Comparative Study of Adsorption Phenomena of Direct Dye Black E by Palm Nut Shell Carbon and Treated Flyash Residue With Respect to Activated Charcoal Carbon

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ABSTRACT

Many researchers[1-3] aimed to study the removal of colouring matter from textile dyeing industrial effluent using the carbon derived from natural sources. Because adsorption of the dyes on carbon is easily, cost effective when comparing to the other techniques. Hence we aimed at the preparation and characterization of the carbon from the natural sources like palm nut shell and flyash. These carbons have been used for adsorption of direct dye Black E. The effect of pH, carbon dose and equilibration period were examined along within the Langmuir and Freundlich isotherm studies. The application of these carbons was investigated on adsorption and colour removal from effluent and synthetic samples, which consists of commercial direct dye Black E.

Keywords: Adsorption phenomena, palm nut shell carbon, treated flyash residue, direct dye Black E

1. INTRODUCTION

Dyeing is one of the fundamental operation in textile industry. The textile wastes are one of the most potential pollutants of our aquatic environment. Dyes are aromatic amines consisting of different types of organic functional groups like phenols[4] and heavy metals embodied in the basic structure and are confirmed carriers by heavy metals like chromium[5], copper[6] and cobalt[7]. Textile dye effluents are complex in chemical nature, highly coloured materials and exhibit toxicity to both aquatic and non-aquatic biota.

Adsorption process is the most powerful technique and used for separating organic and inorganic pollutants from water and waste water and it is embodied in carbon adsorption systems and ion exchangers. Poots *et al.*[8] studied the removal of dyes from effluent using natural adsorbents like wood and peat.

Adsorption process was first observed in solution phase by Lowitz[9]. The significance of the carbon surface chemistry in the adsorption process was first raised by Hassler[10].

Researchers[11] have investigated the removal of dyes from the effluent water which was released by large tiny printing and dyeing units in the sanganer town- now a part of Jaipur city, using activated charcoal as adsorbent. In this direction we have undertaken an investigation on the effluent pollutions caused by the textile industries situated at Tirpur in South Tamilnadu where direct dyes were used mainly.

The present paper aims to develop a low cost adsorbent and apply it for removal of the direct dye Black E. Low cost carbon was prepared from palm nut shells. Treated flyash residue (carbon enriched flyash) also selected. The adsorbent capacities of the low cost carbon and Treated Flyash Residue (TFR) were compared with that of a commercial Activated Charcoal Carbon (ACC).

2. EXPERIMENTAL METHODS

Four parts of dry palm nut shells were treated with two parts of concentrated H_2SO_4 and keeping it in an air oven at 140-170 °C for 24 hours. The carbonized material was filtered and washed with water to remove the excess acid and direct at 110 °C and was designated as PNSC.

The flyash was obtained from Neyveli Lignite Corporation of Tamilnadu, India. The raw flyash was treated with cold and hot running water and then with 400 ml of concentrated H_2SO_4 and kept it in an air oven at 110-140 °C for five hours. The settled residue (mostly carbon) material was filtered and washed with water to remove the excess acid and dried at 105-110 °C.

The dried treated flyash carbon was washed to with organic solvents (benzene, ether, acetone) and dried at in an air oven. The dried residue is designated as Treated Flyash Residue (TFR). The ACC, PNSC and TFR materials were grounded well and sieved to an average diameter of 0.5mm. The activated charcoal carbon (ACC) was obtained from chemical laboratory of qualigens make (Analytical grade).

3. RESULTS AND DISCUSSION

3. 1. Charaterization of carbon sample

The carbon samples (adsorbents) were characterized after following ISI code and the results were tabulated in Table 1.

3. 1. 1. SEM of Carbon Sample

The shape and size of the particles of the carbon samples were examined through SEM photographs (Fig. 1-3). The surface of the carbon samples were irregular and not spherical as expected. In the crystallinity is found to be more in activated charcoal carbon (ACC) than that of palmnut shell carbon (PNSC). In the case of treated fly ash residue (TFR) the conglomeration of carbon particles results into bulky mass. This conglomeration reduces the surface area and hence except low adsorption. Another future identifiable is low degree of spherical shape. This is not present in other two samples. ACC is more crystalline but not spherical in shape.

Among the direct dyes Black E (λ_{max} : 585 nm) was extensively used and discharged into the drain system. The direct dye black E was obtained from Tirupur dyeing industries in Tamilnadu, India. We concentrate on the adsorption of direct dye Black E from the effluent wastewater using palmnut shell carbon and treated flyash residue as an adsorbents.

