



Studies on Adsorption of Basic Dyes on Activated Carbon Derived from *Phragmites australis* (Common Reed)

Shouman M.A* and Rashwan W.E

Surface Chemistry and Catalysis Laboratory, Physical Chemistry Department, National Research Centre, Egypt

* Corresponding author: monashouman@yahoo.com

Abstract:

In this study, the adsorption of two basic dyes, namely, Crystal Violet (CV) and Rhodamine B (RB) from aqueous solution by phragmite *australis* treated with 40% H_3PO_4 was investigated. Batch experiments were conducted to study the effect of temperature, contact time, pH and carbon dose. Equilibrium adsorption isotherms and kinetics were investigated. The equilibrium experimental data were analyzed by using the Langmuir, Freundlich, Temkin and Harkin – Jura isotherms. The kinetic data obtained was analyzed using a pseudo – first order, pseudo – second order and intra – particle diffusion equations. Dye adsorption was best described by the Langmuir model and with the pseudo – second order kinetic model. Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°), and entropy changes (ΔS°) were evaluated. The surface morphology of modified *phragmite australis* was characterized by FT – IR spectroscopy, scanning electron microscope (SEM), surface area and Boehm titrations.

Keywords: *Phragmite australis*, Crystal violet, Rhodamine B, adsorption isotherms, thermodynamic parameters, kinetics

1.0 Introduction:

Water is one of the basic necessities required for the sustenance and continuation of life. However, this is becoming increasingly difficult in views of large scale pollution caused by industrial, agricultural and domestic activities. These activities generate wastewater which contains both organic and inorganic pollutants. Some of the common pollutants are phenols, dyes, detergents, insecticides, pesticides and heavy metals (Nemerow, 1971). Dyes in industrial water are visible pollutants that are difficult to treat due to their complex molecular nature and synthetic origin. The dyes released into the environment can lead to acute effects on exposed organisms due to the toxicity of the dyes (Tsuboy *et al.*, 2007; Vinitnantharat *et al.*, 2008). In addition, some dyes or their metabolites are mutagenic or carcinogenic (Zollinger, 1991). Dye ions can be classified as anionic (direct, acid, and reactive dyes), cationic (basic dyes), and non – ionic (disperse dyes) (Wong and Yu, 1999). Basic dyes include different chemical structures based on substituted aromatic groups (Eren and Afsin, 2007). Also, they carry a positive charge in their molecule due to the presence of protonated amine or sulphur containing groups (Netpradit *et al.*, 2004), furthermore it is water soluble and yield colored cations in solution. Basic dyes are highly visible and have high brilliance and intensity of colors

(Mishra and Tripathy, 1993). Cationic dyes were used intensely as a model in dye adsorption studies such as Crystal violet (Chinnigounder *et al.*, 2011) and Rhodamine B (Anandkumar and Mandal, 2011).

Several physical, chemical and biological treatment techniques have been applied to remove dyes from wastewater, such as, photodegradation (Wahi *et al.*, 2005), reverse osmosis (Gupta *et al.*, 1990), chemical oxidation (Neamtu *et al.*, 2004), electrocoagulation – electroflotation (Bennajaha *et al.*, 2010), and adsorption. Among these methods, adsorption is commonly used owing to its high efficiency and ability to separate a wide range of chemical compounds (Cherifi *et al.*, 2009), simplicity of design (Tan *et al.*, 2008) and economic feasibility. Adsorption using activated carbon has been successfully used as an adsorbent for the removal of dye from wastewater. Activated carbon is widely used as an adsorbent due to its high adsorption capacity, high surface area, microporous structure, and high degree of surface area, respectively. Activated carbon is effective but expensive due to its high cost of manufacturing. However, several researchers have been studying the use of various alternate inexpensive materials. Therefore, in recent years, many studies have examined the preparation of activated carbons from low-cost and readily available materials, mainly industrial and

agricultural by-products (Pollard *et al.*, 1992). Such alternatives include quantenized rice husk (Jaszlo, 1996), tree fern (Ho *et al.*, 2005), rice bran (Suzuki *et al.*, 2007), coir pith (Ash *et al.*, 2006), soybean hull and sugar beet fiber (Laszlo and Dintzis, 1994), banana pith (Namasivayam *et al.*, 1993), coconut husk (Low *et al.*, 1998), date pits (Gaid *et al.*, 1995), and orange and banana peels (Annadurai *et al.*, 2002), with little or no modification were applied for the removal of dyes from wastewater.

Phragmites australis (Common reed), is a widespread, dominant flora species in many aquatic ecosystems (Du Liang *et al.*, 2003). If it is not reaped at the end of the growing season, large amounts of decomposing leaves return to the aquatic system, which can affect the cycle of pollutants in the wastewater (Unamuno *et al.*, 2007). Hence, utilization of such agricultural solid waste for wastewater treatment is very desirable. *Phragmites* usually forms vast belts along shores of fresh water, lake, streams, as well as other wetlands. The rapid expansion of reed (Chambers *et al.*, 1999) may just as well represent a serious threat to natural ecosystems due to its aggressive and persistent survival strategies (Marks *et al.*, 1994; Warren *et al.*, 2001). Due to its fast-growing properties and high biomass yields, reed is a promising plant to be used in constructed wetlands for energy/material production and water purification. It can be called as the "multi-functional wetland" (Randy, 1998; Fern, 2000; Hagelberg and Ikonen, 2007). Ethnographic identification of *phragmites* is confused by a variety of common names including reed, common reed, reed grass, common reed grass, cane, wild cane and bent grass. Reed is one of the most widely distributed plant species on Earth covering over ten million hectares (Holm *et al.*, 1977). *Phragmites australis* occurs throughout Egypt (Eid *et al.*, 2010; Eid, 2010) and is a major component of reed stands along the shores of Lake Burullus close to the Deltaic Mediterranean coast (Serag, 1996).

This study focuses on the use of common reed (CR) for the removal of two basic dyes [crystal violet (CV) and rhodamine B (RB)] from aqueous solution. The effect of contact time (t), initial pH of the dye solution, temperature (T), and carbon dose were investigated. Equilibrium isotherms for the adsorption of CV and RB were analyzed by Langmuir, Freundlich, Temkin and Harkin – Jura models using non – linear regression technique. The kinetic parameters were also calculated by fitting various kinetic models. The thermodynamic properties of the adsorption process (ΔH° , ΔG°

and ΔS°) have also been determined. In addition, surface groups were also determined using Boehm titrations.

2.0 Experimental:

2.1 Adsorbate Preparation:

The adsorbates were supplied by Sigma Chemical Company, USA. The chemical structures of the dyes are illustrated in Figure 1. Also, Table 1 shows the characteristics of these dyes. A stock solution of 100 mg/l was prepared by dissolving accurately weighed amounts of CV and RB in separate doses of 1000 ml distilled water. The desirable experimental concentrations of solution (10-100 mg/l) were prepared by diluting the stock solution with distilled water when necessary. Initial concentrations of CV and RB were determined by finding out the absorbance of the characteristic wavelength using a double beam UV/Vis spectrophotometer (Shimadzu Model PC – 2401; Japan).

2.2 Adsorbent Preparation:

Phragmites australis was collected from along the shores in Lake Burullus in Egypt. The precursor was washed with distilled water to remove the residual chemical materials, dried at 60°C for 12 h. The dried *phragmites australis* was crushed in a laboratory mill and sieved to obtain particles ranging between 19.3 to 19.8 μm . An accurate weight of dried precursor was impregnated with 40% phosphoric acid. The mixture was then stirred at room temperature for 24 h. After impregnation, the mass was then transferred to a muffle furnace and heated slowly to reach the desired temperature (400, 450 and 500 °C). At each temperature, the furnace was kept for one hour and then cooled down to room temperature. The activated product was washed with distilled water until neutral pH was obtained. The calcined samples were then dried in a vacuum oven at 100 °C and left overnight. The activated dried samples were given the following notations (CR-Raw, CR-400 °C, CR-450 °C, and CR-500 °C).

