



ADSORPTION ISOTHERMS, KINETICS, THERMODYNAMICS AND DESORPTION STUDIES OF REACTIVE ORANGE16 ON ACTIVATED CARBON DERIVED FROM *Ananas comosus* (L.) CARBON

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ABSTRACT

The study describes the results of batch experiments on removal of reactive orange16 from aqueous solution onto activated carbon prepared from *Ananas Comosus* leaves. The adsorbent has been studied as a function of contact time, temperature, pH and initial dye concentration by batch experiments. The pH 2-3 was found suitable for maximum removal of RO16. A dye adsorption capacity of activated carbon for the RO16 is 147.05 mg/g of adsorbent. Langmuir, Freundlich, Tempkin, Dubinin-Raduskevich isotherm models were applied for the analysis of isotherm data. Thermodynamic treatment of adsorption data showed an exothermic nature of adsorption. The dye uptake process was found to follow second order kinetics.

Keywords: reactive Orange16, *Ananas comosus* L., activated carbon, adsorption, kinetics.

1. INTRODUCTION

Various industries such as dye manufacturing, pulp and paper, tanneries, cosmetics, coffee pulping pharmaceuticals, food processing, electro plating and distilleries spew out colored and toxic effluents to water bodies rendering them murky, dirty and unstable for further use. Among these industries, the textiles industries rank first in consume larger volumes of water and chemicals for the wet processing of textiles. Reactive dyes are extensively used in textile industry, which are usually characterized by nitrogen to nitrogen double bonds (N=N azo bonds). The color of the azo dye is due to this azo bond and the associated chromophores. The dyes are first adsorbed onto the cellulose and then react with the fiber. The reaction occurs by the formation of a covalent bond between the dye molecule and the fiber, which is much more resistant to unusual condition of use than the physico-chemical bond between other classes of dyes and cellulose (Al-Degs *et al.*, 2000). These characteristics facilitate the interaction with the fiber and reduce energy consumption (Camp and Sturrock, 1990).

The reactive system of these dyes react with ionized hydroxyl groups on the cellulose substrate but the hydroxyl ions present in the dye bath, due to the alkaline dyeing condition, compete with cellulose substrate, resulting in a percentage of hydrolyzed dyes no longer able to react with the fiber (Low *et al.*, 2000). Thus approximately 10-50% of the initial dye load will be present in the dye bath, giving rise to a highly colored effluent (Easton, 1995). Reactive dyes are in general, the most problematic among other dyes, as they tend to pass through conventional treatment systems unaffected. Various physical, chemical and biological methods have been used for the treatment of dye containing wastewater. Some chemical oxidations, such as Fenton reagent, ozone, UV plus H₂O₂ or NaOCl, result in aromatic ring cleavage,

which may generate chemical sludge or by-products that are likely to be even more toxic (Robinson. *et al.*, 2001). Municipal aerobic treatment systems, dependent on biological activity were found to be ineffective in the removal of these dyes (Moran. *et al.*, 1997) but anaerobic bioremediation enables water soluble dyes to be decolorized (Carliell. *et al.*, 1996).

Although ion exchange resins can be regenerated easily, the high cost hinders their wide application for the treatment of dye-bearing waste water. Consequently, various types of (bio) sorbents which are able to bind dye molecules and be easily regenerated have been extensively searched and tested (Robinson. *et al.*, 2001 and Won. *et al.*, 2004). Potential areas for practical application of sorbents are in the final decolorization of pretreated mixed waste water or dye removal from rinsing waters (after dyeing processes) for direct water recycling. A suitable sorbent has to meet the following criteria (Karcher. *et al.*, 2001): (i) high affinity and capacity for target compounds, (ii) regeneration possible, (iii) safe and economically viable treatment/disposal of regenerate, (iv) tolerance for wide range of waste water parameters, and (v) usable for all or nearly all- reactive dyes.

Among the various available water treatment technique adsorption is the most reliable and efficient technique for discoloration, in which the recovery and recycling of the adsorbent materials can be achieved along with the distinct advantages of non production of any toxic sludge cost effectiveness. This has encouraged the development of adsorbent that abundantly available and economical. Now a days numerous low cost adsorbents are available including products of agriculture origin such as wood dust, sugarcane, fruit peel (Senthilkumaar. *et al.*, 2006), Wheat straw and apple pomace (Hana. *et al.*, 2006). Certain other low cost adsorbent materials of industrial origin such as activated slag (Srivastava. *et al.*,



1997), and bagasse fly ash (Gupta. *et al.*, 1998), have also been employed in the recent past. Various types of sludge like waste works sludge, sewage sludge, digested sludge and leachate sludge (Sung Wook Won *et al.*, 2006) and Zeolite from fly ash are employed to remove reactive orange dye (Denise Alves Fungaro *et al.*, 2008).

However, still there arises a great need to explore new low cost adsorbent materials with high adsorption capacity. Thus in the present study, keeping the toxic effect in view, attempts have been made to develop an efficient and cost effective technique for the removal of dye from waste water by employing carbon from waste material namely *Ananas comosus* leaves which is easily and abundantly available. The characterization of this carbon is done by X-ray diffraction (XRD) and BET surface area analysis, FT-IR Spectral and SEM analysis. Influence of temperature, pH of the dye solution, effect of contact time and initial dye concentration are studied under stirred condition. Thermodynamic parameters are calculated to know the nature of adsorption. Four different kinetic models for the adsorption of dye are presented. The equilibrium data are tested with Langmuir, Freundlich, Tempkin, Dubinin-Raduskevich isotherm models. This fundamental study will be helpful for further application in designing a batch adsorption for the treatment of dye containing effluent coming out from dye industries.

2. MATERIALS AND METHODS

2.1 Adsorbate

All chemicals used in this study were of analytical grade. Reactive Orange 16 (RO 16) having molecular formula $C_{20}H_{17}N_3O_{11}S_3Na_2$ (Mol. Wt: 617.53, $\lambda_{max} = 496$) with CI. No.17757, (E. Merck, India) was used as a model reactive dye in this work. As shown in Figure-1, RO16 has two sulfonate groups which have negative charges in aqueous solution (Figure-1).

