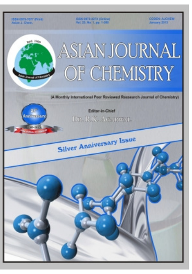
Asian Journal of Chemistry; Vol. 25, No. 3 (2013), 1331-1338

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.12975



Orthophosphoric Acid Activated *Ananas comosus* Leaves Carbon as an Adsorbent for the Removal of Basic Yellow 2

R. Parimalam[1], V. Raj[2] and P. Sivakumar[3]

[1]Department of Chemistry, Sri Meenakshi Government College for Women, Madurai-625 002, India
[2]Department of Chemistry, Periyar University, Salem-636 011, India
[3]Department of Chemistry, Arignar Anna Government Arts College, Namakkal-637 002, India

*Corresponding author: Fax: +91 452 2650374; Tel: +91 452 2534988; E-mail: pari_ramachandran@yahoo.co.in

(*Received*: 31 October 2011; *Accepted*: 8 September 2012) AJC-12108

Removal of basic yellow 2 from aqueous solution by adsorbing it on an activated carbon prepared from *Ananas Comosus* (L) leaves was investigated by batch method. The studies were conducted by varying the pH, initial dye concentration, contact time and temperature. The sorption data was analyzed using the Langmuir, Freundlich, Tempkin isotherm and Dubinin-Radushkevich (D-R) isotherm models. The maximum monolayer adsorption capacity was found to be 227.27 mg/g. The Freundlich model is more appropriate to explain the adsorption phenomena with good fit. The data were also analyzed in terms of their kinetic behaviour and was found to obey the pseudo second order equation with an r^2 value of 0.999.

Key Words: Adsorption, Activated carbon, Basic yellow-2 dye, Kinetics, Equilibrium.

INTRODUCTION

The coloured effluent from the textile industries is a major pollutant in the industrial sector in terms of the volume and effluent composition[1]. Hence, treatment is necessary to reduce the dye concentration to acceptable level before releasing into water bodies. The discharge of highly coloured effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological process within a stream. In addition, many dyes are found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high. Basic yellow 2 (Auramine-O) is one such basic dyes, which has positive electrical charge and are used for anionic fabrics which are negative charge bearing, such as wool, silk, nylon and acrylics where bright dyeing is the prime consideration for textiles, leather and paper[2]. It has also been used as an antiseptic or a fungicide. It may enter the environment from industrial discharge or spills. It may be a carcinogen in humans since it has been shown to cause liver and lymphatic cancers in animals[3]. Chemicals similar to this dye can destroy or disturb the ability of the blood to carry oxygen, continuous exposure have caused liver, kidney damage and bladder cancer. Therefore a method to treat dye wastewater containing such dye is highly desirable.

Effluent containing dyes are difficult to treat because most of these chemicals are resistant to aerobic digestion[4]. There are several methods for the removal of pollutants from effluents. However, there is no single process which is capable of treating these effluents because of the complexity of the matrix[5]. Practically, a combination of different processes is often used to achieve the desired water quality in the most commercial way. Liquid-phase adsorption is one of the most studied methods for the removal of pollutants from wastewater, since it generally produce a high-quality treated effluent[6-8]. The treatment of wastewaters by adsorption process is an excellent choice especially if the sorbent is inexpensive and does not require any additional pre-treatment step before its application.

Adsorption has been found to be superior to other techniques for water re-use in terms of its initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutant[9-11]. The process also does not result in the formation of harmful substance like in many other cases. The main sorbents used to remove dyes in wastewater employs activated carbon because of good adsorption ability[12,13]. The use of activated carbon, however, is restricted due to its high cost. An attempt to develop low cost and effective adsorbents and many non-conventional adsorbents such as clay materials, zeolites, siliceous material, effective adsorbents and industrial waste products have also been suggested[14-16]. In this paper the attention is focused on the use of activated carbon prepared from *Ananas comosus* leaves as an alternative low cost adsorbent for the removal of basic yellow 2 (BY 2) from aqueous solution due to the reason that many textile manufacturers use this and release to environment is a potential carcinogen. The data shall be used to evaluate the adsorption parameters with the help of model equations and also find out the adsorption kinetics.

EXPERIMENTAL

Basic yellow 2 obtained for this investigation was from E. Merck, India. All chemicals used in this study were of analytical grade. The molecular structure of the dye is shown in Fig. 1. Basic yellow 2 (BY 2) having molecular formula $C_{17}H_{21}N_3HCl$ (m.w.: 303.83, λ_{max} = 434 nm) with CI. No. 41000. Stock solution (1000 mg/L) of basic yellow (Fig. 1) is prepared by dissolving appropriate amount of dye (based on % of purity) in 1000 mL of double distilled water. The stock solution was diluted with double distilled water to obtain required standard solution.

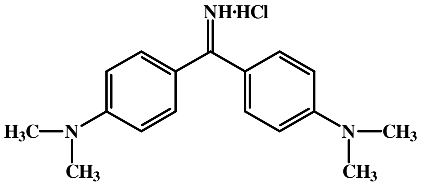


Fig. 1. Molecular structure of basic yellow 2

Preparation of activated carbon: Raw material (*Ananas comosus* leaves) used for the preparation of activated carbon was collected locally, cut into pieces of 1-2 cm size, dried in sunlight for 7 days. The dried material soaked in a boiling solution of 10 % H_3PO_4 for 1 h and kept at room temperature for overnight, then the material was separated, air dried and carbonized in muffle furnace at 400 ºC for 20 min. The carbonized material was powdered, activated in a muffle furnace at 600 ºC for a period of 10 min. Then the material was washed with plenty of distilled water to remove residual acid, dried, sieved 45-300 µm size and stored in a tight lid container for further adsorption studies. The activated carbon will be designated as ACC.

