and McKay G., Equilibrium studies for acid dye Adsorption onto chitosan, *Langmuir.*, 19, 7888 (2003).
- Bulut Y. and Aydin H., A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, *Desalination.*, 194, 259 (2006).
- Freundlich H., "Colloid and Chemistry", *Methien*, London, (1926).
- Stephen Inbaraj B. and Sulochana N., Basic Dyes Adsorption on a Low Cost Carbonaceous Sorbent Kinetic and Equilibrium Studies, *Indian J. Chem. Technol.*, 9, 201 (2002).
- Gupta V. K., Mittal A. and Gajbe V., Adsorption and Desorption Studies of a Water Soluble Dye, Quinoline Yellow, Using *Waste Materials*, *J. Colloid. Interface Sci.*, 284, 89 (2005).
- Gupta V. K., Ali, I. and Mohan D., Equilibrium Uptake and Sorption Dynamics for the Removal of a Basic Dye (Basic Red) Using Low Cost Adsorbent, *J. Colloid Interface Sci.*, 265, 257 (2003).
- Crank J(Ed)., The Mathematics of Diffusion, *Clarendon, Oxford*, (1956).
- Weber W. J. Jr. and Morris C. J., Kinetics of Adsorption on Carbon from Solution, *J. Sanit.Engg. Div.*, 89, 31 (1963).
- Michelson L.D., Gideon P.G., Page A.G. and Kutal L.H., Removal of soluble mercury from wastewater by complexing technique, *U.S.D.I. Office Water Res. Technol. Bull.*, 74, 33 (1975).
- Bhattacharya A.K. and Venkobachar C., Removal of Cd(II) by low cost adsorbents, *J. Environ. Eng. Div.*, 110, 110 (1984).
- Gupta G.S., Prasad G., Panday K.K. and Singh V.N., Removal of Chrome Dye from Aqueous Solution by Fly Ash, *Water Air Soil Pollut.*, 37, 13 (1988).
- Lakshmanan S., Adsorption Dynamics - Removal of Copper Using Lignite as an Adsorption, *Ph.D., Thesis, Bharathidasan University, India*, (2002).
- Boyd G. E., The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites II. Kinetics, *J. Am. Chem. Soc.*, 69, 2836 (1947).
- Reichenberg D., Properties of Ion - Exchange Resins in Relation to their Structure, III. Kinetics of Exchange, *J.Am.Chem.Soc.*, 75, 589 (1953).

Table 1 : Properties of Reactive Red 2

Parameters	Value
C.I Name	Reactive Red 2
C.I Number	18200
Ionization	Acidic
Molecular Formula	$C_{19}H_{10}Cl_2N_6Na_2O_7S_2$
Molecular Weight	615.33

Table 2: Kinetic Model Values for the Adsorption of Reactive Red 2 on to *Moringa Oleifera* fruit shell waste Activated Carbon.

Concentration	Pseudo First Order Values		Elovich Values			Pseudo Second Order Values			
	$k_{Lager} \times 10^{-2}$	r^2	A	β	r^2	q_e	$k_{Lager} \times 10^{-2}$	h	r^2
20 ppm	1.7300	0.988	0.859	0.506	0.826	16.31	7.106	0.801	0.986
40 ppm	1.7283	0.982	0.758	0.171	0.949	27.90	1.338	0.555	0.988
60 ppm	1.7291	0.985	0.657	0.0996	0.984	49.20	0.356	0.356	0.975

Table 3: Parameters of Langmuir and Freundlich Adsorption Isotherms

Temperature °C	Langmuir Isotherm			Freundlich Isotherm		
	b, L/mg	Q_0 , mg/g	R_L	1/n	n	k_f
30	0.07826	86.170	0.149	0.6704	1.3484	1.99194
45	0.07771	91.7087	0.118	0.6172	1.5694	4.09105
60	0.07694	119.0747	0.128	0.5734	1.6852	6.3375

Table 4: D_p and D_f values for the chosen adsorbent - adsorbate system

S.No.	Dye	Temperature, °C	$t_{1/2}$, s	$D_p \times 10^{-10}$, cm^2	$D_f \times 10^{-9}$, cm^2
1	Reactive Red 2	30°C	3398.72	1.0200	6.613
		45°C	4595.99	0.7543	4.645
		60°C	4695.37	0.6931	4.073

Table 5: Values of energy of activation E_a , entropy of activation ΔS^\ddagger and pre-exponential constant D_0 for the present study

S.No.	Parameter	Value
1.	D_i , cm^2s^{-1}	
	30° C	3876×10^{-11}
	45° C	1.2728×10^{-11}
	60° C	1.0341×10^{-11}
2.	E_a , $KJmol^{-1}$	-9.5735
3.	ΔS^\ddagger , $JK^{-1}mol^{-1}$	-185.02
4.	D_0 , cm^2s^{-1}	9.3325×10^{-12}

Table 6: Thermodynamic Parameters for the adsorption of Reactive Red 2 on to *Moringa Oleifera* fruit shell waste Activated Carbon.

Temperature	ΔG , J mole ⁻¹	ΔS , J mole ⁻¹	ΔH , KJ mole ⁻¹
303 K	-731.56	17.06	-7.964
318 K	-431.905		
333 K	-131.941		