Table 1. Characterization of Carbon Sambles

S. No.	Parameters	ACC	PNSC	TFR
1.	Moisture content (%)	20.8	15.2	13.6
2.	Ash content (%)	0.21	0.72	0.42
3.	Bulk density (g/cc)	0.47	0.67	0.74
4.	pH	7.9	6.8	7.8
5.	Carbon soluble in water (%)	0.95	0.97	0.94
6.	Carbon soluble in acid (%)	1.95	1.05	1.81
7.	Decolourizing power (mg/g) methylene blue	112.5	73.5	72.0
8.	Iron content ($\times 10^{-6}$ gm/gram of carbon)	811.0	1054.3	405.5
9.	Phenol number (mg/lit)	227.5	333.3	370.4
10.	Ion exchange capacity (mg/g)	0.4468	0.3277	0.3872
11.	Surface area (m^2/g) (*p*-nitrophenol method)	474.3	459.1	467.9
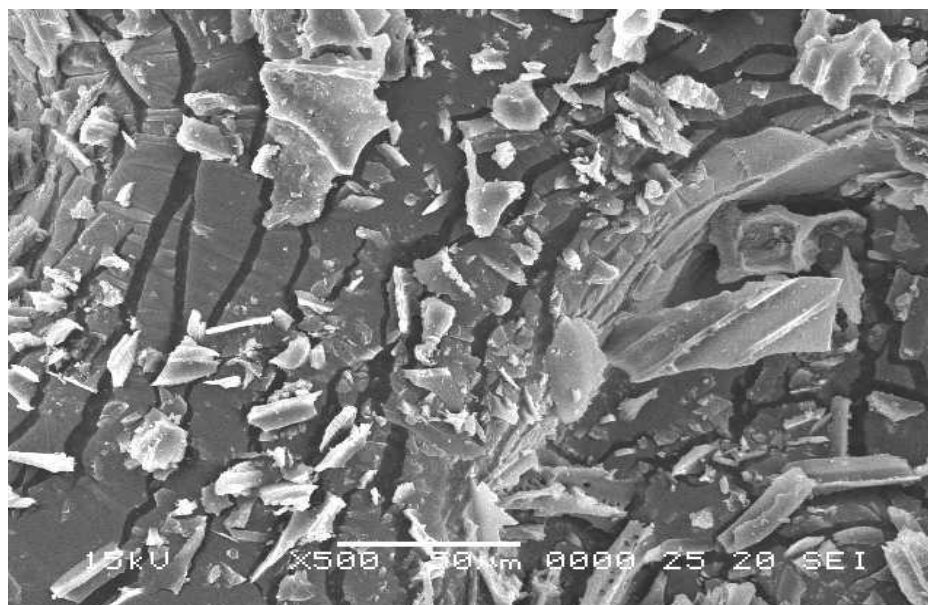
Fig. 1. Activated Charcoal Carbon (ACC)

Fig. 2. Palm Nut Shell Carbon (PNSC)
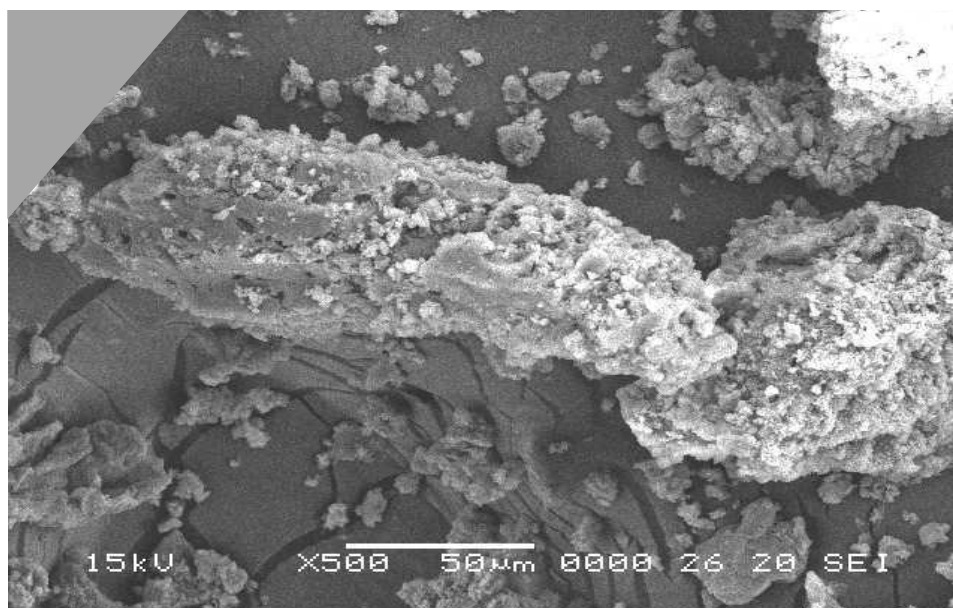
Fig. 3. Treated Flyash Residue (TFR**)**

3. 2. Batch desorption studies

5 gram carbon systems were subjected for the maximum adsorption of the black E dye under optimized condition. The dye adsorbed carbons were filtered off and 0.5 g of each carbons were treated for desorption studies by mineral acid (HCl, H_2SO_4 and $HClO_4$), steam and hydrogen peroxide methods. The desorbed carbons were again used for the adsorption of the dye. The process of adsorption and desorption were repeated for 5 times.

3. 3. Batch isotherm study

A batch experiment was conducted by taking varying amount of adsorbents ranging from 50 mg to 250 mg in polythene bottle and 100 ml of dye solution which vary in concentration from 10-150 ppm under optimum condition. After equilibration period of one hour the absorbance of the supernatant liquid is determined spectrophotometrically at 585 nm.

3. 4. Batch kinetic study

100 ml of dye solution with initial concentration of 10, 15, 20 ppm were treated each with 1 g of carbon and equilibrated for different time intervals of 25, 50, 75 and 100 minutes with constant stirring. The residual dye concentrations after equilibration period were measured spectrophotometerically at 585 nm.

The optimized conditions for maximum adsorption of the dye our the carbons in shown in Table 2.

Table 2. The optimized conditions for maximum adsorption of the dye our the carbons.