SEM photograph of the carbon sample were examined by scanning electron microscope (Hitachi S-3400N). The surface area of the prepared carbon is measured by N_2 adsorption at -195.826 ºC using micrometrics ASAP 2020 V3.00H surface area analyzer. Prior to the analysis, the sample was out gassed at 200 ºC for 12 h. The differential pore volume and pore size distribution were calculated using Horvath and Kawazoe model[17] and BJH model[18]. The median pore width was calculated using Horvath and Kawazoe method. The physico-chemical characteristics of the adsorbent is given in Table-1.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF ACC

Properties	Values
pH	8.93
Conductivity (mS cm^{-1})	0.09
Moisture content (%)	7.4
Ash (%)	15.4
Volatile matter (%)	18.3
Matter soluble in water (%)	0.42
Matter soluble in 0.25 N HCl (%)	1.28
Bulk density (g mL^{-1})	0.43
Specific gravity	0.92
Porosity (%)	53.26
Surface area (BET) (m^2 g^{-1})	807.74
Methylene blue value (mg g^{-1})	345
Iodine Number (mg g^{-1})	948
Fixed Carbon (%)	58.9
Yield	54.6

Batch adsorption experiments: To study the effect of important parameters such as effect of initial concentration, pH, agitation time, temperature, batch studies were performed by agitating 200 mL of dye solution in 250 mL volumetric flasks at 30, 40 and 50 ºC with 100 mg of adsorbent. The mixture was withdrawn at specified interval then centrifugated using electrical centrifuge (Universal make) at 3000 rpm for 10 min and unabsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make Bio-UV visible spectrometer (BL-198) at λ_{max} 434 nm. The effect of pH was studied by adjusting the pH of the adsorptive solution by using 0.1 N NaOH and 0.1 N HCl. The contact time, concentration, temperature *etc*., were altered and variation in the amount of dye taken up was analyzed for the adsorbent. The percentage of dye removal and the amount adsorbed on to unit weight of the adsorbent was calculated using the equations:

$$\text{Percentage of dye removal} = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

The amount of adsorption at equilibrium q_e (mg/g) was calculated by:

$$\text{Amount adsorbed } (q_e) = \frac{C_i - C_e}{C_i} \times \frac{V}{M} \qquad (2)$$

where C_i and C_e are the liquid phase concentration of the dye at initial and equilibrium concentrations (mg/L), respectively. M is the mass (g) of adsorbent and V is the volume of dye solution (mL).

Desorption studies: Desorption studies as a function of pH were conducted to analyze the possibility of reuse the adsorbent for further adsorption and to make the process more economical. After adsorption experiments the dye loaded carbon washed gently with double distilled water to remove any un-adsorbed dye present. Desorption studies were conducted using several such carbon samples. Exactly 50 mg of the dye loaded carbon agitated above the equilibrium time with 50 mL of double distilled water of various pH and the desorbed dye was estimated as stated in the adsorption.

RESULTS AND DISCUSSION

Characterization of the adsorbent: The SEM photographs ascertained that the relative pores with wide ranging cracks. The macro pores clearly visible facilitating the easy diffusion of more number of dye molecules in to the pore structure and also adsorbed on the surface of the adsorbent (Fig. 2).

Nitrogen adsorption/desorption isotherm of the prepared activated carbon: A qualitative information on the adsorption process and the extent of surface area available to

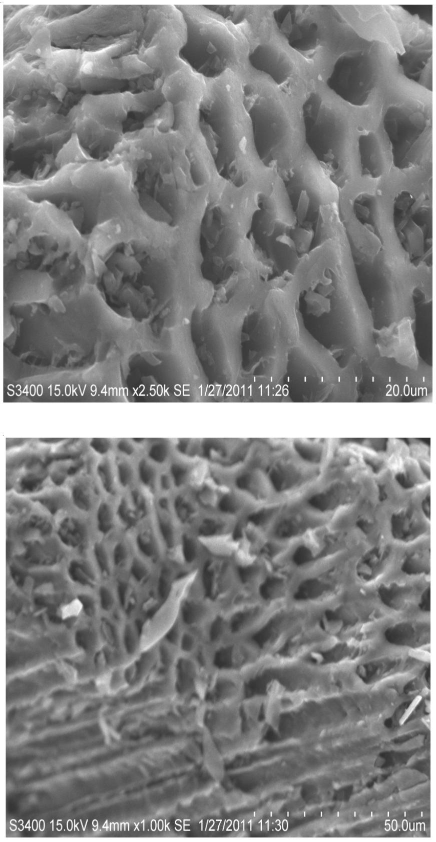


Fig. 2. SEM Photograph of ACC (at 2500 X and 1000X)

the adsorbate is given by the shape of the adsorption. The N_2 adsorption isotherm of the activated carbon prepared from *Ananas comosus* leaves at *ca.* 195.8 °C is shown in Fig. 3. The adsorption isotherm is classified as type I isotherm indicating that the carbon is mainly microporous[19,20] in nature. The hysteresis indicates the presence of mesopores on the surface of the carbon. The amount of nitrogen adsorbed on the adsorbent gradually increases in the whole relative pressure range, implying that this carbon contains a small amount of mesopores. The prepared carbon exhibits a moderately developed porosity with a specific surface area of 807.74 m^2/g and the single point adsorption total pore volume of pores (< 3584.729 Å) is 0.3655 cm^2/g. The BJH average pore radius (2V/A) is 8.5 Å and median pore width by Horvath and Kawazoe is 6.167 Å. The presence of micropores and mesopores in the activated carbon prepared from *Ananas comosus* leaves is given by pore size distribution calculated by Horvath and Kawazoe method and the differential pore volume plot is shown in Fig. 4.

