Adsorption of Dye from Aqueous Solution by CAC, LBC and MPC. Studies on Equilibrium Isotherm and Kinetics of Interactions.

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ABSTRACT

Industrial Wastewater contains several type of dye, causing serious environmental hazard. The discharge of highly colored effluents into natural water bodies not only is aesthetically displeasing, but also impedes light penetration, thus upsetting biological processes within stream and thus required treatment before discharge into a water body. In the present study, Lima Beans Carbon, Musa Paradisiac Carbon converted into a low-cost adsorbent for the removal of Auramine Yellow from effluents of textile industry. Batch studies have been carried out to study the effect of pH, adsorbent doses, adsorbate concentration, temperature and contact time. The results of batch studies reveal that the adsorption of Auramine Yellow is strongly pH dependent and maximum Auramine Yellow removal is observed at equilibrium pH of 7.2. Optimum adsorbent dose and contact time are found to be 10 g/L and 360 minutes respectively. Kinetic studies have been performed to have an idea of the mechanistic aspects and to obtain the thermodynamic parameters of the process. The results also show that the adsorption decreases with increase in temperature, thereby showing the process exothermic in nature. Adsorption data have also been correlated with both Langmuir and Freundlich isotherm models.

Keywords: Lima Beans Carbon, Musa Paradisiac Carbon, adsorption, Auramine Yellow, Langmuir, Freundlich isotherm, adsorbate.

INTRODUCTION

Due to rapid industrialization and urbanization quality of water and air is going to decrease. Dye containing wastewater originates from the textiles, papers, plastics, food and cosmetic industries. Organic dyes are an integral part of many industrial effluents. Most of dyes are toxic, mutagenic and carcinogenic which poses hazard to aquatic life as well as other living organisms [1]. It is estimated that more than 50,000 commercially available dyes with over 3×10^5 tonnes of dye stuff produced annually [2-4]. It is recognized that public perception of water quality is greatly influenced by the colour. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion. Possible methods of colour removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation etc. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [5-7]. Methods of dye wastewater treatment have been reviewed by Pokhrel and Viraraghavan [8], Slokar and Majcen Le Marechal [9], Delee et al. [10], Cooper [11], Crini [12] and Gupta and Suhas [13], Robinson et al. [14] and Banat et al. [15]. Recognizing the high cost of activated carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements. Such materials range from industrial waste products such as waste tyres, baggasse blast furnace slag, fly ash, zeolites and lignin to agricultural products such as wool, rice husk, coconut husk, saw dust, peat moss etc. [16-24].

Fly ash is a waste substance from thermal power plants, steel mills, etc. and is found in abundance in the world. Since wide scale coal firing for power generation began in the 1920s, many millions of tonnes of ash and related by-products have been created. In India about 160 MT/annum of fly ash is generated from burning of coal in power plants. As a matter of fact, the disposal of fly ash will soon be too costly if not forbidden. Throughout the world, much research is being conducted on the use of such waste materials in order to either avert an increasing toxic threat to the environment or to streamline present waste disposal techniques by making them more affordable. It, therefore, follows logically that an economically viable solution to this problem should include utilization of waste materials into new products for other applications rather than disposal in a landfill. In recent years, utilization of fly ash has gained much attention in public and industry, which will help reduce the environmental burden and enhance economic benefit. Auramine Yellow (AY) dye is one of the most commonly used water-soluble cationic dyes in textile, paper, printing and other industries. The structure of Auramine Yellow is shown below in scheme 1. It is generally used in dying textile specially cotton and silk and in some medical.

Experimental

Adsorbent

Lima Beans Carbon (LBC), Musa Paradisiac Carbon (MPC) was collected from Cumbum Village in Theni-625516 District, Tamil Nadu, INDIA and used as an adsorbent in this study. It was collected from natural sources and washed thoroughly under the running tap, followed by distilled water until the dust particles were removed from the adsorbent. The adsorbent was dried in sunlight for 48 hours, grounded and screened through a set of sieves to obtain particles of different sizes and the sieved powder was kept dry in a closed container. It was ensured that there was no color produced by Lima Beans Carbon (LBC), Musa Paradisiac Carbon (MPC) when it was in contact with the dye solution.

ADSORBATE

Auramine Yellow (AY)dye was purchased from Sigma-Aldrich a chemical company, 1.0g of (AY) dye and it was further diluted to prepare the test solutions of various required concentrations (20mg/L-100mg/L). The molecular structure of the AY is shown in Fig-2a.