S. No.	Optimized parameters	ACC	PNSC	TFR
1.	pH	7	9	7
2.	Carbon dose (g)	1.0	0.9	1.1
3.	Equilibration period (min.)	330	360	360

3. 5. Desorption and regeneration studies

The desorption of the dye from the adsorbed carbon is attempted by mineral acids (HCl, H_2SO_4 and $HClO_4$), steam and hydrogen peroxide methods. In acid desorption method, the adsorbed carbon is treated with 0.5 N H_2SO_4 separately for 1 hour and the resulted desorbed dye concentration was identified. In steam method, the adsorbed carbons were subjected to the steam flow (100 °C) for a period of 30 minutes and intermission for 10 minutes.

The collected dye is concentrated and identified. In hydrogenperoxide (30% v/v) method, 0.5 g of adsorbed carbons are mixed with hydrogen peroxide and stirred for 1 hour.

The resulted desorbed dye content is identified. The reusefullness of the carbons are also tested for five times. The results are presented in Table 3. From the table, the adsorbed dye is in most cases is desorbed with much loss reduction in percentage of desorption is 5 to 15%. It is indicates that the adsorption is mostly physical in nature.

3. 6. Equilibration isotherm studies

The variation of amount of dye adsorbed with initial equilibrium dye concentration (Fig. 4) indicates a sharp increase in the amount adsorbed up to 340 mg/lt, 560 mg/lit and 360 mg/lit in the case of ACC, PNSC and TFR carbons without a notch.

This is an indicative of homogenous adsorptions model[13,14]. A plot of x/m Vs equilibration dye concentration results in a L shape[15] (Fig. 4) indicate of Langmuir assumption that the intermolecular forces between sorbate and sorbent.

Table 3. Reusability data

No. of cycles	0.5N H_2SO_4 acid method						Steam method						30% v/v hydrogen peroxide method					
	ACC System (a)		PNSC System (b)		TFR System (c)		ACC System (a)		PNSC System (b)		TFR System (c)		ACC System (a)		PNSC System (b)		TFR System (c)	
	O.D	% of desorption	O.D	% of desorption	O.D	% of desorption	O.D	% of desorption	O.D	% of desorption	O.D	% of desorption	O.D	% of desorption	O.D	% of desorption	O.D	% of desorption
1	0.785	86.9	0.601	71.9	0.640	72.4	0.875	96.9	0.753	90.1	0.800	90.5	0.825	91.4	0.750	89.7	0.790	89.4
2	0.770	85.3	0.590	70.6	0.615	69.6	0.853	94.5	0.741	88.6	0.781	88.3	0.805	89.1	0.720	86.1	0.760	86.0
3	0.743	82.3	0.575	68.8	0.590	66.7	0.809	89.6	0.705	84.3	0.780	88.2	0.775	85.8	0.701	83.8	0.725	82.0
4	0.740	81.9	0.529	63.3	0.545	61.6	0.780	86.4	0.690	82.5	0.753	85.2	0.730	80.80	0.690	82.5	0.705	79.8
5	0.727	80.5	0.508	60.8	0.530	59.9	0.729	80.7	0.685	81.9	0.750	84.8	0.709	78.5	0.658	78.7	0.691	78.2

(a) % of Adsorption out of 95%
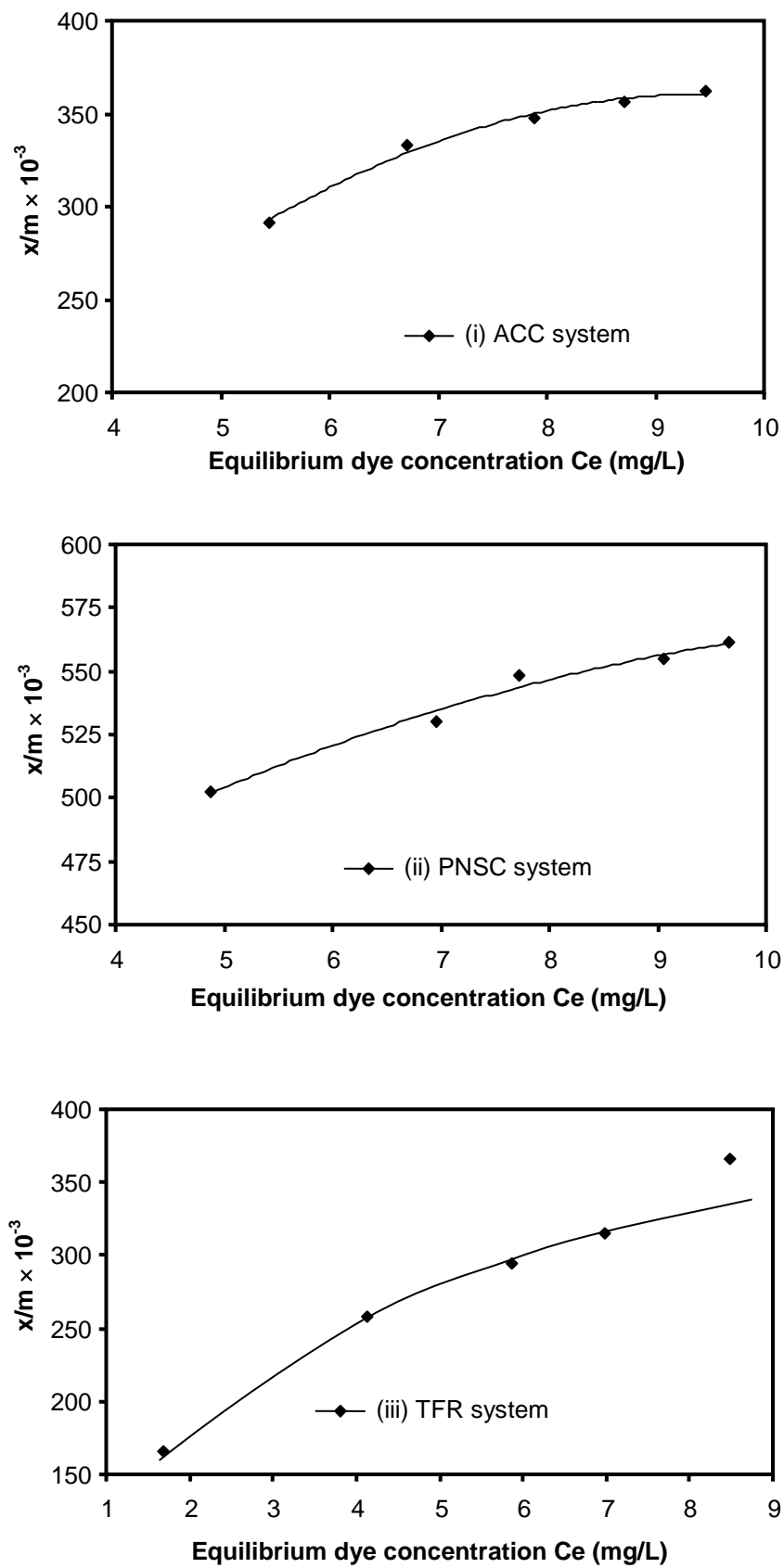(b) % of Adsorption out of 88%
(c) % of Adsorption out of 93%