2.3 Characteristics of Adsorbent:

The surface textures of *Phragmites australis* was examined by means of scanning electron microscopy (SEM, Joel JSM 60). The samples were dried and coated with gold before scanning. The Fourier – Transform Infrared (FT-IR) spectra were obtained using a Perkin – Elmer Model 180 Spectrometer (USA), within the range of 4000 – 400 cm^{-1} , using a 1.5 mg sample mixed with 200 mg of KBr. Samples were pressed into a thin transparent tablet. The physicochemical characteristics of the raw and activated samples treated at different temperatures are given in

Table 2. The specific surface area (BET), average pore diameter and average pore volume were measured using Quantachrome Nova Automated N₂ gas adsorption at -196 °C.

2.4. Batch Adsorption Studies:

Batch experiments were carried out at room temperature (25 °C) to determine the equilibrium adsorption isotherms. A weighed quantity (0.1 g) of the adsorbent was placed in a 250 ml conical flask containing 100 ml of the dye solution. The contents were shaken thoroughly using a mechanical shaker with a speed 120 rpm. The solution was then filtered and the residual dye concentration was determined spectrophotometrically using UV – Vis spectrophotometer at $\lambda_{\max} = 591$ for CV dye and $\lambda_{\max} = 554$ for RB dye. The adsorption experiments were carried out in a batch process at 30, 40 and 60 °C. The effect of variables such as initial concentration, contact time, pH, and temperature were studied thoroughly and reported in the results and discussion part.

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

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg/l) are the liquid – phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry sorbent used (g).

The dye removal percentage can be calculated as follows:

$$\text{Percentage Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

2.5 Titration Studies:

Earlier studies by Boehm (Boehm, 2002) revealed that only strong acidic carboxylic acid groups are neutralized by sodium bicarbonate, whereas those neutralized by sodium carbonate are thought to be lactones, lactol and carboxyl group. The weakly acidic phenolic group reacts only with NaOH. Therefore, by selective neutralization using bases of different strength, the surface acidic functional group in carbon can be characterized both quantitatively and qualitatively. Neutralization with HCl characterizes the amount of surface basic groups that are, for example, pyrones and chromenes. The adsorbent (0.1 g) was mixed with 50 ml of each of 0.1 M NaOH, NaHCO₃ and Na₂CO₃, and shaken continuously for 24h. The supernatants were separated by filtration, and 10 ml of each filtrate was used for titration with 0.1 M HCl to determine the total acidity and 0.1 M NaOH to determine the total basicity. Results from titration studies indicate that the carbon used may possess basic functional groups on its surface

(0.075 μmolm^{-2}) more than acidic functional groups (0.05 μmolm^{-2}).

3. Results and Discussion:

3.1. Fourier Transform Infrared Spectrometer (FT- IR):

The adsorption capacity of activated carbon depends upon porosity as well as the chemical reactivity of functional groups at the surface. This reactivity creates an imbalance between forces at the surface as compared to those within the body, thus leading to molecular adsorption by the Van der Waals force. Knowledge on surface functional groups would give insight to the adsorption capability of the produced activated carbons. Figure 2 shows the functional groups of activated carbon calcined at different temperatures. The broad band around 3400 cm^{-1} can be assigned to the O – H stretching mode of hydroxyl groups and adsorbed water (Staurt, 1996). The position and asymmetry of this band at lower wave numbers indicate the presence of strong hydrogen bonds (Zawadki, 1989). The band at 2900 cm^{-1} is due to aliphatic unit as symmetric and asymmetric stretching C – H, CH₂ or CH₃ bonds. The aldehyde group of – O – CH₃ is found around 2854 cm^{-1} . The strong band at around 1600 cm^{-1} may be ascribed to C = C in alkenes. The band at 1270 represents C – N stretch in aliphatic amines. The bands from 650 – 1000 cm^{-1} may be assigned to = C – H band in alkenes. It is clear from these peaks that the adsorbent has many functional groups. Most probably these functional groups form hydrogen bonding with adsorbate which is responsible for adsorption.

3.2 SEM Analysis of the Activated Carbon:

Scanning electron microscope (SEM) was used in order to obtain information about the surface morphology of the activated carbons investigated. Figure 3 shows the SEM photographs of the raw and phragmite australis treated with 40% H₃PO₄ calcined at 450 and 500 °C. As depicted from Figure 3, an important change in the surface characteristics and the size of the pore spaces is seen after calcinations process. The large pores created by increasing the calcinations temperature promote the activation in the internal surface of carbon particles and also, the possibility of good adsorption properties.

3.3 Effect of pH:

The pH of the solution affects the surface charge of the adsorbents as well as the degree of

ionization of different pollutants (Singh and Nayak, 2004). The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This

subsequently leads to a shift in the reaction kinetics and equilibrium characteristics of adsorption process.

Table 1: Characteristics of the selected dyes for the adsorption study

Properties	CV	RB
λ_{\max} (nm)	591	554
C.I. number	42555	45170
C.I. name	Basic Violet 3	Basic Violet 10
Class	Triarylmethane	Rhodamine
Colour	Blue Violet	Red
Mol.weight	407.9	479.0
Mol.formula	$C_{25}H_{30}N_3Cl$	$C_{28}H_{31}N_2O_3Cl$

Table 2: Textural characteristics of the activated carbon derived from *Phragmites australis* calcined at different temperatures

Sample	CR-400°C	CR-450°C	CR-500°C
BET surface area (m^2/g)	319	303	282
Total pore volume (cm^3g^{-1})	0.16	0.15	0.14
Average pore diameter (Å)	19.8	19.7	19.5

Table 3: Isotherm parameters obtained for the adsorption of CV and RB on phragmites australis ($C_0 = 100$ ppm, CR-450 °C)

Isotherm models	CV			RB		
	30 °C	40 °C	60 °C	30 °C	40 °C	60 °C
<u>Langmuir</u>						
Q_m (mg/g)	38.5	73.5	90.9	45.4	65.3	67.8
K_L (L/mg)	0.14	0.27	0.73	0.44	0.76	0.14
R^2	0.99	0.99	0.99	0.99	0.99	0.99
<u>Freundlich</u>						
$K_F(mg/g)(mg/L)^{1/n}$	12.58	17.78	30.19	15.8	20.9	35.5
n	3.8	3.3	2.7	3.9	1.2	6.4
R^2	0.97	0.97	0.98	0.98	0.97	0.98
<u>Tempkin</u>						
K_T (l/mg)	4.04	1.38	2.62	6.08	5.59	9.49
B	370	166.7	126.8	349.7	223.9	259.6
R^2	0.97	0.96	0.97	0.96	0.97	0.97
<u>Harkin's – Jura</u>						
A		1256			280.1	
B		2.7			1.12	
R^2		0.97			0.98	

Figure 4 shows the effect of pH on the dye removal by adsorption on phragmite australis at an initial concentration of dye (100 mg/l) within pH range from 2 to 12. The results showed that the adsorption capacity of dyes by phragmite australis was dependent on pH. It can also be observed that the removal of CV and RB increased with increasing pH to reach a maximum value at pH range 4-6. No significant increase in removal was observed beyond 7. The amount adsorbed was low at very low pH. The RB uptake, however, decreased significantly in the pH range 6-8. Similar trend in q_e values was observed by other workers for basic dyes (Low *et al.*, 1995; Rajamohan, 2009). This trend may be explained on the basis of the

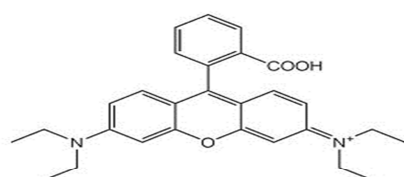
fact that at pH below 6, the RB ions readily enter into the pore structure of the common reed surface, whereas at pH beyond 6, RB will associate in acidic solution to form dimmers and possibly larger micelles. Such a large group of molecules will not have an easy penetration through the surface layer of common reed. The different investigated (CV and RB) dyes will experience different physical and electrostatic forces according to their structure, molecular size and functional groups. Similar views have been expressed by earlier workers (Allen *et al.*, 1989). In this study, the adsorption capacity decreased in the order RB > CV.