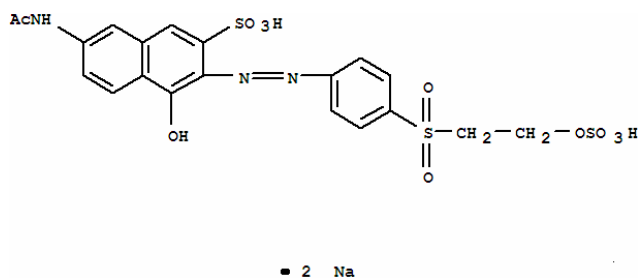


Figure-1. Structure of reactive orange 16.

2.2 Preparation of adsorbent (ACC)

Raw material (*Ananas comosus* leaves) used for the preparation of activated carbon was collected locally, cut into pieces of 1cm to 2cm size, dried in sunlight for 7 days. The dried material soaked in a boiling solution of 10% H_3PO_4 for 1h and kept at room temperature for overnight, then the material were separated, air dried and carbonized in muffle furnace at $400^\circ C$ for 20 min. The carbonized material was powdered, activated in a muffle furnace at $600^\circ C$ for a period of 10 min. Then the material

was washed with plenty of distilled water to remove residual acid, dried, sieved $45 \mu m$ to $300 \mu m$ size and stored in a tight lid container for further adsorption studies (Table.1).

2.3 Characterization

X-ray diffraction patterns of the activated carbon sample were studied using DELTA GX 270 and the patterns were recorded over a 2-theta (2θ) range of 10-75. The FT-IR spectra of the activated carbon sample were scanned by placing KBr pellets in the Parkin Elmer 16 PC spectrometer. The KBr pellets were prepared by mixing the carbon samples with KBr powder, grounding it in an agate mortar and then shaping it into pellets under hydraulic pressure. SEM photograph of the carbon sample were examined by scanning electron microscope (Hitachi S-3400N).

2.4 Adsorption studies

Adsorption characteristics were determined with the help of primary analysis. To study the effect of important parameters such as effect of initial concentration, pH, agitation time, temperature, batch studies were performed by taking 100ml of dye solution in 250ml volumetric flasks at 30, 40, and $50^\circ C$. 100mg of suitable mesh size activated carbon was chosen and added into each flask with intermittent shaking. The mixture was withdrawn at specified interval then centrifuged using electrical centrifuge (Universal make) at 3000 rpm for 10 minutes and unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make Bio-UV visible spectrometer (BL-198) at 496 nm. The effect of pH was studied by adjusting the pH of the adsorptive solution by using 0.1N NaOH and 0.1 N HCl. The adsorbent dose, concentration, etc. were altered and variation in the amount of dye taken up was analyzed for the adsorbent.

Table-1. Physico-chemical characteristics of ACC.

	Properties	Values
1	pH	8.93
2	Conductivity, $mS\ cm^{-1}$	0.09
3	Moisture content, %	7.4
4	Ash, %	15.4
5	Volatile matter, %	18.3
6	Matter soluble in water, %	0.42
7	Matter soluble in 0.25 N HCl, %	1.28
8	Bulk density, $g\ mL^{-1}$	0.43
9	Specific gravity	0.92
10	Porosity, %	53.26
11	Surface area (BET), $m^2\ g^{-1}$	807.74
12	Methylene blue value, $mg\ g^{-1}$	345
13	Iodine number, $mg\ g^{-1}$	948
14	Fixed carbon, %	58.9
15	Yield	54.6



2.5 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. 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 studies (Hsieh and Teng, 2000).

3. RESULTS AND DISCUSSIONS

3.1 Characterization of the adsorbent

The XRD spectrum of the adsorbent showed the broad peaks, which indicate the presence of amorphous form of carbon. It does not give any major peak which could be due to lack of inorganic substances in the activated carbon (Figure-2).

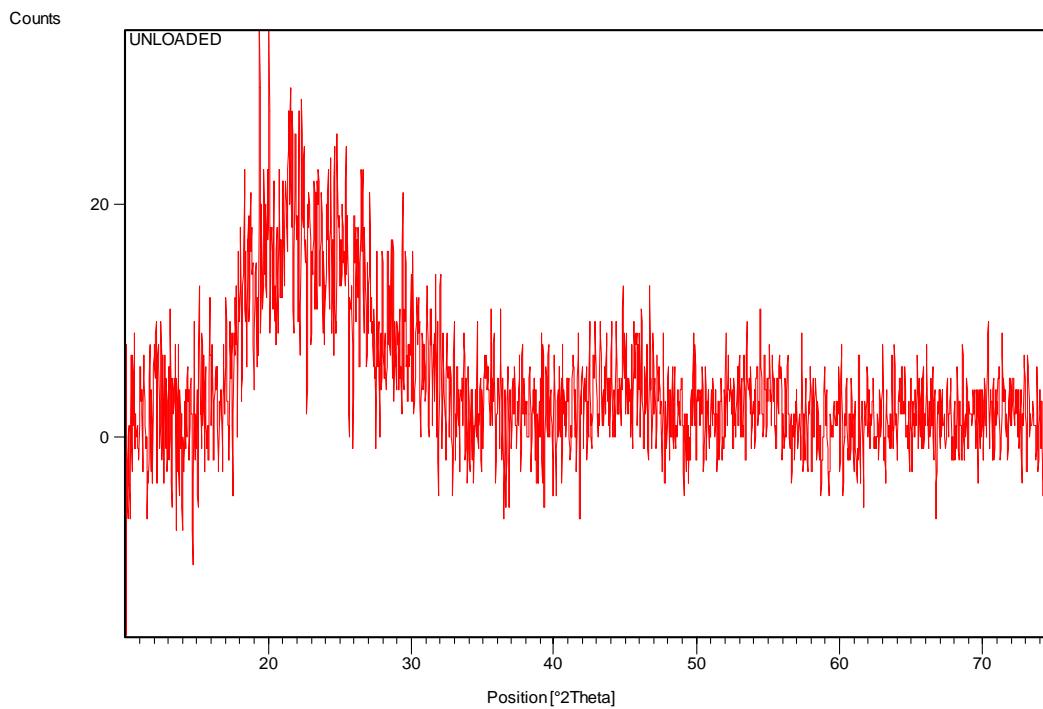


Figure-2. XRD Spectrum of ACC.