Effect of pH: The initial pH of the dye solution is an important parameter, which controls the adsorption process particularly the adsorption capacity, pH of the solution may change (1) the surface charge of the adsorbent, (2) the degree of ionization of the adsorbate molecule and (3) extent of dissociation of functional groups on the active sites of the adsorbent. To observe the effect of pH on the extent of dye adsorption, dye solution pH varied from 2-11. The percentage of dye removal at different pH is shown in Fig. 5 for the initial dye concentration of 50 mg/L. From this study it is observed that maximum adsorption takes place at pH value of 8. Fig. 5 also shows that the removal of dye increases with the increase of pH up to 8 and then it gradually decreases. This is attributed to increasing electronegative charge on the adsorbent as the pH of the solution is increased. As the adsorbent is negatively charged, the increasing electrostatic attraction between positive adsorbate dye species and the negative adsorbent particle would lead to increased adsorption of dyes.

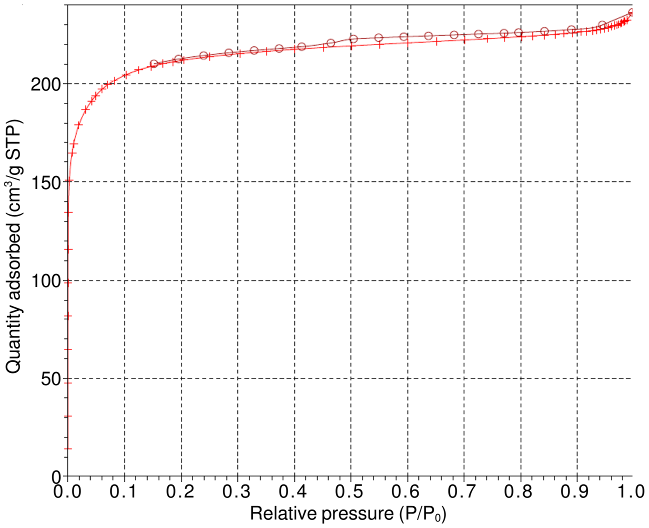


Fig. 3. Nitrogen adsorption /desorption isotherm of the prepared activated carbon

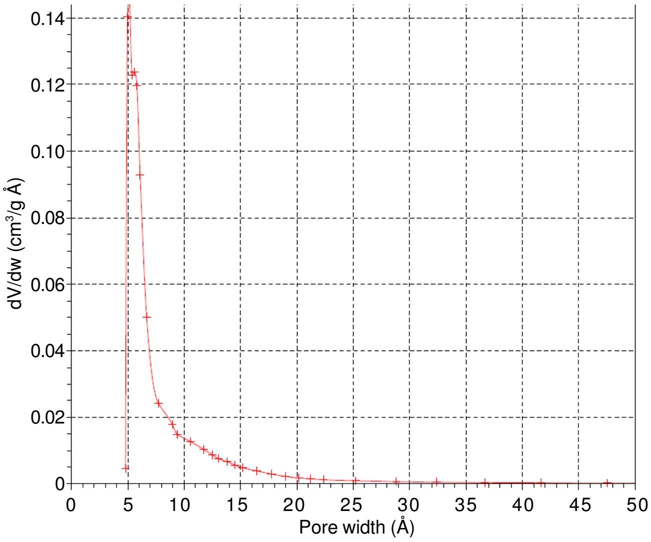


Fig. 4. Horvath-Kawazoe differential pore volume plot for the prepared activated carbon

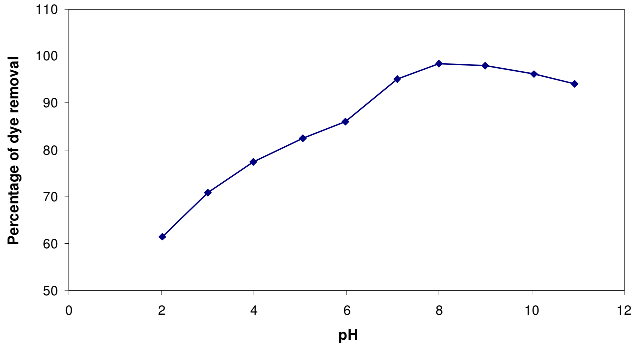


Fig. 5. Effect of pH for the adsorption BY 2 onto ACC at 303 K

Effect of contact time and initial dye concentration: The variation in amount removal of dye with contact time at different initial concentration ranging from 25-100 mg/L is presented in Fig. 6. It is observed from the figure that the maximum amount of dye adsorption taking place within the contact time of 40 min and becomes gradual there after. This indicates that the rate of adsorption is very fast.

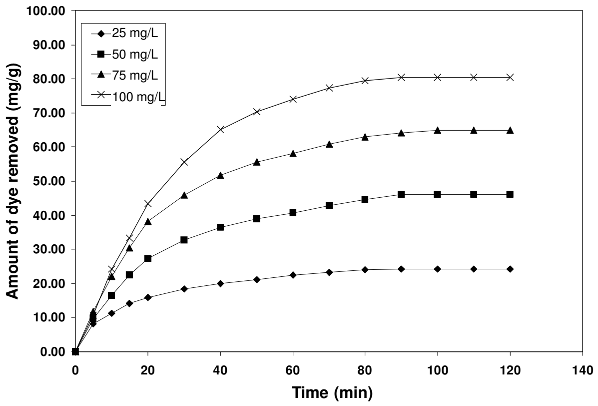


Fig. 6. Effect of agitation time on the removal of BY 2 onto ACC at 303 K

After 90 min there is no significant change in the extent of adsorption. For an initial concentration of 75 mg/L more than 90 % adsorption was observed, whereas for 100 mg/L, the percentage removal of dye is 85.03 %. From the above observation, it is evident that, at lower concentration of dye, the adsorption process is very fast. The percentage removal of dye decreases with increase in initial concentration and takes longer time to reach equilibrium because of the fact that with increase in dye concentration, there will be increased competition for the active adsorption sites and the adsorption process will increasingly slowing down.