Table 4: Kinetic parameters for the removal of CV and RB by *Phragmite australis* calcined at different temperatures ($C_0=100$ ppm)

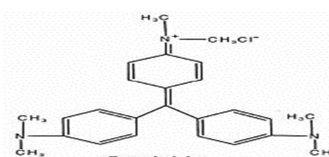
Kinetic Model	Dye	Temperature			
		CR-400 °C	CR-450 °C	CR-500 °C	
<u>Pseudo-first order</u>	Crystal Violet	CR-400 °C	CR-450 °C	CR-500 °C	
$K_1(\text{min}^{-1})$		0.004	0.007	0.005	
$q_{e1}(\text{mg g}^{-1})$		23.71	25.11	23.5	
R_1^2		0.86	0.86	0.87	
<u>Pseudo-second order</u>		$K_2(\text{g mg}^{-1}\text{min}^{-1})$	0.001	0.0007	0.001
$q_{e2}(\text{mg g}^{-1})$		40.0	37	26.6	
R_2^2		0.96	0.95	0.96	
<u>Intraparticle diffusion</u>		$K_{id}(\text{mg g}^{-1}\text{min}^{-1/2})$	3.5	3.2	2.6
$C(\text{mg g}^{-1})$		7.5	5	5.5	
R^2	0.99	0.99	0.99		
<u>Pseudo-first order</u>	Rhodamine B	0.008	0.009	0.01	
$K_1(\text{min}^{-1})$		26.3	33.1	34.7	
$q_1(\text{mg g}^{-1})$		0.87	0.86	0.87	
R_1^2		0.009	0.002	0.0008	
<u>Pseudo-second order</u>		$K_2(\text{g mg}^{-1}\text{min}^{-1})$	53.5	50	47.6
$Q_2(\text{mg g}^{-1})$		0.99	0.98	0.99	
R_2^2		3.77	4.45	3.22	
<u>Intraparticle diffusion</u>		$K_{ip}(\text{mg g}^{-1}\text{min}^{-1/2})$	22	20.5	12.5
$C_{ip}(\text{mg g}^{-1})$		0.96	0.96	0.97	
R^2					

Table 5: Thermodynamic parameters for adsorption of CV and RB on *Phragmites australis* ($C_0 = 100$ ppm)

Temperature (K)	CV dye		
	ΔG° (KJmol ⁻¹)	ΔH° (KJmol ⁻¹)	ΔS° (Jmol ⁻¹ K ⁻¹)
303	-29.68	24	159.95
313	-30.20		
333	-34.87		
RB dye			
303	-30.85	34.5	191.84
313	-28.88		
333	-35.43		



Rhodamine B



Crystal violet

Figure 1: Structure of the selected basic dyes for the adsorption study

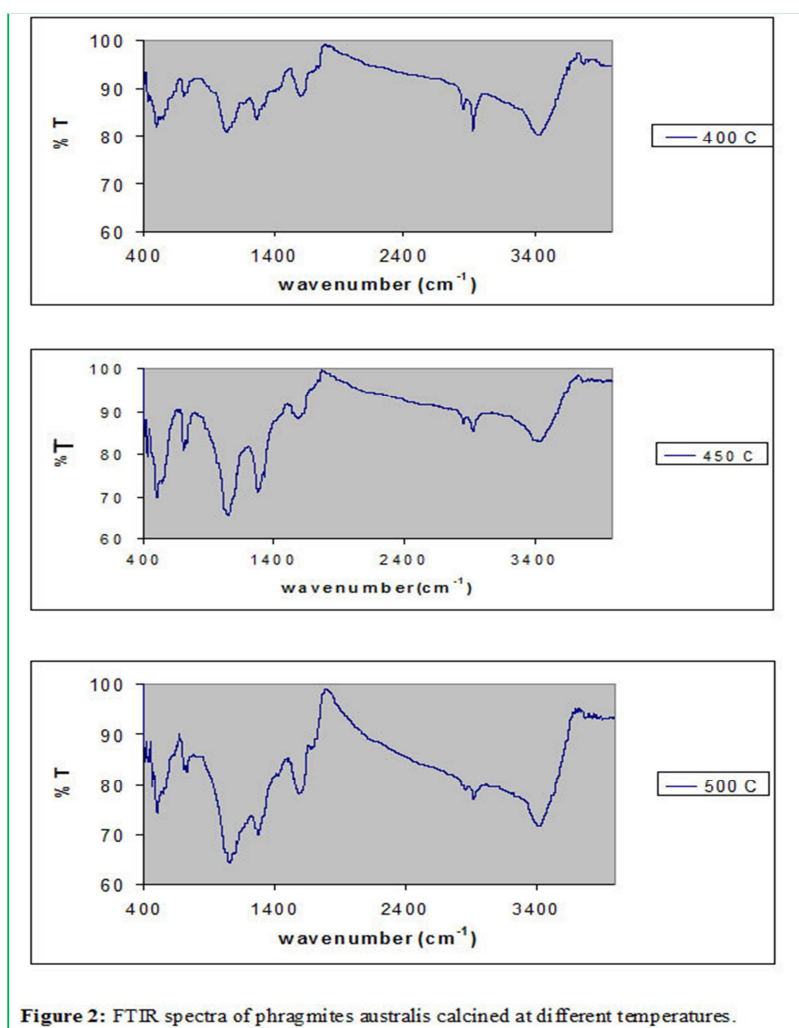
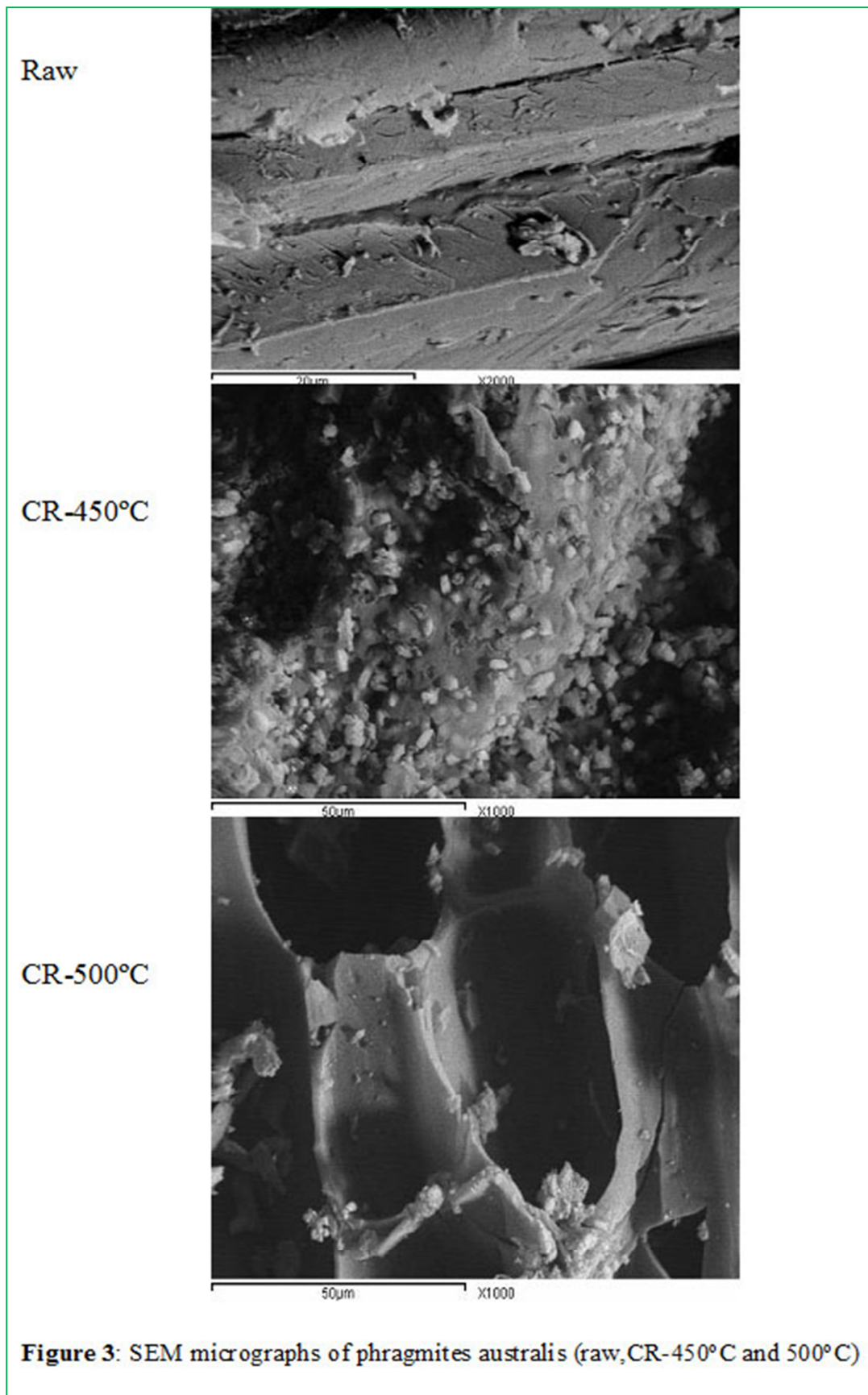