The SEM photographs ascertained that the relative porous 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 (Figure-3).

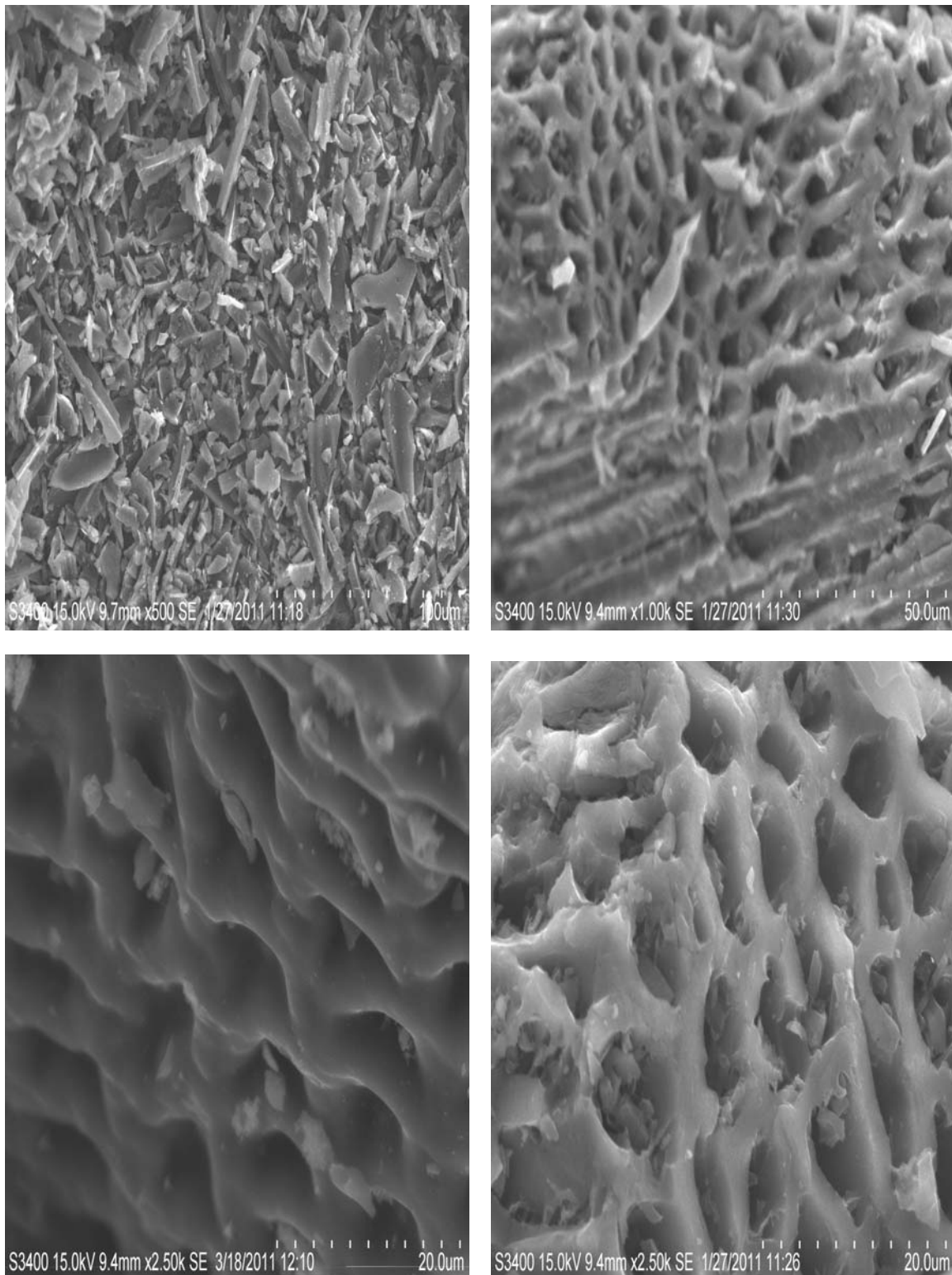


Figure-3. SEM Photograph of ACC.

The FT-IR spectra of the activated carbon showed the characteristic bands at 3787 cm^{-1} due to O-H stretching, 3428 cm^{-1} represents O-H stretching vibrations of the carboxylic acid, peaks at 2336.84 cm^{-1} represents the $\text{C}\equiv\text{C}$ stretching, peaks at 1563.36 cm^{-1} represents the

$\text{C}=\text{C}$ stretching, peak appears at 1441 cm^{-1} shows the C-H bond in CH_3 , 1138.04 cm^{-1} and 1099.46 cm^{-1} peaks represents the presence of C-O stretching, peaks appear at 1022.31 cm^{-1} represents the C-O stretching, 797.56 cm^{-1} is due to C-H deformation (Figure-4).