Effect of temperature on the dye removal: The percentage of basic yellow 2 sorption by ACC increases from 90.28 to 97.26 % while increasing the temperature from 303 to 323 K. The adsorption increases with temperature indicates that the sorption of basic yellow 2 by ACC is endothermic in nature Fig. 7. This may the result of increase in the mobility of the larger dye ion with increasing temperature. However , the maximum amount of basic yellow BY 2 adsorbed between 303 and 323 K are close to each other and thus the temperature has a small effect on adsorption.

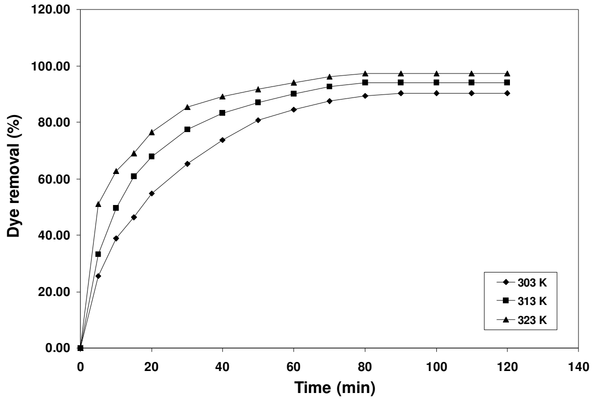


Fig. 7. Effect of temperature for the adsorption of basic yellow 2 onto ACC

Kinetic studies: Four kinetic models were applied to adsorption kinetic data in order to investigate the behaviour of adsorption process of basic yellow 2 onto ACC. These models are pseudo-first-order, pseudo second order, Elovich and the intra-particle diffusion models.

Pseudo-first-order model: The pseudo first order model is given as[21]

$$\log\,(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

where, q_e and q_t are the amount adsorbed (mg g^{-1}) at equilibrium and time t (min^{-1}), respectively and k_1 is pseudo-first-order rate constant. The values of k_1 at different temperatures were calculated from the slope of the respective linear plots of log (q_e – q_t) *versus* time (Table-2). Typical pseudo-first order plots for adsorption of BY 2 on ACC at different concentrations are also shown in Fig. 8. The correlation coefficient for the pseudo first order model was in the range of 0.951-0.982. The calculated q_e values did not agree with the experimental data. The results indicated that the adsorption of basic yellow 2 onto ACC does not follow the pseudo first order kinetics.

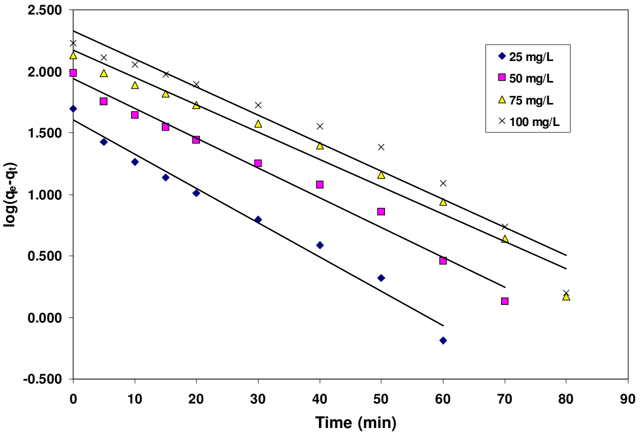


Fig. 8. Pseudo first order plot for the adsorption of basic yellow 2 onto ACC at 303 K

Pseudo second order model: The pseudo second order model[22] has the following form

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

where, k_2 is the rate constant of the pseudo-second-order equation (g mg^{-1} min^{-1}).

The straight line plots of t/q_t *versus* t have been used to obtain the rate parameter. The values of k_2 (g mg^{-1}) and correlation coefficients, r^2 at different concentrations and temperatures were calculated from these plots (Table-2). Fig. 9 and 10 show the plot of pseudo second order model for an different initial dye concentrations and different temperatures, respectively.

Good correlation were obtained by fitting the experimental data to eqn. 4, indicating that the adsorption process for the dye is the pseudo second order. The pseudo second order rate constants indicate that the uptake of dyes increases with increase of concentration from 25 to 100 mg/L and decreases with the increasing solution temperatures. These results may

TABLE-2
CALCULATED KINETIC PARAMETERS FOR THE ADSORPTION OF BY 2
ONTO ACC AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Concentration (mg/L)	25	50 h	75	100	Temperature		
					303 K	313 K	323 K
First order kinetics							
$k_1 \times 10^{-2}$ (min^{-1})	0.06218	0.05527	0.05066	0.05066	0.0511	0.0566	0.0564
q_e cal (mgg^{-1})	40.27	87.096	145.54	212.32	147.43	132.46	107.32
q_e exp (mg g^{-1})	49.95	96.53	135.42	170.07	135.42	141.10	145.89
r^2	0.980	0.982	0.974	0.951	0.9741	0.9833	0.9843
SSE (%)	3.061	2.983	3.2002	13.36	4.003	2.732	11.629
Second order kinetic							
$k_2 \times 10^{-4}$ (g mg^{-1} min^{-1})	27.9	9.0	3.396	1.44	3.319	6.34	10.48
q_e cal (mgg^{-1})	55.55	111.11	166.66	250	158.73	156.25	153.84
h	8.609	11.11	9.432	9.0	9.372	15.478	24.802
r^2	o.9990	0.9980	0.9970	0.9940	0.9976	0.9992	0.9996
SSE (%)	1.496	3.896	8.349	21.362	6.229	4.075	2.124
Elovich model							
α (mg g^{-1} min^{-1})	0.1198	0.0523	0.0297	0.0213	0.0283	0.0498	0.0498
β (gm g^{-1})	40.27	33.909	20.585	18.82	19.181	36.265	144.09
r^2	0.942	0.971	0.981	0.976	0.9908	0.9806	0.9795
Intra particle diffusion model							
Kdiff (mgg-1 min)	3.382	8.3759	10.42	14.887	5.960	6.223	4.650
r^2	0.973	0.983	0.999	1.000	0.966	0.987	0.993
l	23.27	29.07	18.00	36.44	79.56	85.73	104.1