Figure 2: FTIR spectra of phragmites australis calcined at different temperatures.



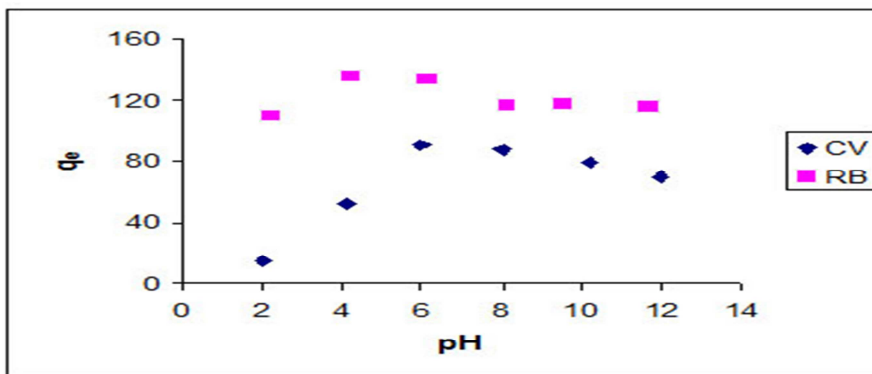


Figure 4: Effect of pH on the adsorption of dyes onto phragmite australis

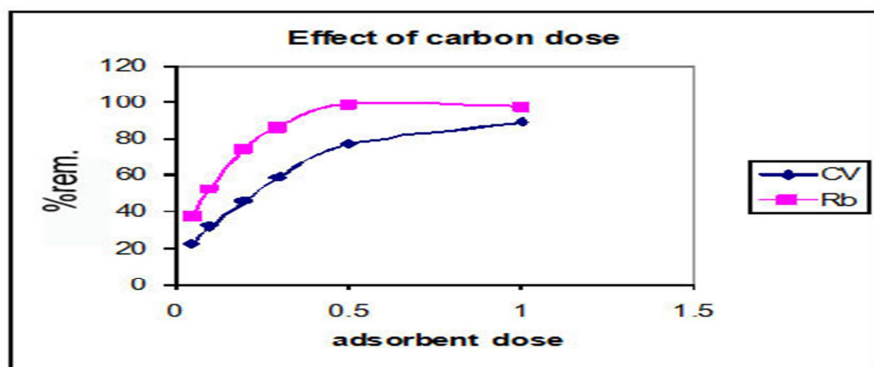


Figure 5: Effect of adsorbent mass on the adsorption of dyes by phragmites (temperature=30°C, initial dye concentration. =100 mg/l)

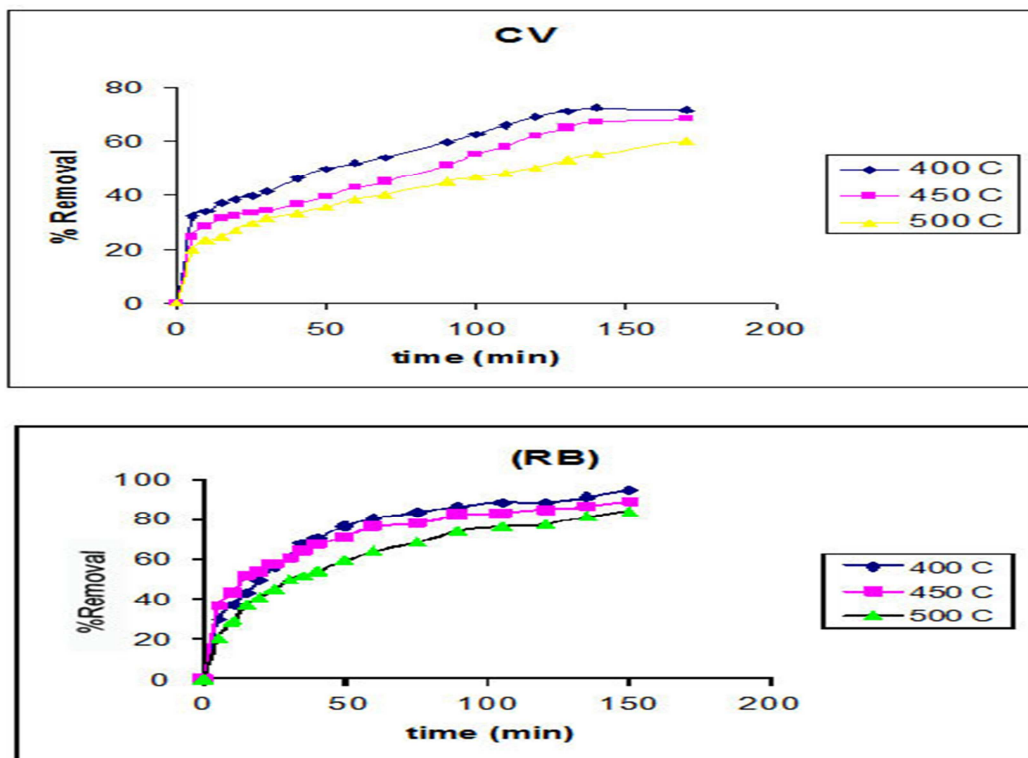


Figure 6: Effect of contact time on the adsorption of dyes onto phragmite australis at different temperatures

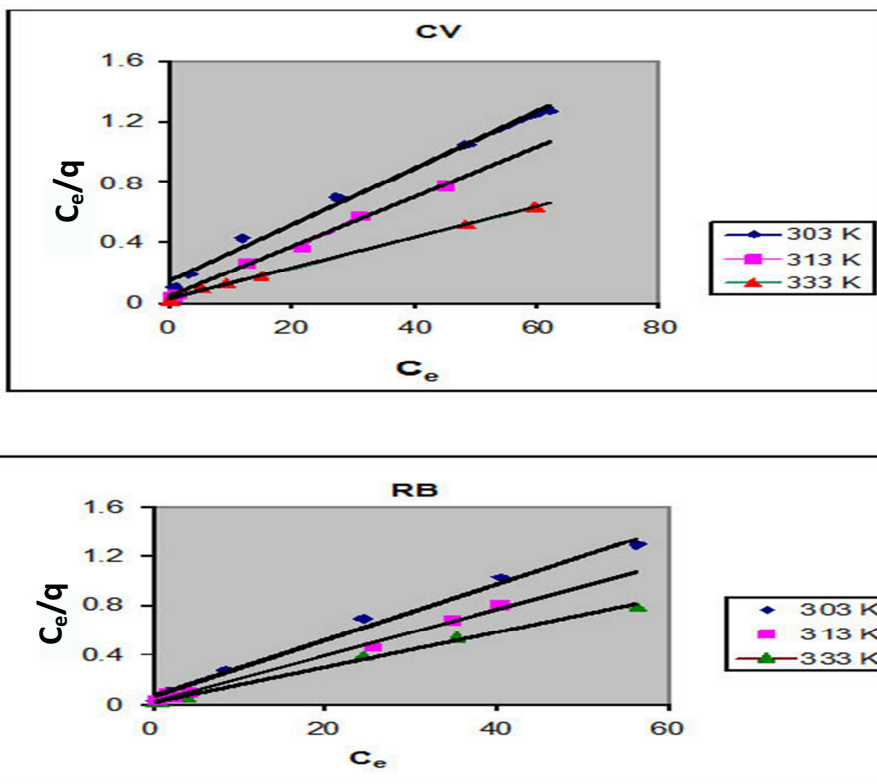


Figure 7: Langmuir adsorption isotherms for the adsorption of CV and RB onto phragmites australis at different temperatures