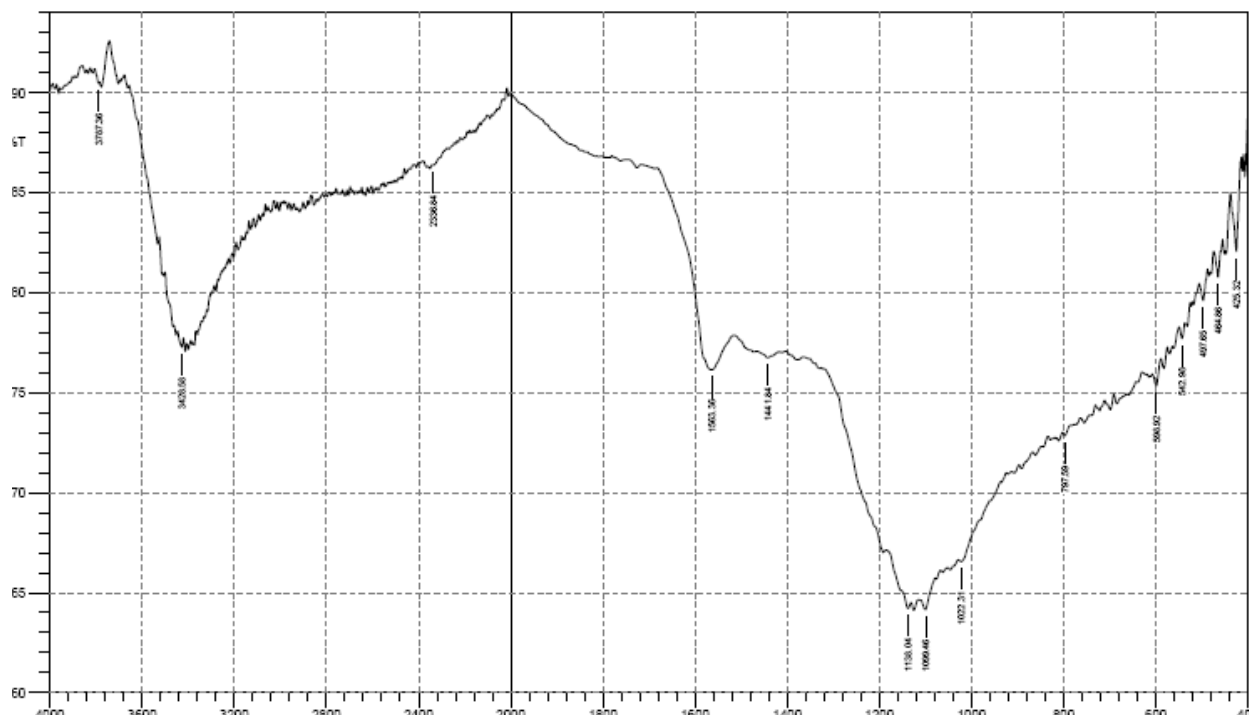


Figure-4. FT-IR Spectrum of ACC.

3.2 Effect of pH

The initial pH of the dye solution is an important parameter which controls the adsorption process particularly the adsorption capacity. The pH of the solution may change the surface charge of the adsorbent, the degree of ionization of the adsorbate molecule and 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 is varied from 2 to 11. The percentage of dye removal at different pH is shown in Figure-2 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. Figure.5 also shows that the removal of dye increases with increase of pH up-to 8 and then it gradually decreases. The variation in the dye up take with respect to the initial solution pH can be explained on the basis of the structure of dye molecule and point of zero charge of activated carbon. For this carbon the point of zero charge is estimated to be at 8.0. Above this pH the carbon particle acquires a negative surface charge leading to a lesser dye uptake since dye molecule becomes neutral at that pH. At a pH lower than pH_{ZPC} the surface of the carbon acquires positive charge and dye molecules also become positive charge. Due to this there is an electrostatic repulsion between dye molecules and activated carbon that causes decrease in the dye uptake.

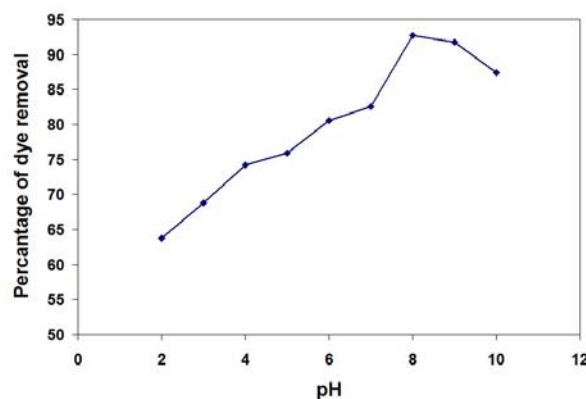


Figure 5. Influence of pH on the adsorption of RO 16 onto ACC.

3.3 Effect of contact time and initial dye concentration

The variation in percentage removal of dye with contact time at different initial concentration range from 25 ppm to 100 ppm was selected and 0.1 gm of the adsorbent was added to these solutions. It was observed from the figure that the maximum amount dye adsorption taking place within the contact time of 20 min and becomes gradual thereafter. This indicates that the rate of adsorption is very fast. Data has been taken up-to 90 min of operation which closes to attain equilibrium. After that there is no significant change in the extent of adsorption (Figure-6).

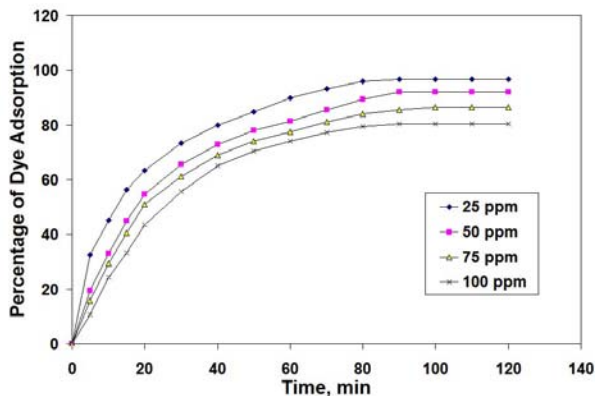


Figure-6. Effect of agitation time on the adsorption RO 16 onto ACC at 303 K.

For the initial concentration of dye up-to 75 ppm more than 85% adsorption has been observed, where as for 100ppm the percentage removal of dye is 80%. From the above observation, it is evident that for lower initial

concentration of dye, the adsorption is fast. The percentage removal of dye decreases with increase in initial dye 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. This explains the more adsorption time for higher concentration [Table-2].

3.4 Effect of temperature

Figure-4 represents the uptake of RO 16 onto ACC at 30, 40, and 50 °C by keeping the initial dye concentration at 50 mg/L. The equilibrium sorption capacity, q_e (mg/g) of RO 16 onto ACC decrease with increase of temperature from 30°C to 50°C. The amount of RO 16 uptake decreases from 55.86 mg/g to 51.8 mg/g while increasing the temperature from 30°C to 50 °C. It can therefore, be inferred that the adsorption is exothermic in nature (Nandi. *et al.*, 2009). This trend obtained in agreement with the general adsorption processes (Figure-7).