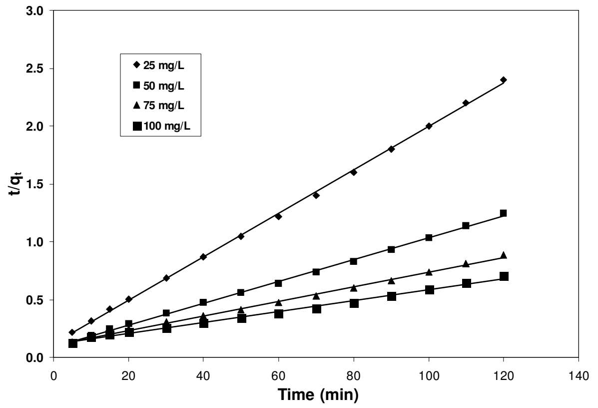


Fig. 9. Pseudo second order plot for the adsorption of basic yellow 2 onto at 303 K

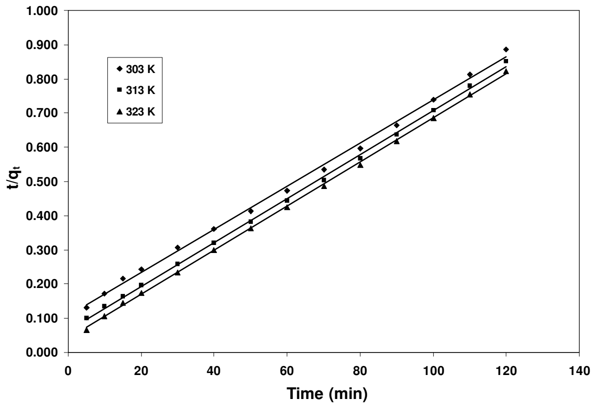


Fig. 10. Pseudo second order plot for the adsorption of basic yellow 2 onto ACC

be attributed to the fact that increasing the temperature of the solution increases the rate of the approach to the equilibrium adsorption capacity due to enhanced mobility of ions at high temperature[23].

Elovich model: The Elovich equation is mainly applicable for chemisorptions kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous[24]. The Elovich model is generally expressed as:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (5)$$

Integrating this equation for the boundary conditions, gives:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (6)$$

where, α is the initial adsorption rate (mg/g min) and β is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg).

A plot of q_t *versus* ln t gives a linear trace with a slope of (1/β) and an intercept of 1/β ln (αβ). The results of Elovich plot for the adsorption of BY 2 by ACC at various initial dye concentration and temperatures are given in Table-2 (Figure not shown). The plot is linear with good correlation coefficient (r^2 = 0.942-0.981). The initial adsorption rate a, decreases from 40.27 to 18.82 on increasing initial concentration from 25 to 100 mg/L.

Intra particle diffusion model: It is known that adsorption is a multi step process involving transport of solute molecules from the aqueous phase to the surface of the solid particles. Webber and Morris[25] reported that the intra-particle diffusion equation is

$$q_t = k_d t^{1/2} + 1 \quad (7)$$

where, *l* is the intercept and k_d is the intra particle rate constant. The intercept l represents the effect of boundary layer thickness. Maximum is the intercept length, adsorption is less boundary layer controlled.

Figs. 11 and 12 show that the intra particle diffusion plots for BY 2, the plots of q_t *versus* $t^{1/2}$ present a multi linearity

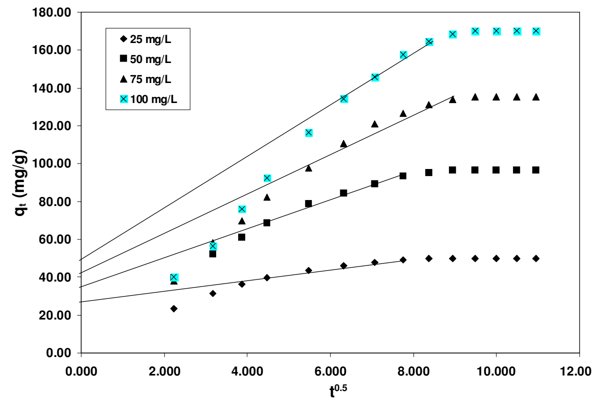


Fig. 11. Intra particle diffusion for the adsorption of basic yellow 2 onto ACC at 303 K