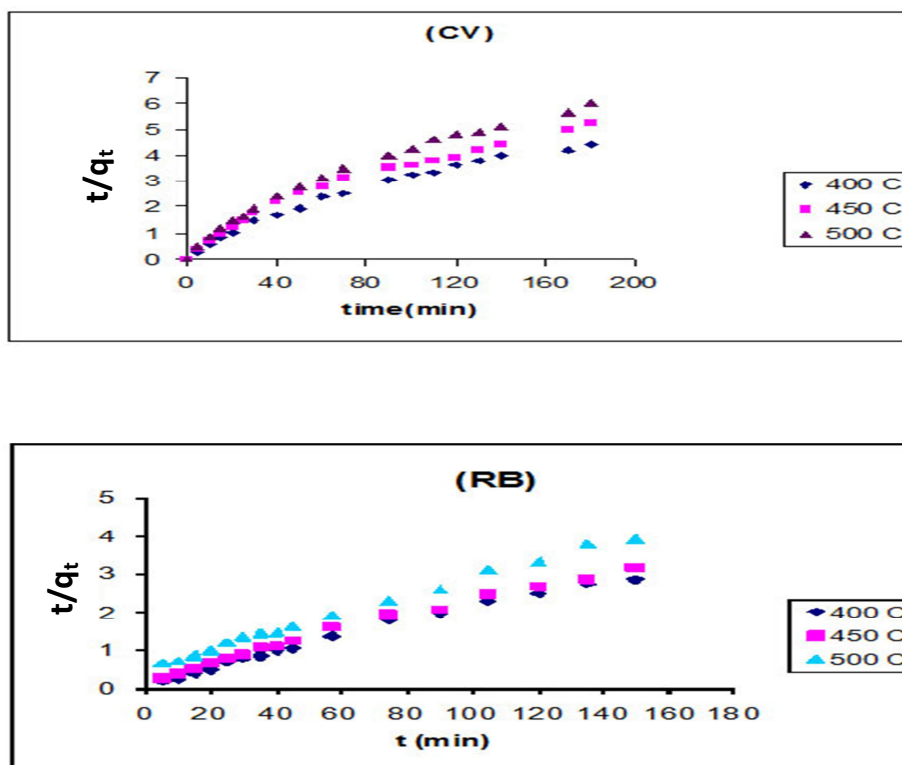


Figure 8: Pseudo-second order kinetic plots for the adsorption of CV and RB onto phragmite australis at different temperatures

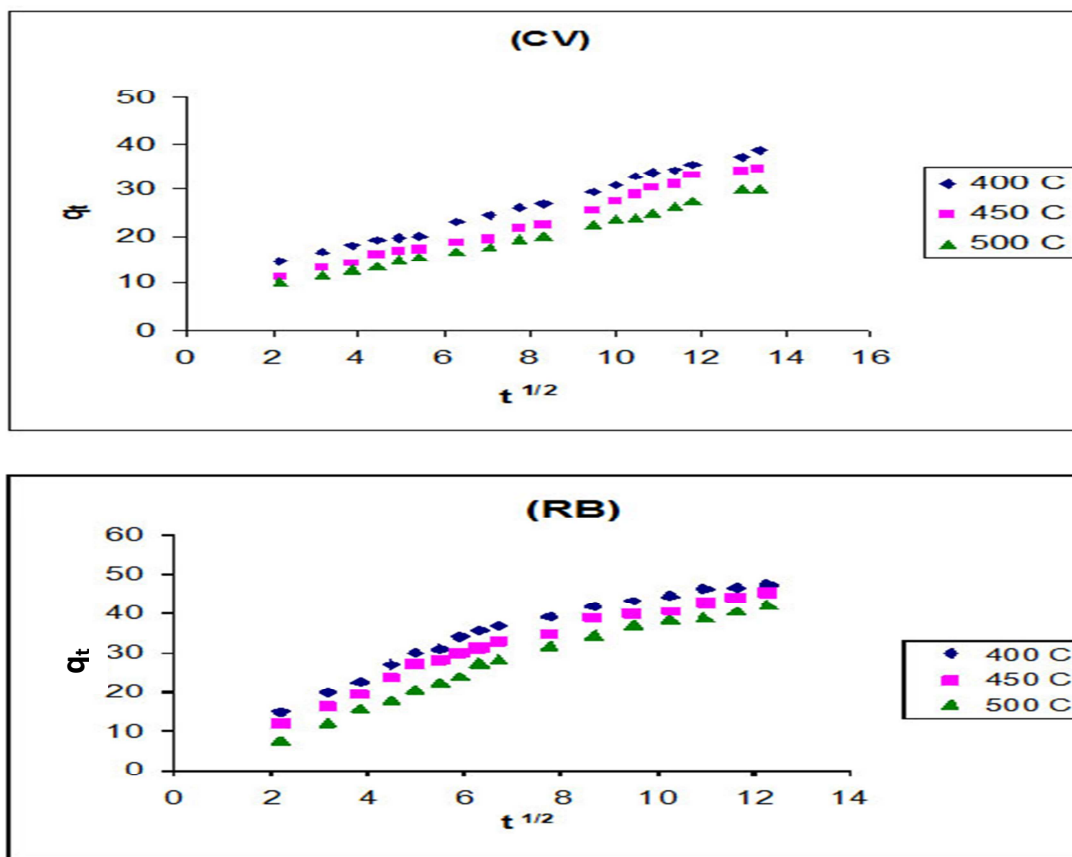


Figure 9: Intraparticle diffusion plots for the removal of CV and RB dye by *phragmites australis*

3.4 Effect of Adsorbent Dose:

The effect of common reed dosage on removal of RB and CV dyes is shown in Fig.5. To study the effect of adsorbent dose on dyes adsorption, different amounts of adsorbents varying from 0.05g to 1g were respectively added to initial concentration 100 mg/L RB and CV solution. The mixtures were shaken into 250 ml stoppered flasks at 30°C until equilibrium time was reached. It can be seen from Figure 5 that the percentage removal increased with the increase in the activated carbon dosage from 0.05 to 0.1 g. The CV percentage removal increased from 23 to 89% while RB percentage removal increased from 38 to 97%, respectively. This increase was due to the availability of more surface active sites and porosity resulting from the increased dose of the adsorbent (Kannan and Sundaram, 2001; Garg *et al.*, 2003).

3.5 Effect of Contact Time:

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. In physical adsorption, most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal

that the uptake of adsorbate species is fast at initial stages of the contact period, and thereafter, it becomes slower near equilibrium. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The effect of contact time on the adsorption of CV and RB by the adsorbents calcined at different temperatures was studied for a period of 3h. It has been observed that the amount of adsorption increases rapidly in the beginning till 40 min then attains equilibrium afterwards. For CV and RB adsorption onto common reed, the percentage removal of the dye was found to be CV>RB at any contact time. This trend was observed because CV which has a smaller size could get adsorbed more deeply than RB which was big enough not to adsorb much greater size. Fig.6 represents the effect of contact time on the adsorption of dyes onto common reed at different temperatures. From this figure, it is shown that all the curves of contact time are single, smooth and continuous leading to saturation. These curves indicate the possible monolayer coverage of dye on the surface of common reed (Inbraj and Sulochana, 2002).