Table-2. Calculated kinetic parameters for the adsorption of RO 16 onto ACC at various concentrations and temperatures.

	Concentration (mg/L)				Temperature (°C)		
	25	50	75	100	30	40	50
First order kinetics							
$K_1 \times 10^{-2}$ (min ⁻¹)	0.0428	0.0359	0.04076	0.0430	0.0359	0.03730	0.03915
q_e cal (mg g ⁻¹)	24.19	46.07	65.343	80.42	46.07	37.87	31.83
q_e exp (mg g ⁻¹)	24.19	46.07	64.92	86.00	46.07	47.64	48.43
R^2	0.9871	0.9943	0.9903	0.9985	0.9943	0.9827	0.9618
SSE (%)	0.9569	1.248	0.1337	1.764	1.248	3.0895	5.2493
Second order kinetic							
$K_2 \times 10^{-4}$ (mg g ⁻¹ min ⁻¹)	26.63	8.134	5.225	3.016	8.136	14.3	23.31
q_e cal (mg g ⁻¹)	27.397	55.865	80.00	106.38	55.86	53.19	51.813
H	1.9988	2.5385	3.344	3.413	2.5387	4.048	6.257
R^2	0.9987	0.9981	0.9959	0.9786	0.9981	0.9986	0.9989
SSE (%)	0.857	2.617	4.030	6.938	3.096	1.7519	1.0697
Elovich model							
A (mg g ⁻¹ min ⁻¹)	0.1837	0.0816	0.0560	0.0417	0.07845	0.09576	0.1209
B (mg g ⁻¹)	4.952	5.4396	7.1102	7.497	5.217	10.6639	31.278
R^2	0.9857	0.9898	0.9866	0.9777	0.9962	0.9991	0.9957
Intra particle diffusion model							
kdif(mg g ⁻¹ min)	2.016	3.420	3.874	4.845	3.417	3.034	2.448
R^2	0.993	0.987	0.994	0.994	0.997	0.991	0.987
Xi	7.233	14.07	23.54	25.13	14.07	18.01	25.01

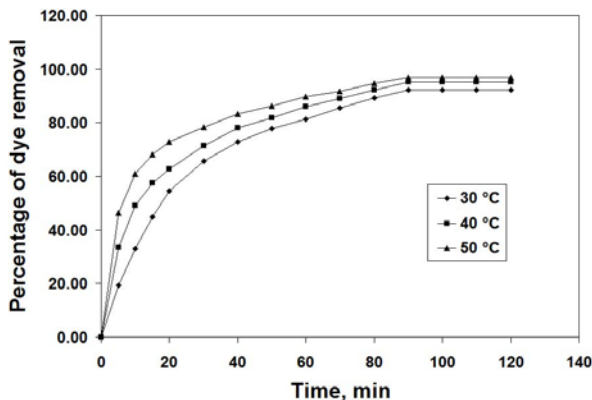


Figure-7. Effect of agitation time on the adsorption RO 16 onto ACC at various temperatures.

3.5 Adsorption studies

In order to evaluate the kinetic mechanism which controls the process, the pseudo first order (Lagergren 1898), pseudo second order (Ho, Y. S. McKay, G., 1998), Elovich model (Namasivayam, and Kavitha, 2002) and intra particle diffusion (Weber, and Morris, 1962) models were tested and the validity of the models were verified by linear equation analysis $\log(q_e - q_t)$ vs t , (t/q_t) vs t and q_t vs $t^{1/2}$, respectively. Good correlation with the kinetic data explains the dye adsorption mechanism in the solid phase' (Ho and McKay, 1999; Wu, *et al.*, 2001; Chiou, and Li, 2002 and Uzun, 2006).

3.5.1 Pseudo-first order model

Eq. (1) represents the pseudo-first-order equation:

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

Where k_1 (min^{-1}) is the pseudo- first-order adsorption kinetic parameter; q_t is the amount adsorbed at time t (min); and q_e denotes the amount adsorbed at equilibrium, both in mg g^{-1} . The plot of the $\log(q_e - q_t)$ as a function of t provides the k_1 and q_e values. The results of first order kinetics at various temperatures are given in Table-2. The pseudo first order rate constant increases with increase of temperature. An irregular trend was noticed while increasing the concentration, which may be due to poor fit of the data with the pseudo first order kinetic model. Large deviation noticed between the experimental q_e (exp) and calculated q_e (cal) values. Hence, the adsorption of RO16 onto ACC not obeys the Lagergren pseudo first order kinetic model.

3.5.2 Pseudo-second-order model

The pseudo - second-order equation based on the adsorption capacity at equilibrium may be expressed by the following equation:

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

Where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second - order adsorption kinetic parameter. From the slope and

intercept of the (t/q_t) as a function of t , k_2 and q_e can be obtained.

The plots according to Equation (2) provided excellent linearity $R^2 > 0.99$. The pseudo second order plot at various initial dye concentrations and temperatures are given in Figures 5 and 6 and results are given in Table-2. The pseudo second order rate constant decrease from 8.13×10^{-4} to $23.31 \times 10^{-4} \text{ g mg}^{-1} \text{ min}$, when the temperature increased from 30 to 50 °C. The experimental q_e (exp) and calculated q_e (cal) values are well in close at various concentrations as well as various temperatures of study. The adsorption of RO16 by ACC is explained well by pseudo second order kinetics with a very high correlation coefficient. Adsorption passes through several stages involving the transport of the adsorbate from the aqueous phase to the adsorbent surface and diffusion of the adsorbate into the interior of the adsorbent pores, which is a slow process (Figure-8).