Fig. 4. Equilibrium sorption curves of Black E

3. 6. 1. Langmuir adsorption isotherm

The langmuir plot of Ce/x/m Vs equilibrium dye concentration results in a linear relation was obtained and presented in Fig. 5. From the plot, the essential characteristics of sorption intensity "a" (mg/L) and sorption capacity "b" (mg/g) and linearized Langmuir equations are present in Table 4.

Table 4. Essential characteristics of Langmuir plot

S. No.	Carbon system	Sorption intensity 'a' mg/L	Sorption capacity 'b' mg/g	$\dfrac{Ce}{x/m} = \dfrac{1}{ab} + \dfrac{1}{b}Ce$
1.	ACC	0.234	0.532	$\dfrac{Ce}{x/m} = 8.02 + 1.88\,Ce$
2.	PNSC	0.748	0.637	$\dfrac{Ce}{x/m} = 2.10 + 1.57\,Ce$
2.	TFR	0.266	0.503	$\dfrac{Ce}{x/m} = 7.46 + 1.99\,Ce$

3. 6. 2. Freundlich adsorption isotherm

The experimental data was presented in the form of Fig. 6 was fit into the Freundlich model which is represented by

$$\log (x/m) = \log K + 1/n \log Ce$$

The fit in the data indicates the heterogeneity of the system. The essential characteristics of Freundlich plot are presented in Table 5.