3.6 Theory of Adsorption Isotherms:

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface (Astoe and Dalton, 2000) and give a comprehensive understanding on the nature of interaction. The parameters obtained from different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis.

3.6.1 Langmuir Isotherm:

The Langmuir theory assumes homogeneous type of adsorption within the sorbent and predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent (Langmuir, 1918). The Langmuir adsorption isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions (Hameed *et al.*, 2007; Tan *et al.*, 2007). The linear form of the Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_o} + \frac{1}{K_L Q_o} \quad (1)$$

where C_e is the equilibrium concentration (mg/L), Q_o is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g) and K_L is the Langmuir adsorption constant related to the adsorption efficiency. The linear plots of C_e / Q_e versus C_e suggest the applicability of the Langmuir isotherms. The Langmuir constants Q_o and b were determined from the slope and intercept of the plot and are represented in Table 3. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption and is expressed as $R_L = \frac{1}{1+b C_o}$ where C_o is the highest initial concentration of adsorbate (mg/L) and b (L/mg) is the Langmuir constant. The parameter R_L indicates the nature of shape of the isotherm as given:

R_L	Adsorption
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

In the present investigation, the R_L values were less than one which shows that the adsorption process was favorable. From the results, it is clear that the values of Q_o (adsorption efficiency) and b (adsorption energy) of the carbon increases on increasing the temperature. From these values, it is concluded that the maximum adsorption corresponds to a saturated monolayer of

adsorbate molecules on the adsorbent surface. The values of Q_o and K_L are given in Table 2.

3.6.2 Freundlich Isotherm:

The Freundlich isotherm considers multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules (Freundlich, 1906). The linear Freundlich isotherm is expressed as:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (2)$$

where k_F is the Freundlich constant and is related to the binding energy, and n is a measure of the adsorption intensity or surface heterogeneity (a value closer to zero represents a more heterogeneous surface). A plot of $\log q_e$ versus $\log C_e$ enables the empirical constants k_F and n to be determined from the intercept and slope of the linear regression. The values of k_F and n are given in Table 2 and the linear plots are represented in Figure 7.

3.6.3 Temkin Isotherm:

Temkin isotherm takes into account the effect of some indirect adsorbate/adsorbate interactions on adsorption isotherms. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with a coverage due to adsorbate – adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Gottipati and Mishra, 2010). The linear form of Temkin isotherm is represented by the following equation:

$$q_e = B \ln A + B \ln C_e \quad (3)$$

where B is the Temkin constant and is related to the heat of adsorption and is equal to RT/b and A is the equilibrium binding constant (L/mg). A plot of q_e versus $\ln C_e$ enables the determination of the constants A and B . The constants A and B together with the R^2 values are shown in Table 2.

3.6.4 Harkin's – Jura Isotherm:

Harkin's – Jura isotherm assumes the presence of multilayer adsorption with the existence of heterogeneous pore distribution (Gurses *et al.*, 2006). The Harkin's – Jura isotherm is expressed as:

$$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \frac{1}{A} \log C_e \quad (4)$$

where C_e is the equilibrium concentration of the dye in solution (mgL^{-1}), q_e is the amount of dye adsorbed onto the adsorbent (mgg^{-1}) and A, B are the isotherm constants. The plot of $\frac{1}{q_e^2}$ versus $\log C_e$ represents a linear plot. The isotherm

constants as well as the correlation coefficient are given in Table 2.

The non – linear R^2 values, based on the actual deviation between the experimental points and the theoretically predicted data points, provide a better correlation of experimental data and are shown in Table 3. It was observed that the Langmuir isotherm fits better to the experimental data than do the other adsorption isotherms studied for the CV and Rb dye adsorption on the activated carbon derived from phragmite australis.

3.7 Adsorption Dynamics:

The kinetics of adsorption is one of the important characteristics in defining the efficiency of adsorption. It also describes the rate of adsorbate uptake on activated carbon. Three kinetic models were studied and used to fit the experimental data from the adsorption of dyes onto phragmite australis (common reed). These models are the pseudo – first order, pseudo – second order and intraparticle diffusion model.

3.7.1 Pseudo – first order Kinetic Model:

The pseudo – first order kinetic model can be represented by the following Lagergren rate equation (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (5)$$

where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity in equilibrium (mg/g), K_1 is the pseudo – first order rate constant (min^{-1}). The values of q_e and K_1 for the pseudo – first order kinetic model were determined from the intercepts and the slopes of the plots of $\log(q_e - q_t)$ versus t , respectively. The parameters of the pseudo – first order model are given in Table 4. The correlation coefficient (R^2) changed in the range 0.86-0.87 for CV and RB, respectively. This suggests that the kinetics of CV and RB adsorption on phragmite australis did not follow the pseudo – first order kinetic model.

3.7.2 Pseudo – second order Kinetic Model:

The adsorption mechanism over a complete range of the contact time is explained by the pseudo – second order kinetic model (Liu, 2008). The integrated linear form of the model is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at contact time t (mg/g) and K_2 is the rate constant of the pseudo – second order adsorption (g/mg.min).

A plot of $\frac{t}{q_t}$ versus t gives a linear relationship, from which q_e and K_2 can be determined from the slope and intercept of the plot respectively. The data for the adsorption of CV and RB onto phragmite australis applied to pseudo – second order model is shown in Figure 8 and the results are given in Table 4. This procedure is more likely to predict the behavior over the whole range of adsorption. The corresponding correlation coefficients (R^2) values for the pseudo – second order kinetic model were greater than 0.99 for all CV and RB concentrations, indicating the applicability of the pseudo – second order kinetic model.

3.7.3 Intraparticle Diffusion Model:

The adsorption mechanism may proceed in several steps, the slowest of which will be the rate determining step. In general, pore and intraparticle diffusion are often rate limiting in a batch reactor system. However, the pseudo – first and pseudo – second order models can not give information or evaluate the contribution of intraparticle diffusion to the sorption mechanism. For this reason, Weber and Moris suggested a kinetic model to identify the diffusion mechanisms and rate controlling steps that affect the adsorption process (Weber and Chakravarthi, 1974). It is empirically a functional relationship, common to adsorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t (Hameed *et al.*, 2008). According to this theory, the intraparticle diffusion equation is expressed as follows:

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

where k_{id} is the intraparticle diffusion rate constant (mg/g.min^{1/2}) and C is the intercept (mg/g). According to equation 7, a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept C when adsorption follows the intraparticle diffusion process. Value of the intercept give an idea about the thickness of the boundary layer, i.e., the larger the intercept the greater is the boundary layer effect (Kannan and Sundaram, 2001). Figure 9 shows the amount of dye adsorbed versus $t^{1/2}$ for the removal of CV and RB dye by phragmite australis. The data is given in Table 4. As seen from figure 9, the plots are not linear over the whole time range, which indicates that more than one mode of adsorption, is involved in the dye adsorption. The adsorption mechanism for any dye removal by an adsorption process may be assumed to involve the following four steps: (i) bulk diffusion; (ii) film diffusion; (iii) pore diffusion or intraparticle diffusion; and (iv) adsorption of dye on the sorbent surface (Khaled

et al., 2009). From figure 9, it may be seen that there are two separate regions – the first straight portion is attributed to macropore diffusion (phase I) and the second linear portion to micropore diffusion (phase II) (Allen *et al.*, 1989). The first part of the curve ($t^{1/2}$ from 0 to 5 min) can be attributed to mass transfer effects taking place with boundary layer diffusion, while the final linear parts indicate intraparticle diffusion (very slow diffusion of the adsorbates from the surface film into the micropores, which are least accessible sites of adsorption). The intercept, however, did not cross the origin in any of the test conditions, thereby suggesting that pore diffusion is the only controlling step and not film diffusion.