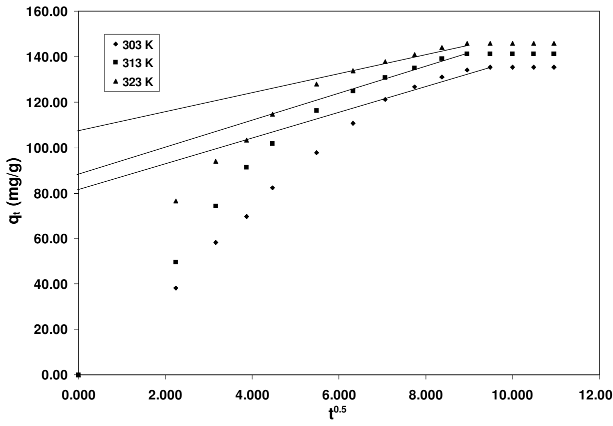


Fig. 12. Intra particle diffusion plot at various temperatures

correlation, which indicates that two steps occur during the adsorption process. The first portion is a gradual adsorption stage, where diffusion of the solute molecules on the surface of adsorbent can be rate controlling. The second stage is the final equilibrium stage, where the diffusion of the solute molecules into the interior of the pores starts to slow down due to low solute concentration in solution[26]. Values of the intra-particle diffusion constant, k_d was obtained from the slopes of the linear portion of the plots (Table-2). The correlations coefficient for the intra particle diffusion model (r^2) were 0.9782 to 0.9999, for various initial concentrations. Both the lines does not passes through the origin that concludes that both film diffusion and intra particle diffusion are simultaneously occurring during the adsorption of BY 2 onto ACC. Similar result is found for adsorption of cationic dye using silkworm pupa as adsorbent[24].

Adsorption isotherm: Adsorption properties and equilibrium parameters, commonly known as adsorption isotherms, describe how the adsorbate interacts with adsorbents and comprehensive understanding of the nature of interaction. Isotherms help to provide information about the optimum use of adsorbents. In order to optimize the design of an adsorption system to remove dye from solutions. It is essential to establish the most appropriate correlation for the equilibrium curve. There are several isotherm equations available for analysis of experimental sorption equilibrium parameters and three important isotherms are selected in this study are the Langmuir, Freundlich and Tempkin isotherm models.

Langmuir isotherm: The application of Langmuir isotherm suggests that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not nearby sites are occupied and that the adsorbent is saturated after one layer of adsorbate molecules formed on the adsorbent surface. The equation of Langmuir isotherm[27].

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_0}{Q_0} \tag{8}$$

where, Q_0 (mg/g) and b (L/mg) are the Langmuir isotherm constants determined from the plot of C_e *versus* C_e/q_e as shown in Fig. 13 (Table-3). An essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter, R_L, which is defined by the eqn. 9[28]:

$$R_L = \frac{1}{(1 + bC_0)} \tag{9}$$

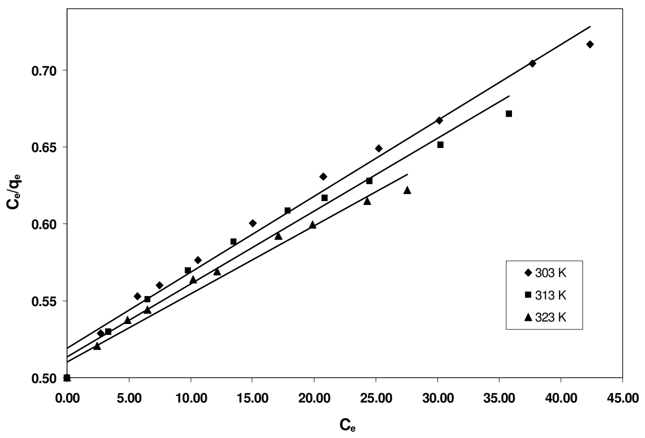


Fig. 13. Langmuir isotherm for the adsorption of basic yellow 2 onto ACC

TABLE-3
RESULTS OF VARIOUS ISOTHERM PLOTS
FOR THE ADSORPTION OF BY 2 ON TO ACC

Temperature (K)	303	313	323
Langmuir			
Q_0 (mg g^{-1})	204.08	212.76	227.27
b × 10^{-2} (Lm g^{-1})	0.9439	0.9156	0.8629
R_L	0.4307	0.4382	0.4528
K_L	1.9263	1.9481	1.9611
r^2	0.9855	0.9732	0.9734
Freundlich			
1/n	0.2662	0.2702	0.2759
n	3.7565	3.7009	3.624
k_f ($mg^{1-1/n}L^{1/n}g^{-1}$)	71.76	78.05	87.17
r^2	0.9903	0.9803	0.9854
Tempkin			
α (Lg^{-1})	2.7577	3.4126	4.2447
β (mgL^{-1})	40.27	42.002	44.928
b	0.01598	0.01547	0.01673
r^2	0.9898	0.9539	0.9613
Dubinin-Radushkevich			
Q_m (mg g^{-1})	177.06	176	187
k (× 10^6 mol^2 kJ^{-2})	1.8	0.6	1.4
E (kJ mol^{-1})	0.5270	1.1785	0.5050
r^2	0.8805	0.635	0.653

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 b is the Langmuir constant and C_0 is the highest initial concentration (mg/L). The value of R_L was found to be in the range 0.4307-0.4528 for various temperatures, which suggests that the adsorption of BY 2 is a favorable process.

Freundlich isotherm: The Freundlich isotherm model is an exponential equation that applies to adsorption on heterogeneous surface with interaction between adsorbed molecules and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and correspondingly that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. The well- known expression for the Freundlich model is given as[29].

$$q_e = k_F C_e^{1/n} \tag{10}$$

where, k_F is the Freundlich constant [mg/g(L/g)$^{1/n}$] related to the binding energy and n is the heterogeneity factor and is a measure of the deviation from linearity of the adsorption. It indicates the degree of non-linearity between solution concentration and adsorption. The value of n in the range of $0 < n > 1$ represents favorable adsorption conditions[30]. A plot of log q_e *versus* log C_e (Fig. 14) used to calculate the Freundlich constant k_F and n. The value of n was found to be 3.625-3.7 for various temperatures, which indicate favorable adsorption of basic yellow 2 by ACC. Based on the r^2 values the linear form of the Freundlich isotherm fits well than other two model.