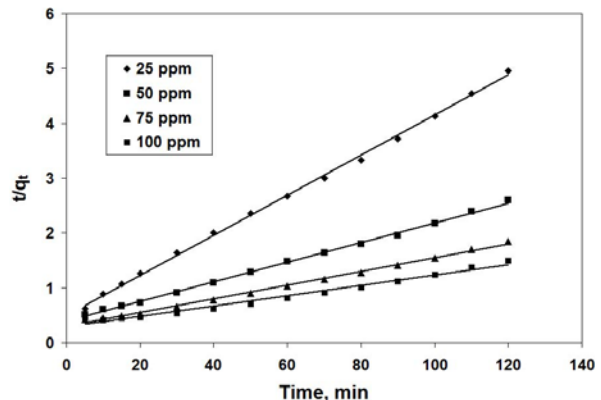


Figure-8. Pseudo second order plot for the adsorption RO 16 onto ACC at various concentrations.

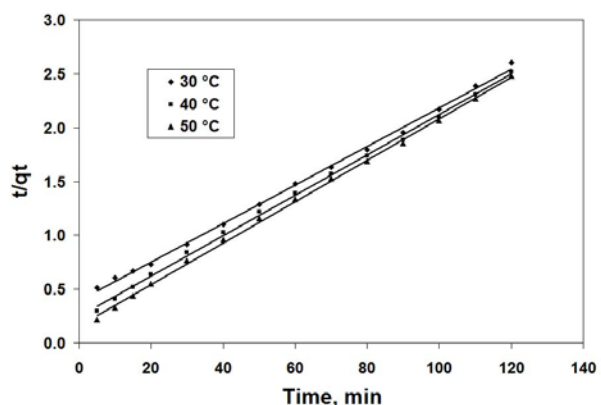


Figure-9. Pseudo second order plot for the adsorption RO 16 onto ACC at various temperatures.

3.5.3 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 (Namasivayam and Kavitha 2002). The Elovich model is generally expressed as



$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (3)$$

Integrating this equation for the boundary conditions, gives:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (4)$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}$) and β is related to the extent of surface coverage and the activation energy for chemisorptions (g mg^{-1}).

A plot of q_t vs. $\ln t$ gives a linear trace with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$. The results of Elovich plot for the adsorption of RO 16 by ACC at various initial dye concentrations and at various temperatures are given in Table-2 (Figure-10). The plot is linear with good correlation coefficient ($r^2 = 0.9962$ to 0.9991). The initial adsorption rate, α , decreases from 0.1837 to $0.0417 \text{ mg g}^{-1} \text{min}$ while increasing the initial dye concentration from 25 to 100 mg/L .

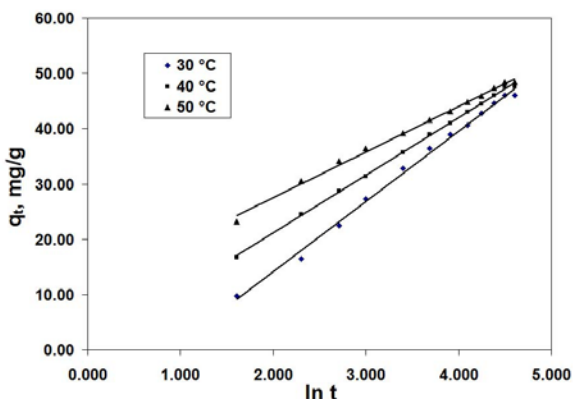


Figure-10. Elovich plot for adsorption of RO 16 onto ACC at various temperature.

3.5.4 Intra particle diffusion model

The intra particle diffusion model (Weber and Morris, 1962) was applied to describe the competitive adsorption. In a liquid-solid system, the fractional uptake of the solute on particle varies according to a fraction of D the diffusivity within the particle and r is the particle radius. The initial rate of intra particle diffusion are obtained by linearization of the curve $q_t = f(t^{0.5})$. The plot of q_t against $t^{0.5}$ may present multi-linearity (Allen *et al* 1989). This indicates that two or more steps occur in the adsorption processes. The first sharper portion is external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage where the intra particle diffusion is rate-controlled. The third portion is the final equilibrium stage, where the intra particle diffusion starts to slow down due to the extremely low solute concentration in solution. Figure-11 shows the plot of q_t against $t^{0.5}$ for the competitive adsorption occurring in solution. The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through the origin. This variation from the origin or near saturation may due to the variation of mass transfer in

the initial and final stage adsorption (Pandey *et al* 1986, Mohanty *et al* 2005). The values are given in Table-2.

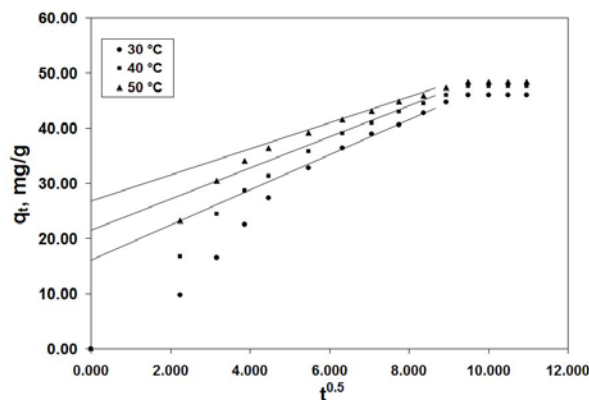


Figure-11. Intra particle diffusion plot for adsorption of RO 16 onto ACC at various temperatures.

3.6 Test of kinetic models

Besides the value of r^2 , the applicability of both kinetic models are verified through the sum of error squares (SSE, %). The adsorption kinetics of RO 16 on ACC was tested at different initial concentrations. The validity of each model was determined by the sum or error squares (SSE, %) given by;

$$\text{SSE (\%)} = \frac{\sum (q_{e \text{ exp}} - q_{e \text{ cal}})^2}{N} \quad (3)$$

Where N is the number of data point.

The higher is the value of r^2 and lower is the value of SSE; the better will be the goodness of fit. Table-4 lists the calculated results. It is found that the adsorption of RO 16 on ACC can be best described by the second-order kinetic model. Similar phenomena processes have been in the adsorption of direct dyes on activated carbon prepared from sawdust (Malik, 2004) and adsorption of Congo red dye on activated carbon from coir pith (Uzun, 2006).