3.8 Effect of Temperature and Thermodynamic Parameters:

A range of reaction temperatures (30, 40 and 60 °C) were used and the flasks were agitated for 90 min. A 0.1 g sample of activated carbon derived from phragmite australis was added to 50 ml volume of dye solution set at optimum pH and agitated at 200 rpm for all the experiments. The experiments were carried out at initial dye concentration 100 mg/L for all the studies. It has been believed that the temperature generally has two major effects on the adsorption process. Increasing the temperature will increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (Al-Qodah, 2000). Results show that the amount of CV adsorbed increased from 38.5% to 90% and that of RB increased from 45% to 67% when the temperature increased from 30 to 60°C. These results imply that adsorption process for MB and CV would be endothermic.

Thermodynamic parameters such as change in free energy ΔG° (KJ/mol) and enthalpy ΔH° (KJ/mol) and entropy ΔS° (J/K/mol) were determined using the following equations:

$$k_o = C_{solid}/C_{liquid} \quad (8)$$

$$\Delta G^\circ = -RT \ln k_o \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

$$\ln k_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (\text{Van't Hoff Equation}) \quad (11)$$

where k_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/l), C_{liquid} is the liquid phase concentration at equilibrium (mg/l), T is the temperature in Kelvin, and R is the general gas constant. ΔH° and ΔS° values obtained from the slope and intercept of

Van't Hoff plots are represented in Table 5. The positive value of ΔH° indicate the endothermic nature of adsorption which governs the possibility of physical adsorption. In case of physical adsorption, increasing the temperature of the system leads to an increase in the extent of dye adsorption. This indicates that there is no possibility of chemisorptions (Arivoli *et al.*, 2007). The low values ΔH° depicts that the dyes are physisorbed onto phragmite australis. The negative values of ΔG° (Table 5) show that the adsorption is highly favorable and spontaneous. The positive values of ΔS° (Table 5) show the increased disorder and randomness at the solid solution interface of CV and RB with the phragmite adsorbent. The enhancement of adsorption capacity of the activated carbon at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface (Gong *et al.*, 2005).

4. Conclusions:

The equilibrium, kinetics and thermodynamics for the uptake of Rhodamine B and Crystal Violet by phragmite australis from aqueous solution were studied. The adsorption data was fitted best in the Langmuir adsorption model. The fitness of Langmuir's model indicated the formation of monolayer coverage of the sorbate on the outersurface of the adsorbent. The kinetic data agreed well with the pseudo – second order rate equation. The result of intraparticle diffusion model suggests that pore diffusion is the only controlling step and not film diffusion. The negative values of ΔG° and positive values of ΔH° and ΔS° indicated that the adsorption is spontaneous, endothermic and favorable. Phragmite australis used in this work offers greater wastewater treatment than other activated carbons prepared from waste materials which suggests to be a promising low – cost adsorbent for the removal of CV and RB from aqueous solution.

References:

- 1) Allen, S.J, Mckay, G., and Khader, K.Y.H. (1989): Intraparticle diffusion of a basic dye during adsorption onto sphagnum peat. *Environ.Pollution*, 56: 39-50.
- 2) Allen, S.J., McKay, G., and Khader, K.Y.H. (1989): Equilibrium adsorption isotherms for basic dyes onto lignite. *J.Chem.Tech.Biotech.*, 45: 291-302.
- 3) Al-Qodah Z. (2000): Adsorption of dyes using oil ash. *Water Res.*, 34(17): 4295-4303.

- 4) Anandkumar, J., and Mandal B.(2011): Adsorption of chromium (V) and rhodamine B by surface modified tannery waste: kinetic, mechanistic and thermodynamic studies. *J. Hazard. Mater.*, 186(2-3): 1088-1096.
- 5) Annadurai, G., Juang, R.S., and Lee, D.J (2002): Use of cellulose based waste for adsorption of dyes from aqueous solutions. *J.Hazard. Mater*, 92: 263-274.
- 6) Arivoli S. *et al.*, (2007): Comparative study on the adsorption kinetics and thermodynamics of metal ions onto acid activated low cost carbon. *E.J.Chem*, 4: 238-254.
- 7) Ash B. *et al.*, (2006): Characterization and application of activated carbon prepared from waste coir pith. *J. of Scientific and Industrial Research*, 65: 1008-1012.
- 8) Astoe, J.E., and Dalton, J.S. (2000): Dynamic surface tension and adsorption mechanisms of surfactants at the air water interface. *Adv.Colloid Interface Sci*, 85: 103-144.
- 9) Bennajaha M. *et al.*, (2010): A variable order kinetic model to predict deflouridation of drinking water by electrocoagulation-electroflotation. *Int.J.Eng.Sci.Tech.*, 2(12): 45-52.
- 10) Boehm, H.P. (2002): Surface oxides on carbon and their analysis: a critical assessment. *Carbon*, 40:145-149.
- 11) Chambers, R.M., Meyerson, L.A., and Saltonstall, K. (1999): Expansion of Phragmites australis into tidal wetlands of North America. *Aquatic Botany*, 64: 261-273.
- 12) Cherifi, H., Haninia, S., and Bentahar, F. (2009): Adsorption of phenol from wastewater using vegetal cords as a new adsorbent. *Desalination*, 244(1-3): 177-187.
- 13) Chinniagounder, T., Shanker, M., and Nageswaran S. (2011): Adsorptive removal of crystal violet dye using agricultural waste cocoa (theobroma cocoa) shell. *Journal of Chemical Sciences*, 17: 38-45.
- 14) Du Liang, G., Tack, F.M.G., and Verloo, M.G. (2003): Performance of selected destruction methods for the determination of heavy metals in reed plants (Phragmite australis). *Anal.Chim.Acta*, 479:191-198.
- 15) Eid, E.M. *et al.*, (2010): Effects of abiotic conditions on Phragmite australis along geographic gradients in Lake Burullus , Egypt., *Aquatic Botan*, 92(2) :86-92.
- 16) Eid, E.M., (2010): Dynamics of carbohydrate translocation between the above-and underground organs of Phragmites australis in Lake Burullus, Egypt. *Egyptian Journal of Aquatic Research*, 36 (1):107-113.
- 17) Eren, E., and Afsin, B.(2007): "Investigation of a Basic Dye Adsorption from Aqueous Solution onto Raw and Pre-treated Sepiolite Surfaces. *J. Dyes Pigment*, 73:162-167.
- 18) Fern, K., (2000): Plants for a future: edible & useful plants for a healthier world. 2nd ed. Hampshire, UK, Permanent Publications; White River Junction, VT, distributed in the USA by Chelsea Green Pub. Co.: 267-273.
- 19) Freundlich, H. (1906): Concerning adsorption in solutions. *J.Phys.Chem. Stoichiometrie Verwandtschaftslehre.*, 57A: 385-470.
- 20) Gaid A. *et al.*, (1995): Surface mass transfer processes using activated date pits as adsorbent. *Water SA*, 20(4): 1-6.
- 21) Garg, V.K. *et al.*, (2003): Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresour.Technol*, 89:121-124.
- 22) Gong R.*et al.*, (2005): Effect of chemical modification on dye adsorption capacity of peanut hull. *Dyes and Pigments*, 67:179.
- 23) Gottipati, R., and Mishra, S. (2010): Application of biowaste (waste generated in biodiesel plant) as an adsorbent for the removal of hazardous dye – methylene – blue from aqueous phase. *Braz.J.Chem.Eng*, 27: 357.
- 24) Gupta, G.S., Prasad, G., and Singh, V.N (1990). Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal. *Water Res.*, 24: 45-50.
- 25) Gurses, A. *et al.*, (2006): The adsorption kinetics of the cationic dye methylene blue onto clay. *J.Hazard.Mater*, 131: 217-228.
- 26) Hagelberg, E., and Ikonen, I., (2007): Read Up on Reed" Southwest Finland Regional Environmental Centre, Turku,Finland: 94-101.
- 27) Hameed, B.H., Ahmad, A.L., and Lattif, K.N.A. (2007): Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes and Pigments*, 75: 143-149.
- 28) Hameed, B.H., Din, A.T.M., and Ahmad A.L. (2007): Adsorption of methylene blue onto bamboo – based activated carbon: kinetics and equilibrium studies. *J.Hazard.Mater*, 141: 819-825.
- 29) Hameed, B.H., Tan, I.A.W., and Ahmad, A.L. (2008): Adsorption isotherm, kinetic modeling and mechanism of 2, 4, 6-trichlorophenol on coconut husk-based activated carbon. *Chem.Eng.J*, 144(2): 235-244.