Table 5. Essential characteristics of Freundlich plot

S. No.	ACC System		PNSC System		TFR System	
	K	1/n	K	1/n	K	1/n
1.	0.148	0.406	0.378	0.180	0.129	0.473

In the present studies only one line is resulted which testifies the formation of monolayer only on the adsorbent surface[16]. From the adsorption isotherm studies, it is found out that the order of preference for removal of dye is PNSC > ACC > TFR.
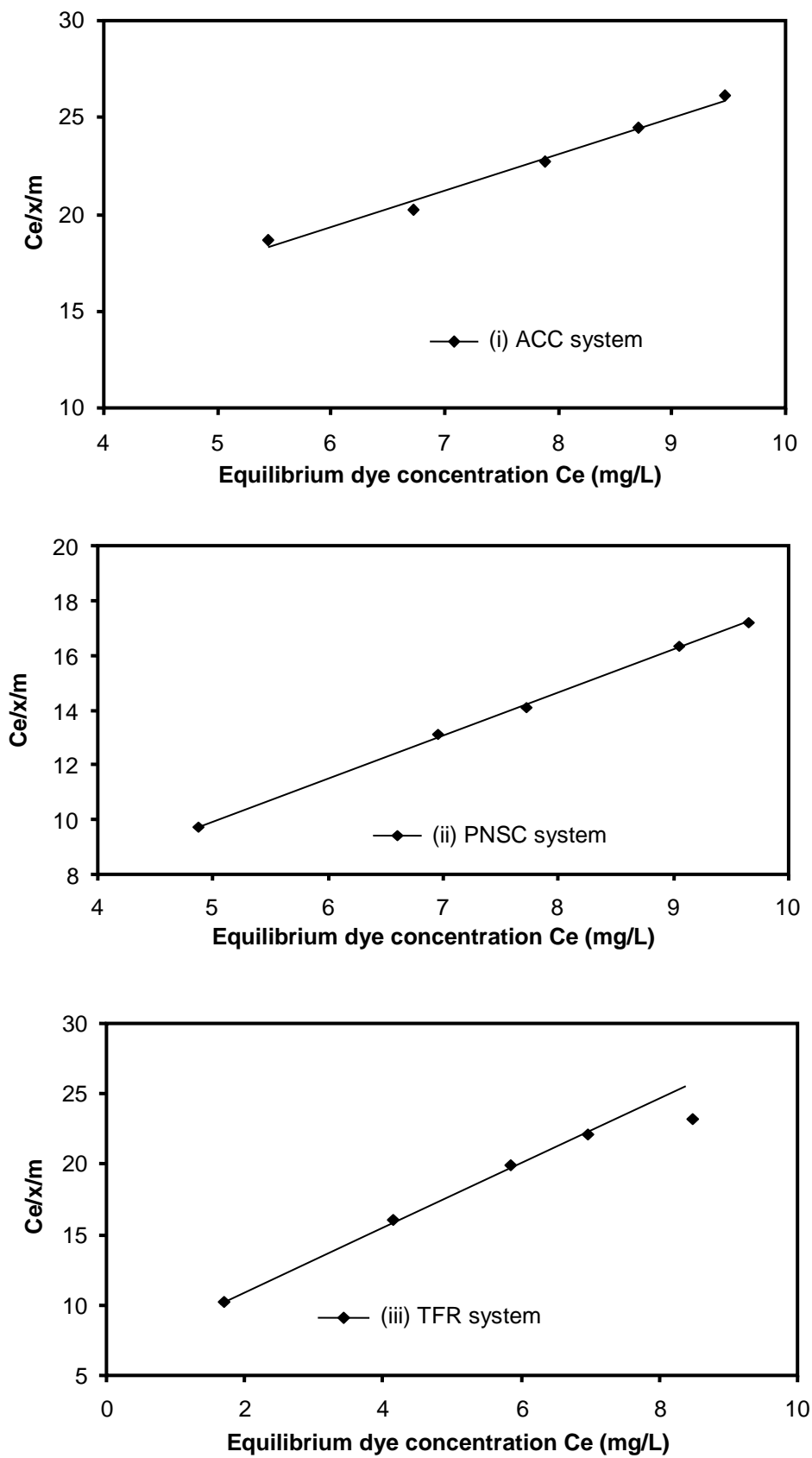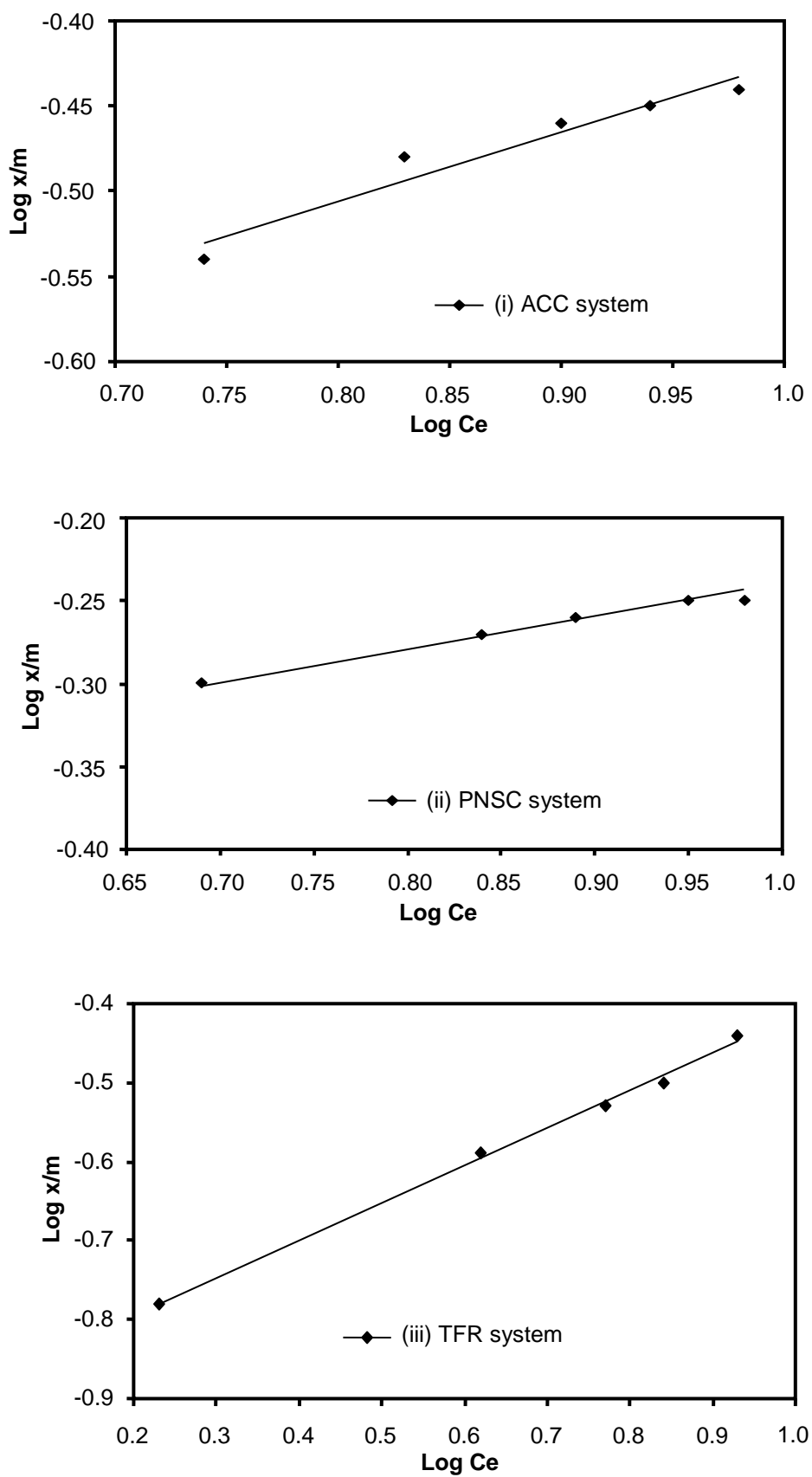
Fig. 5. Langmuir plot of Black E