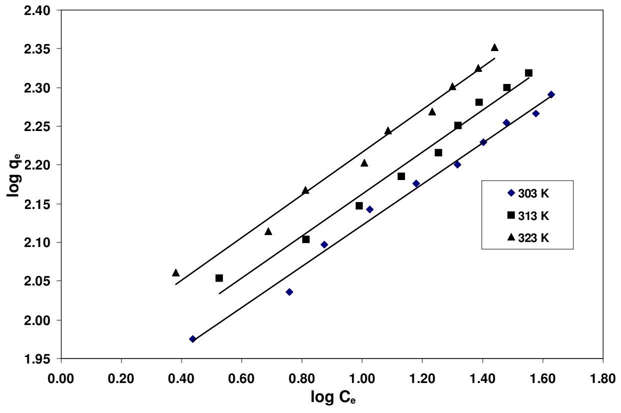


Fig. 14. Freundlich isotherm for the adsorption of BY 2 onto ACC

Tempkin isotherm: Tempkin isotherm takes into account of the effect of indirect adsorbate-adsorbate interaction and suggests that the heat of adsorption of all molecules in the adsorbent surface layer would decrease linearly with coverage[31]. The Tempkin Isotherm can be expressed as[32].

$$q_e = \frac{RT}{b} \ln (AC_e) \tag{11}$$

The Tempkin isotherm eqn. 11 can be simplified to the following form

$$q_e = \beta \ln \alpha + \beta \ln C_e \tag{12}$$

where, β = (RT)/b, T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 J(mol K)$^{-1}$. The constant b is related to the heat of adsorption. The adsorption data were analyzed according to the linear form of the Tempkin isotherm (eqn. 12). The linear isotherm constants and coefficients were determined from a plot of ln C_e *versus* q_e as shown in Fig. 15 and the results are presented in Table-3. The heat of BY 2 adsorption onto ACC was found to increase from 0.1547-0.167 kJ mol^{-1} with increase of temperature from 303-323 K. The correlation coefficient obtained from Tempkin model were comparable to that obtained for Langmiur and Freundlich equations, which explain the applicability of Tempkin model to the adsorption of BY 2 onto ACC.

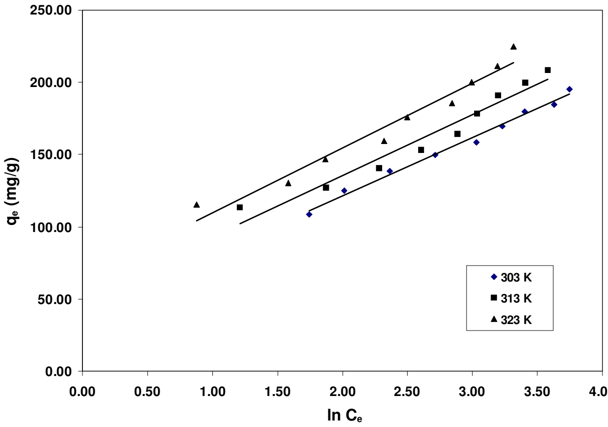


Fig. 15. Tempkin isotherm for the adsorption of BY 2 onto ACC

Dubinin-Radushkevich (D-R) isotherm: The D-R model was also applied to estimate the porosity apparent free energy and the characteristics of adsorption[33-35]. The D-R isotherm does not assumes a homogeneous surface or constant sorption potential. The D-R model has commonly been applied in the following linear form can be shown in eqn. 13:

$$\ln q_e = \ln Q_m \times k\varepsilon^2 \tag{13}$$

where, k is a constant related to the adsorption energy, Q_m the theoretical saturation capacity, ε the polanyi potential, calculated from the following equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{14}$$

The slope of the plot of ln q_e *versus* ε^2 (Fig not given) gives k (mol^2 (kJ^2)$^{-1}$) and the intercept yields the adsorption capacity, Q_m (mg g^{-1}). The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the k value using the following relation[35].

$$E = \frac{1}{\sqrt{2k}} \tag{15}$$

The calculated value of D-R parameters is given in Table-3. The values of E calculated using eqn. 15 are 0.5050 to 1.172 kJ mol^{-1}, which indicating that the physico-sorption process play the significant role in the adsorption of BY 2 onto ACC.

Thermodynamics of adsorption: Thermodynamic parameters like ΔH^o, ΔS^o and ΔG^o were measured based on Van't Hoff's plot.

$$\ln k_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{16}$$

where, k_L is the Langmuir equilibrium constant, ΔH^o and ΔS^o are the standard enthalpy and Entropy changes of adsorption, respectively and the values of ΔH^o and ΔS^o are calculated from the slopes and intercepts of the linear plot of ln k_L *versus* 1/T. The free energy of specific adsorption ΔG^o (kJ/mol) is calculated from the following expression.

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{17}$$

The thermodynamical parameters calculated from Eyring's plot are given in Table-4. Negative standard free energy of adsorption indicates that the adsorption process is favorable and spontaneous in nature.

TABLE-4
THERMODYNAMICAL PARAMETERS FOR THE ADSORPTION OF BY 2 ONTO ACC

Temperature (K)	ΔH^o (kJ/mol)	ΔS^o (J/K/mol)	ΔG^o (kJ/mol)
303	-305.12	3.375	-1.327
313			-1.361
323			-1.395

The negative value of ΔH^o for the system confirms the exothermic nature of adsorption. Similar results were reported for the adsorption of methylene blue by red mud[36] and malachite green by neem saw dust[37]. Physical adsorption is an exothermic process, which occur during physico-chemical process such as adsor ption.