3.6.1 Adsorption isotherms

The adsorption of reactive orange 16 onto adsorbents was studied at all three temperatures, viz, 30, 40, and 50 °C. The paper deals mainly with four different kinds of isotherms, namely Langmuir, Freundlich, Tempkin, and D-R isotherms.

3.6.2 Langmuir isotherm

The Langmuir isotherm assumes that the surface of any adsorbent material contains a number of active sites where the adsorbate attaches itself. This attachment can either be physical or chemical. When the attachment is via Van der waals interactions it is known as physisorption and when via covalent bond it is known as chemisorptions. It says that there is not much interaction between the adsorbate molecules and once a saturation value has been reached no further adsorption would take place (Langmuir, 1916).



$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \tag{5}$$

Where q_e is the amount of dye adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the dye (mg L^{-1}) Q_0 is the maximum adsorption capacity (mg g^{-1}) and b is the energy of adsorption (L mol^{-1}).

A linear plot obtained for Langmuir isotherm is shown in Figure-12. This isotherm holds good for reactive orange and ACC system which is indicated by the linear plots obtained for $1/q_e$ against $1/C_e$ at each temperature. Various Langmuir constants have been calculated at 30, 40, and 50°C and depicted in Table-3.

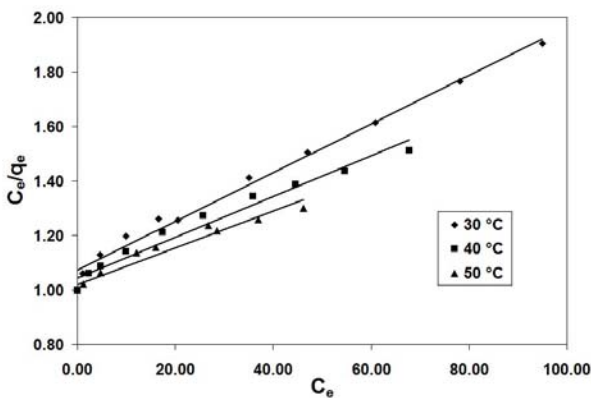


Figure-12. Langmuir isotherm for the adsorption RO 16 onto ACC at various temperatures.

The essential feature of the Langmuir isotherm can be expressed by means of dimensionless constant separation factor which is calculated using;

$$R_L = 1 / (1 + b_L C_0) \tag{6}$$

Where b denotes the Langmuir constant and C_e the initial concentration (Weber and Chakrabarti 1974). At all temperatures r values have been found less than unity indicating there by the adsorption process favorable.

Temperature, C	30	40	50
Langmuir			
$Q_0(\text{mgg}^{-1})$	112.35	133.33	147.05
$B \times 10^{-2}(\text{Lmg}^{-1})$	0.00829	0.00718	0.00667
k_L	0.9313	0.9573	0.9805
R_L	0.4587	0.4105	0.4284
r^2	0.9883	0.9695	0.9561
Freundlich			
$1/n$	0.3954	0.4128	0.3836
N	2.5290	2.4224	2.6068
$k_f(\text{mg}^{1-1/n}\text{L}^{1/n}\text{g}^{-1})$	19.81	24.705	35.489
r^2	0.9716	0.9712	0.8512
Tempkin			
$A(\text{Lg}^{-1})$	0.9637	1.4732	4.745
$B(\text{mgL}^{-1})$	23.971	27.362	25.806
B	0.00952	0.01050	0.00944
r^2	0.9776	0.9777	0.9161
Dubinini-Radushkevich			
$Q_m(\text{mgg}^{-1})$	88.09	100.0	114.58
$K(\times 10^6 \text{mol}^2\text{kJ}^{-2})$	2.4	0.6	2.1
$E(\text{kJmol}^{-1})$	2.946	11.78	33.67
r^2	0.7770	0.7316	0.5477

3.6.3 Freundlich isotherm

The Freundlich model (Chilton *et al.*, 2002 and Osma *et al.*, 2007) is given by the relation;

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{7}$$

Where q_e is the amount adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), k_f and n , the Freundlich constants are related to adsorption capacity and desorption intensity, respectively. The model is based on the assumption that adsorption occurs on a heterogeneous adsorption surface having unequally available sites with different energy of adsorption (Figure-13). Depict the plots obtained for the Freundlich constants were calculated and are presented in Table-3.

Table-3. Results of various isotherm plots for the adsorption of RO 16 on to ACC.

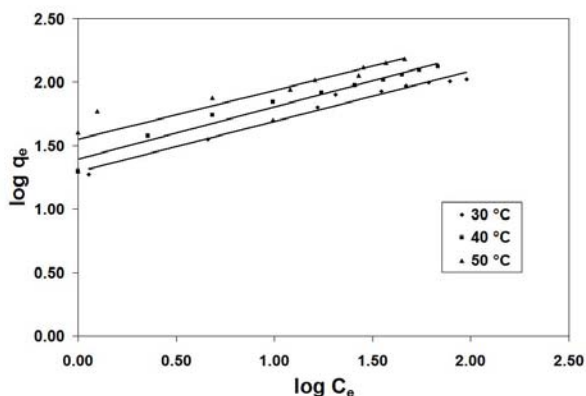


Figure-13. Freundlich isotherm for the adsorption RO 16 onto ACC at various temperatures.

3.6.4 Tempkin isotherm

The Tempkin isotherm assumes that the heat of adsorption of all the molecules increases linearly with coverage (*Allen et al 2004*). The linear form of this isotherm can be given by

$$q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_e \quad (8)$$

Q_e is the amount adsorbed at equilibrium in mg/g; k_1 is the Tempkin isotherm energy constant. The slopes and intercept obtained from the graphical plot q_e against $\ln C_e$ were used to calculate the Tempkin constants (Table-3).