Fig. 6. Freundlich plot of Black E

3. 7. Kinetics of adsorption

The kinetics of adsorption plots are constructed to the concentration of the dye (mg/L) with different time intervals Vs various initial dye concentrations are presented in Fig. 7. All the plots show similar trends with in the limits of study. A significant fact to be noticed is increased percentage of adsorption with increase in initial concentration. The equilibrium concentration also increases with increased initial concentration. Hence, the rate of adsorption also increases with increased initial concentration.
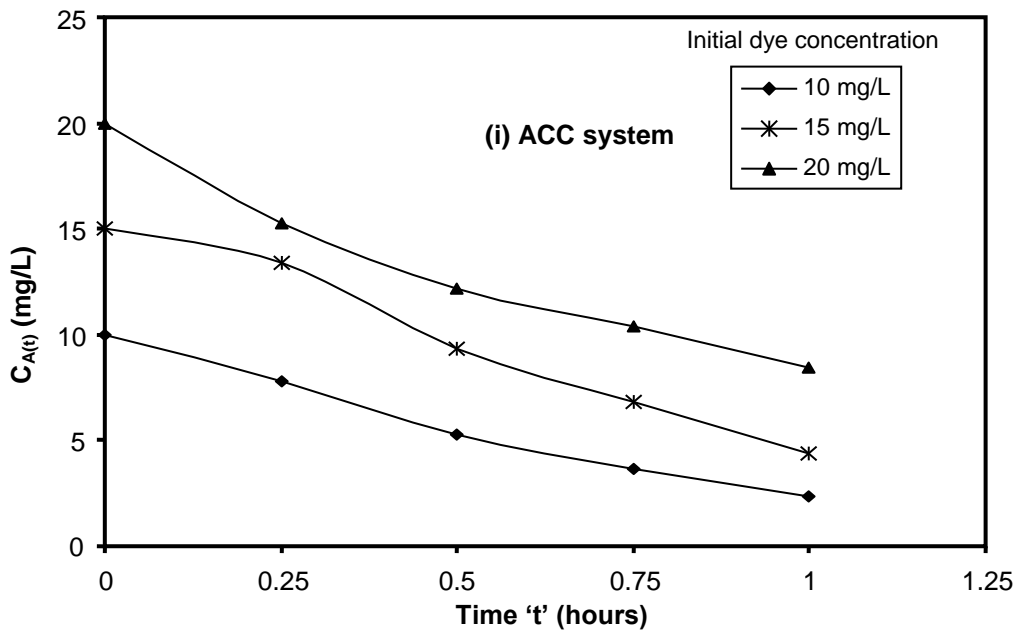
(i) ACC system
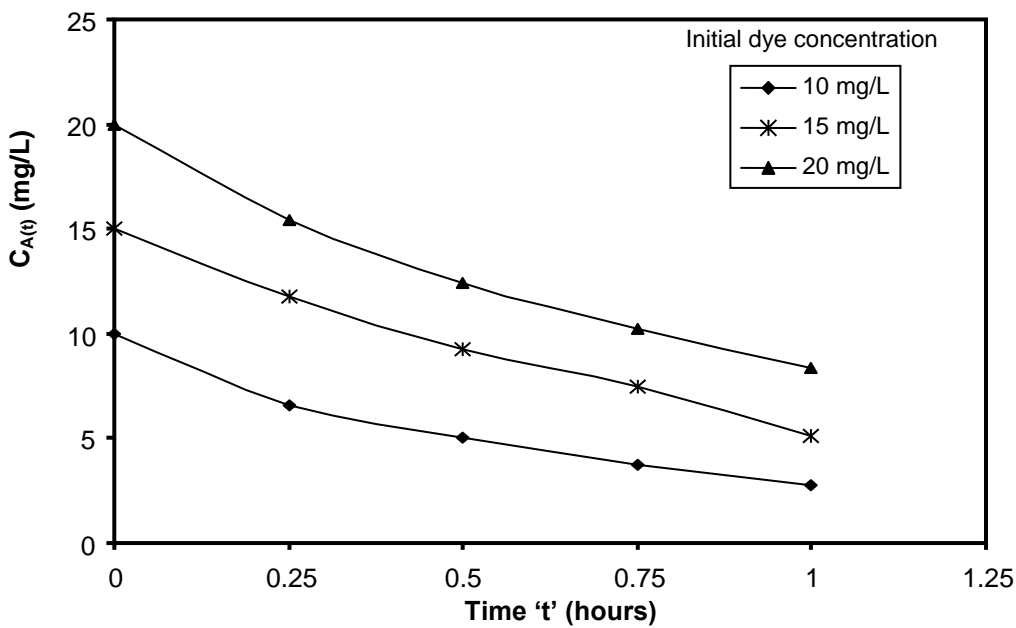
(ii) PNSC System
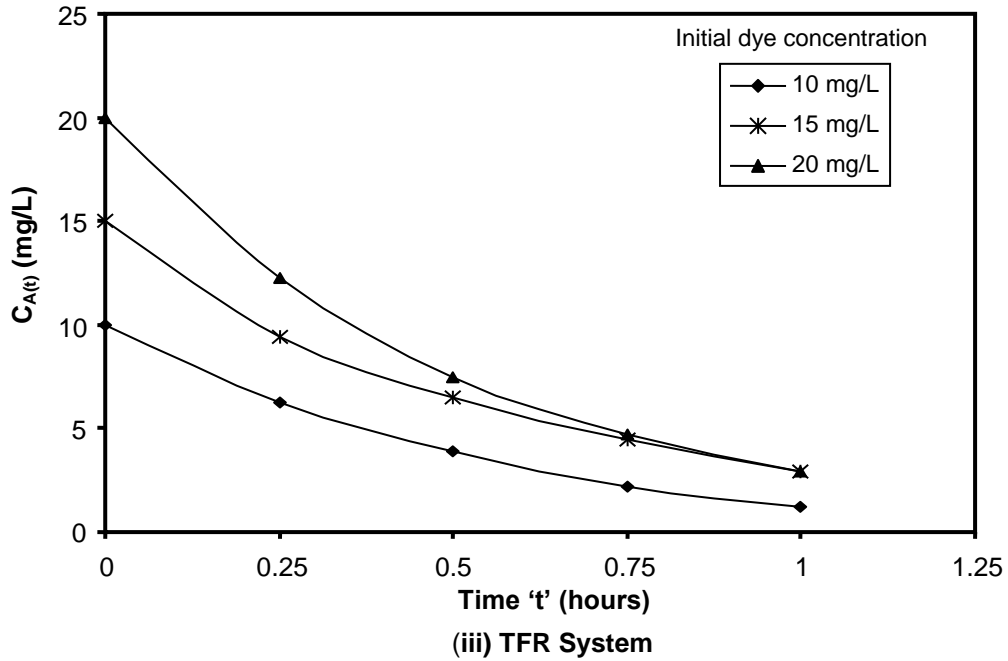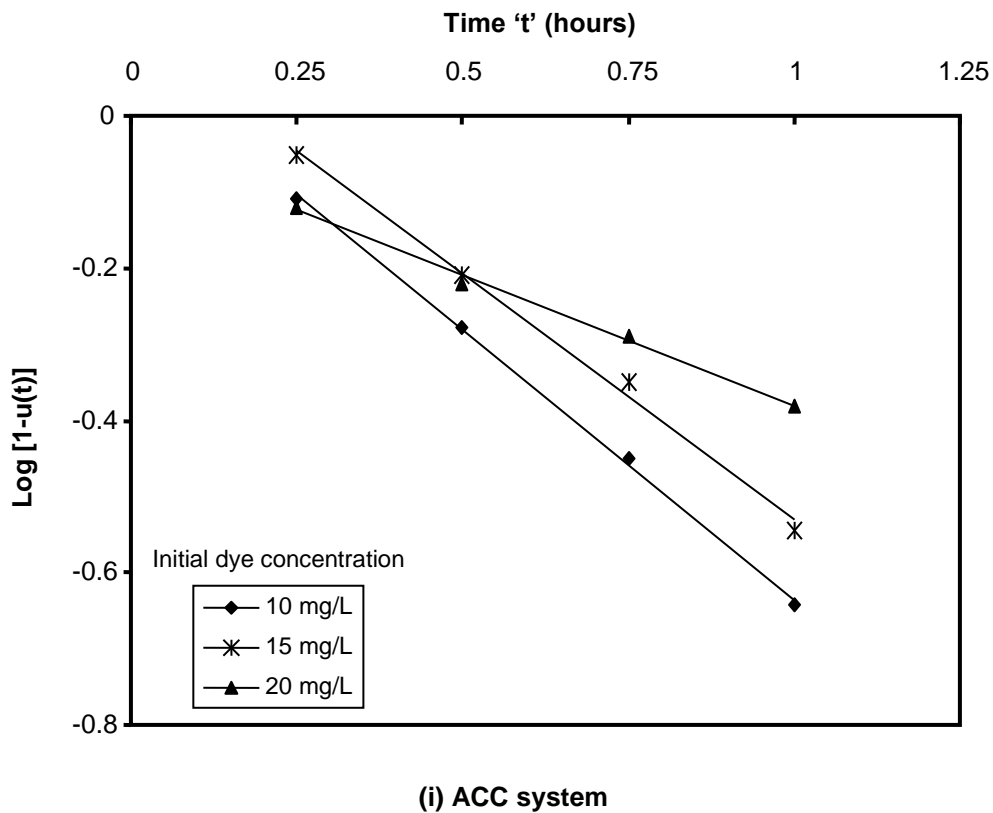
(iii) TFR System