The positive value of ΔS^o observed for the adsorption of dye molecules suggested the increased randomness at the solid-solution interface during adsorption process. The dye molecules in the aqueous media are hydrated. When the dye molecule get adsorbed on the adsorbent surface, the water molecules previously hydrogen bonded to the dye molecules get released and dispersed in the solution, this results in an increased in the entropy. The positive values of entropy changes also reflect good affinity of the dye towards the adsorbent. The entropy changes in the present study are in excellent agreement with adsorption of methylene blue on red mud[36], wheat shell[28] and alumina[38].

Desorption studies: A good adsorbent should be regenerable, otherwise waste have to be disposed of and fresh sorbent should be used. Desorption increases with increase of pH from 2-4. Then gradually decreases above pH 4. The maximum percentage of desorption observed at pH 4 was 47.86 %.

Conclusion

The results show that the adsorbent has a good BET surface area of 807.74 m^2/g with a total pore volume of 0.3655 cm^2/g. The equilibrium data fitted well with the Freundlich isotherm, confirming the heterogeneity of the adsorbent surface. The kinetics of basic yellow 2 adsorption on the ACC follows the pseudo second order model. The material used in this study is an agricultural waste product, freely and abundantly available and hence it can be used as alternative to the other commercial activated carbons used for dye removal in wastewater treatment process.

REFERENCES

1. M. Hema and S. Arivoli, *Int. J. Phys. Sci*., **2**, 010 (2007).
2. H. Zollinger, In Colour Chemistry; VCH; New York, edn. 1 (1987).
3. N.I. Sax, Cancer causing Chemical, DC 9625000, VNR: New York, edn. 1 (1981).
4. I.A. Alaton, B.H. Gutsoy and J.E. Schmidt, *Dyes Pigments*, **78**, 117 (2008).
5. S.M. Ghoreishi and R. Haghighi, *Chem. Eng. J*., **95**, 163 (2003).
6. S. Al. Asheh, F. Banat and L. Abu-Aitah, *Sep. Sci. Technol*., **21**, 451 (2003).
7. M.A. Khraisheh and M.S. Alg-Houti, *Adsorption*, **11**, 547 (2005).
8. A.R. Cestai, E.F.S. Viera and J.A. Mota, *J. Hazard. Mater*., **160**, 337 (2008).
9. D. Mohan, K.P. Singh, G. Singh and K. Kumar, *Ind. Eng. Chem. Res*., **41**, 3644 (2002).
10. G. McKay and S.J. Allen, *J. Sep. Proc. Technol*., **4**, 1 (1983).
11. S. Wang and H. Li, *Dyes Pigments*, **72**, 308 (2007).
12. I.A.W. Tan, B.H. Hameed and A.L. Ahmad, *Chem. Eng. J*., **127**, 111 (2007).
13. M.J. Iqbal and M.N. Ashiq, *J. Hazard. Mater*., **139**, 57 (2007).
14. S.B. Bakaullah, M.A. Rauf and S.S. Al Ali, *Dyes Pigm*., **24**, 85 (2007).
15. M. Lehocky and A. Mracek, *Czech. J. Phys*., **56**, 1277 (2006).
16. G. Cirini, *Bioresour. Technol*., **589**, 67 (2006).
17. G. Horvath and K. Kawazoe, *J. Chem. Eng. (Japan)*, **16**, 470 (1983).
18. E.P. Barrett, L.G. Jaoyner and P.P. Halenda, *J. Am. Chem. Soc*., **73**, 373 (1953).
19. C.T. Hsieh and H. Teng, *J. Colloid Interf. Sci*., **230**, 171 (2000).
20. P.K. Malik, *Dyes Pigments*, **56**, 239 (2003).
21. A. Ozcan and A.S. Ozcan, *J. Hazard. Mater*., **B125**, 252 (2007).
22. Y.S. Ho and G. McKay, *Process Safety Environ. Protect*., **76**, 183 (1998).
23. K. Ravikumar, B. Deebika and K. Balu, *J. Hazard. Mater*., **122**, 75 (2005).
24. B. Noroozi, G.A. Sorial, H. Bahrami and M. Arami, *J. Hazard. Mater*., **B139**, 167 (2007).
25. W.J. Weber Jr., J.C. Morriss and J. Sanit, *Eng. Div. Am. Soc. Civil Eng*., **89**, 31 (1963).
26. Q. Sun and L. Yang, *Water Res*., **37**, 1535 (2003).
27. I. Langmuir, *J. Am. Chem. Soc*., **40**, 1361 (1981).
28. Y. Bulut and H. Aydin, *Desalination*, **194**, 259 (2006).
29. M.K. Purkait, D.S. Gusain, S. Das Gupta and S. De, *Sep. Sci. Technol*., **39**, 2419 (2004).
30. M.J. Tempkin and V. Pyzhev, *Acta Physiol. Chem. U.S.S.R*., **12**, 217 (1941).
31. C. Aharoni and D.L. Sparks, In eds.: D.L. Sparks and D.L. Suarez, Kinetics of Soil Chemical Reactions-A Theoretical Treatment, Rate of soil Chemical Processes, Soil Science Society of America, Madison, Wt, pp. 1-18 (1991).
32. M.M. Dubinin, *Chem. Rev*., **60**, 235 (1960).
33. M.M. Dubinin, *Zh. Fizich. Khim*., **39**, 1305 (1965).
34. L.V. Radushkevich, *Zh. Fizich. Khim*., **23**, 1410 (1949).
35. S. Kundu and A.K. Gupta, *Colliods Surf. A*, **273**, 121 (2006).
36. A. Ramesh, D.J. Lec and J.W.C. Wang, *J. Colliod Interf. Sci*., **291**, 588 (2005).
37. S.D. Khattri and M.K. Singh, *Water, Air Soil Pollut*., **120**, 283 (2000).
38. M.J. Iqbal and M.N. Ashiq, *J. Chem. Soc. Pak*., **32**, 419 (2010).