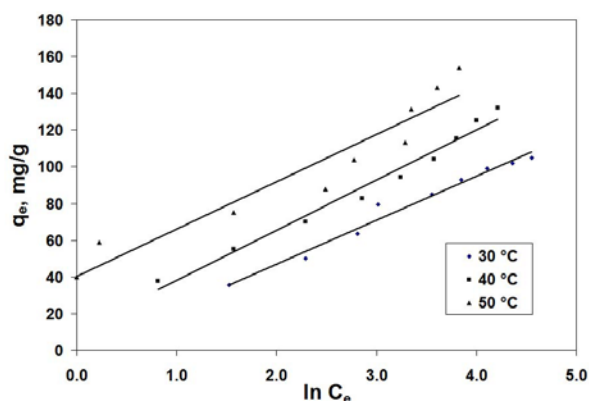


Figure-14. Tempkin isotherm for the adsorption RO 16 onto ACC at various temperatures.

3.6.5 Dubinin-Radushkevich isotherm

The linear form of the Dubinin-Radushkevich isotherm (*Padmesh et al., 2006*) can be given as;

$$\ln q_e = \ln q_D - B\varepsilon^2 \quad (9)$$

Where q_D is the theoretical saturation capacity (mg g^{-1}), B is a constant related to mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) and ε is the polanyi potential which is related to equilibrium as follows;

$$\varepsilon = RT \ln(1+1/C_e) \quad (10)$$

Where, R is the Universal gas constant (8.314 J/mol/K) and T is the temperature in Kelvin. E the mean sorption energy, is calculated using the following relation (Table-3)

$$E = 1/(2B)^{1/2} \quad (11)$$

Based on this energy of activation one can predict whether an adsorption is physisorption or chemisorptions. If the energy of activation is $< 8 \text{ KJ/mol}$, the adsorption is physisorption and if the energy of activation is $8-16 \text{ KJ/mol}$, the adsorption is chemisorptions in nature (*Ozcan, et al 2005*). The activation energy of adsorption increases with temperature. At 30°C E is < 8 hence; the adsorption is physisorption in nature. At 40°C and 50°C E is $> 11 \text{ KJ/mol}$ indicates the adsorption is chemisorptions in nature (normally chemisorptions will occur at high temperature).

3.6.6 Thermodynamics of adsorption

It has been observed that with increase in temperature, adsorption capacity decreases. This implies that for the initial dye concentration of each solution, the adsorption is exothermic in nature.

The thermodynamic parameters change in Gibb's free energy (ΔG°), change in enthalpy ΔH° , and change in entropy ΔS° for the adsorption of reactive orange 16 over ACC has been determined by using the following equation (*Purkait et al 2004*).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

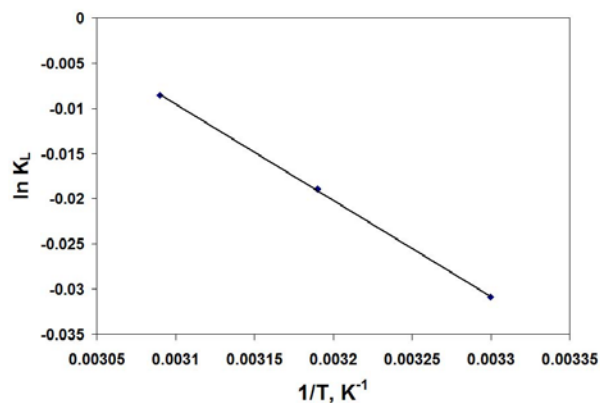


Figure-15. Thermodynamic plot for adsorption RO 16 onto ACC at various.

The values of ΔH° and ΔS° are calculated from the slope and intercepts of the linear plot of $\ln k_L$ Vs $1/T$ in Figure-10 and the values are given in Table-4. Once these two parameters are obtained ΔG° is determined from the above equation.12. The exothermic nature is also indicated by the decrease in the amount of adsorption with temperature. The higher heat of adsorption obtained in this work indicates that chemisorptions rather than the physisorption are prevalent in this case. The negative value of ΔH° and ΔG° indicate that the adsorption process is spontaneous and exothermic in nature. An increase in randomness is indicated by positive values of entropy change.



3.7 Desorption studies

To be a good adsorbent for dye removal, the dye loaded sorbent should be regenerable, otherwise waste have to be disposed of and fresh sorbent should be used. Desorption decreases with increase of pH from 2 to 11. There is no considerable change in desorption above pH 4. The maximum percentage of desorption observed at pH 3 was 44.7%.

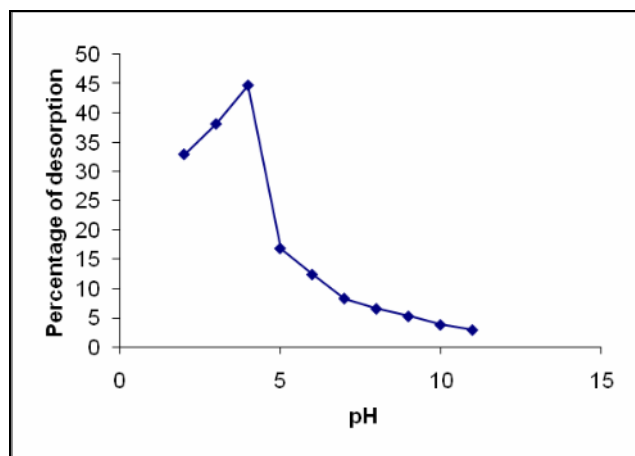


Figure-16. Influence of pH on the desorption of RO 16 onto ACC.

4. CONCLUSIONS

The present study shows that the activated carbon prepared from *Ananas Comosus* leaves is effective adsorbents for the removal of reactive orange 16 from aqueous solution. Higher percentage of RO 16 by ACC was possible provided that the concentration of RO 16 in the solution was low. Optimum dosage was 100 mg L⁻¹. The optimum equilibrium time for adsorption onto ACC was 90 minutes. The adsorption capacity of RO 16 on ACC is comparable. Adsorption kinetics was found to follow second order rate expression. Equilibrium adsorption data was best represented by the Langmuir, Freundlich and Tempkin isotherms. Adsorption of RO 16 is favorably influenced by a decrease in the temperature indicating exothermic nature of the adsorption process. Overall RO 16 is excellently adsorbed by ACC from the aqueous solution.

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