Table 7. Essential characteristics of Freundlich plot

3. 8. Rate constant studies

The interpretation of the adsorption data can be best explained with the help of linearized Lagergrem's equation (Fig. 8). The forward and backward rate constant, overall rate of the adsorption and equilibrium constant were calculated and presented in Table 6.
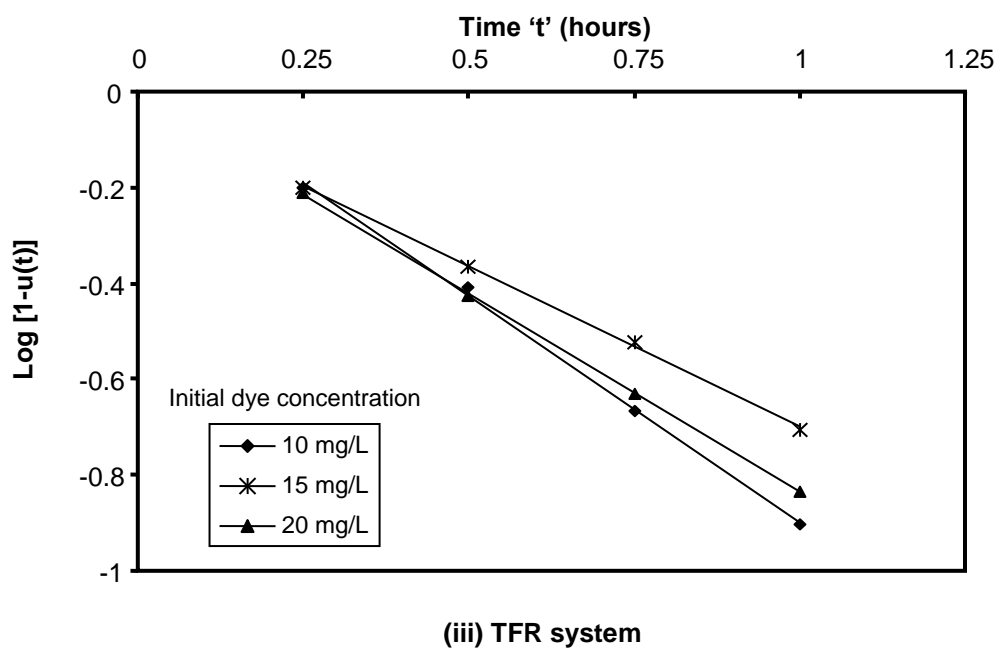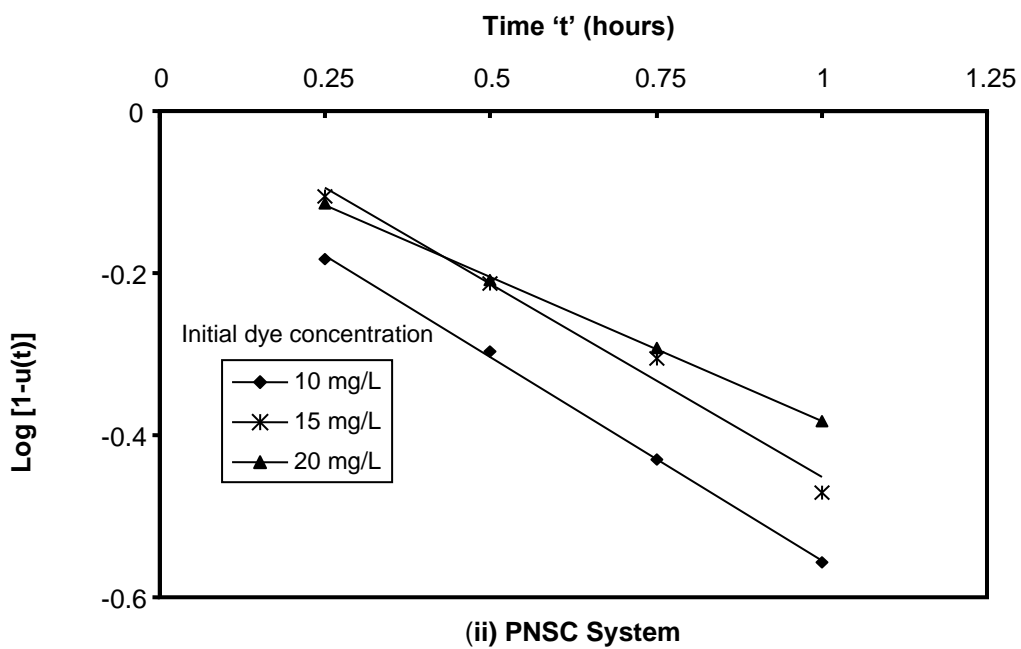

(i) ACC system

Time 't' (hours)

(**ii) PNSC System**

Time 't' (hours)

(iii) TFR system

Fig. 8. Rate Constants of Carbon System with Black-E

Table 6. Rate constants of carbon systems

S. No.	Initial dye conc. (mg/L)	ACC System				PNSC System				TFR System			
		K	k_1	k_{-1}	k_C	K	k_1	k_{-1}	k_C	K	k_1	k_{-1}	k_C
1.	10	-0.9453	-1.890×10^{-4}	-0.9451	2.000×10^{-4}	-0.5027	-7.539×10^{-4}	-0.5019	1.502×10^{-3}	-0.7087	-8.787×10^{-3}	-0.6999	12.555×10^{-3}
2	15	-0.6682	-3.564×10^{-4}	-0.6678	5.336×10^{-4}	-0.4766	-1.652×10^{-3}	-0.4749	3.479×10^{-3}	-0.6478	-7.557×10^{-3}	-0.6402	-11.804×10^{-3}
3	20	-0.8270	-10.332×10^{-4}	-0.8259	12.516×10^{-4}	-0.3564	-2.423×10^{-3}	-0.3539	6.846×10^{-3}	-0.3416	-3.945×10^{-3}	-0.3376	-11685×10^{-3}

$$K \quad = \text{ Overall rate of the adsorption}$$
$$k_1 \quad = \quad K \text{ adsorption}$$
$$k_{-1} = \quad K \text{ desorption}$$
$$k_C \quad = \quad \text{Equilibrium constant}$$

4. CONCLUSION

The carbons (PNSC & TFR) are prepared from locally available cheap materials like, palm nut shells and fly ash. The properties of (PNSC & TFR) are closed with ACC. The direct dye black E was obtained by commercially and using this dye a coloured solutions are prepared. The carbon have been used to adsorb the colouring matter from Black -E dye solution and to be adsorbed effectively and the adsorption of the dye on the carbon are almost 90-95%. The adsorption of the dye depends upon the initial concentration of the dye and upon pH condition and the carbon after use can be disposed without any effects are burnt easily.

The carbon can be reused at least five times without much reduction in the adsorption capacity. The Langmuir and freundlich constant are calculated for Black-E dye and also bed depth service time analysis has been done and depth to time dependency has been evaluated.

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