- 30) Ho, Y.S., Chiang, T.H., and Hsueh Y.M. (2005): Removal of basic dye from aqueous solution using tree fern as a biosorbent. *Process Biochem*, 40: 119-124.
- 31) Holm, L.G. *et al.*, (1977): *The World's Worst Weeds*. Honolulu, Hawaii, USA: University Press of Hawaii
- 32) Inbraj, B.S., and Sulochana, N. (2002): Basic dye adsorption on low cost carbonaceous sorbent – kinetic and equilibrium studies. *Indian J.Technol*, 9: 201-208.
- 33) Jaszlo, J.A. (1996): Electrolyte effects on hydrolyzed reactive dye binding to quaterize cellulose. *Textile Chem. Colorist*, 27: 25-27.
- 34) Kannan, K., and Sundaram, M.M. (2001): Kinetics and mechanism of removal of methylene blue by adsorption on various carbons – a comparative study. *Dyes and Pigments*, 51: 15-40.
- 35) Khaled, A. *et al.*, (2009): Treatment of artificial textile dye effluent containing direct Yellow 12 by orange peel carbon. *Desaination*, 238: 210-232.
- 36) Lagergren S. (1989): About the theory of so – called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24(4): 1-39.
- 37) Langmuir, I. (1918): The adsorption of gases on plane surface of glass, mica and platinum. *J.Am.Chem.Soc*, 40: 1361.
- 38) Laszlo, J.A., and Dintzis, F.R. (1994): Crop residues as ion – exchange materials: Treatment of soybean hull and sugar beet fiber (pulp) with epichlorohydrin to improve cation – exchange capacity and physical stability. *J.Appl. PolySc.*, 52: 521-528.
- 39) Liu Y. (2008): New sights into pseudo – second order kinetic equation for adsorption. *Colloids and Engineering Aspects*, 320(1-3): 275-278.
- 40) Low, K.S., Lee, C.K., and Lee, K.L. (1998): Removal of Reactive Dyes by Quaternized Coconut Husk. *J.Environ.Sci.Health, Part A.*, 33(7): 1479.
- 41) Low, K.S., Lee, C.K., and Tan, K.K., (1995): Bisorption of basic dyes by water hyacinth roots. *Biores. Technol*, 52: 79-83.
- 42) Marks, M., Lapin, B., and Randall, J. (1994): *Phragmites australis* (P. communis): Threats, Management, and Monitoring. *Natural Areas Journal*, 14:285-294.
- 43) Mishra, G., and Tripathy M. (1993): A critical review of the treatment for decolorization of textile effluent. *Colourage*, 40: 35-38.
- 44) Namasivayam, C., Kanchana, N., and Yamuna, R.T. (1993): Waste banana pith as adsorbent for the removal of Rhodamine B from aqueous solution. *Waste Manag*, 13: 89-95.
- 45) Neamtu, M. *et al.*, (2004): Yediler A., Siminiceanu I., Macoveanu M., and Kellrup A., "Decolorization of disperse red 354 azo dye in water by several oxidation processes – a comparative study. *Dyes Pigments*, 60: 61-68.
- 46) Nemerrow, N.L. (1971): *Liquid Waste of Industry*". California: Addison Wesley Publishing Company.
- 47) Netpradit, S., Thiravetyan P., and Towprayon S. (2004): Adsorption of three azo reactive dyes by metal hydroxide sludge: effect of temperature, pH, and electrolytes. *Journal of Colloid and Interface Science*, 270: 255-261.
- 48) Pollard, S.J.T. *et al.*, (1992): Low – cost adsorbents for waste and wastewater treatment: a review. *Sci.Total Environ*, 116: 31-52.
- 49) Rajamohan, N. (2009): Equilibrium studies on adsorption of an anionic dye onto acid activated water hyacinth roots. *Afr.J.Environ.Sci.Technol*, 3: 399-404.
- 50) Randy G.W., (1998): *Invasive plants: changing the landscape of America: fact book*. Washington, D.C.: Federal Interagency Committee for the Management of Noxious and Exotic Weeds:10-17.
- 51) Serag M.S., (1996): Ecology and Biomass of *Phragmites australis* (Cav.) Trin.Ex.Steud. in the north- eastern region of the Nile Delta, Egypt. *Ecoscience*, 3(4): 473-482.
- 52) Singh, B.K., and Nayak, P.S. (2004): Sorption equilibrium studies of toxic nitro – substituted phenols on fly ash. *Adsorp.Sci.Technol*, 22: 295.
- 53) Staurt, B. (1996): *Modern Infrared Spectroscopy*", Wiley, Chichester, UK.
- 54) Suzuki, R.M. *et al.*, (2007): Preparation and characterization of activated carbon from rice bran. *J.Biores.Technol* , 98(10) :1985-1991.
- 55) Tan, I.A.W., Ahmad, A.L., and Hameed, B.H. (2008): Preparation of activated carbon from coconut husk: Optimization study on removal of 2,4,6 – trichlorophenol using response surface methodology. *J.Hazard.Mater*, 153: 709-719.
- 56) Tan, I.A.W., Hameed, B.H., and Ahmad, A.L. (2007): Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chem.Eng.J*, 127: 111-119.

- 57) Tsuboy, M.S., *et al.*, (2007): Gentoxic, Mutagenic and Cytotoxic Effects of the Commercial Dye CI Disperse Blue 291 in the Human Hepatic Cell Line HepG2. *Toxicology in Vitro.*, 21(8) :1650-1655.
- 58) Unamuno, V.I.R.*et al.*, (2007): Cu sorption on Phragmites australis leaf and stem litter: A kinetic study. *Chemosphere*, 69(7): 1136-1143.
- 59) Vinitnantharat, S., Chartthe, W., and Pinisakul A. (2008): Toxicity of Reactive Dye 141 and Basic Red 14 to Algae and Water Fleas. *Water Science and Technology.*, 58(6) :1193-1198.
- 60) Wahi, R.K.*et al.*, (2005): Photodegradation of Congo red catalyzed by nanosized TiO₂. *J.Molecular Catal. A: Chem*, 242: 48-56.
- 61) Warren, R.S.*et al.*, (2001): Rates, patterns, and impacts of Phragmites australis expansion and effects of experimental Phragmites control on vegetation, macroinvertebrates, and fish within tidelands of the lower Connecticut River. *Estuaries*, 24: 90-107.
- 62) Weber, W.J., and Chakravarthi, R.K (1974): Pore and solid diffusion modules for fixed bed adsorbent. *J.Am.Inst.Chem.Eng*, 22: 228-238.
- 63) Wong, Y., and Yu J.(1999): Laccase Catalysed Decolorisation of Synthetic Dyes. *Water Res.*, 33(16): 3512-3520.
- 64) Zawadzki, J. (1989): Infrared spectroscopy in surface chemistry of carbons. In: Thrower PA.Editor. *Chemistry and Physics of carbon*" NewYork: Marcel Dekker. 21: 147-386.
- 65) Zollinger, H. (1991): *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments*. 2nd edn, Wiley VCH, NewYork. : 413-414.