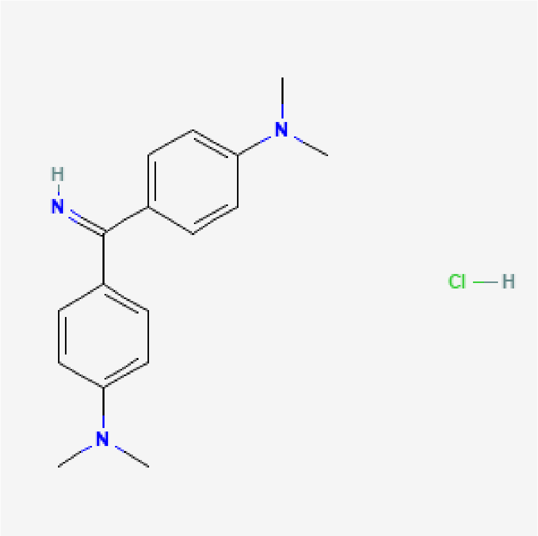


Fig-2a- Structure of Auramine Yellow

Adsorption Experiments

Adsorption experiments were conducted in batch process. The effect of various adsorption parameters such as the effect of contact time, the effect of initial concentration and the effect of temperature were studied.0.2g of CAC, LBC & MPC was added to 50 mL of AY stock solution of known concentrations taken in a set of 250 mL Erlenmeyer flasks. All the samples were taken from an orbital shaker and kept in centrifugation at 4000 rpm for mins. Final concentrations of supernatant were examined by using a UV spectrometer at a maximum wavelength of 455nm to find the dye concentration in the aqueous solution. The amount of dye (mg/g), adsorbed by CAC, LBC &MPC can be represented by the following equation

$$qe = \frac{(Co - Ce)V}{M}$$

Where Co is the initial AY concentration and Ce is the AY dye concentration of at equilibrium in mg/L, V is the volume of dye solution (L) and ‘m’ is the mass of the adsorbent (g) used.

Characterization Studies

UV-Studies

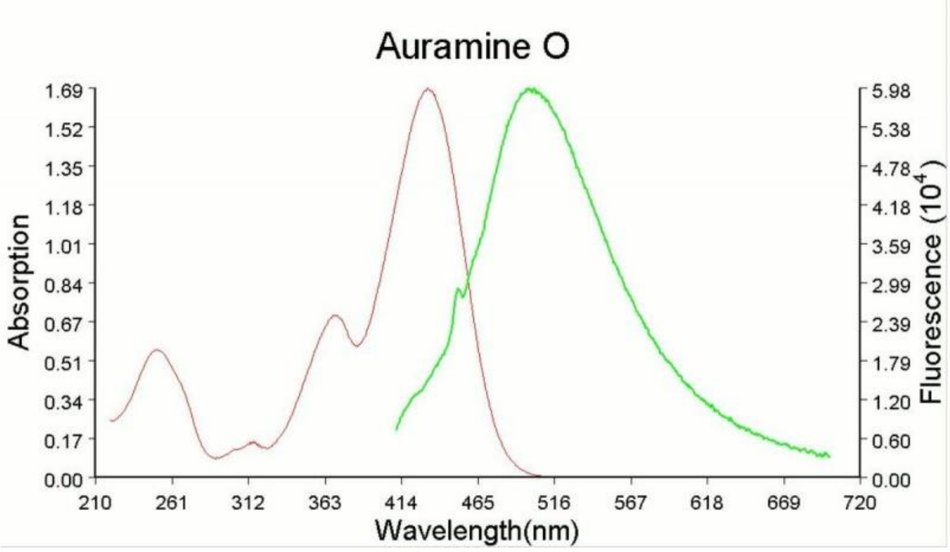


Fig- 3.1a. UV-After and Before adsorption AY dyes on IPACs.

FT – IR STUDIES:

The Fourier Transform Infra-Red (FT–IR) spectra were recorded for the AC. The values of frequency (ν in cm^{-1}) of some of the characteristic absorption peaks observed in AC

The FT - IR spectra of ACs indicate the presence of various surface functional groups like C = O, -OH, - COOH, = C = C=, = C = S, etc,. These surface functional groups are responsible for the adsorption of dye. This observation also concludes the fact that these ACs could be used as low-cost adsorbent materials as alternatives to CAC, for the removal of dye by adsorption from water and wastewater like dye industrial effluent.

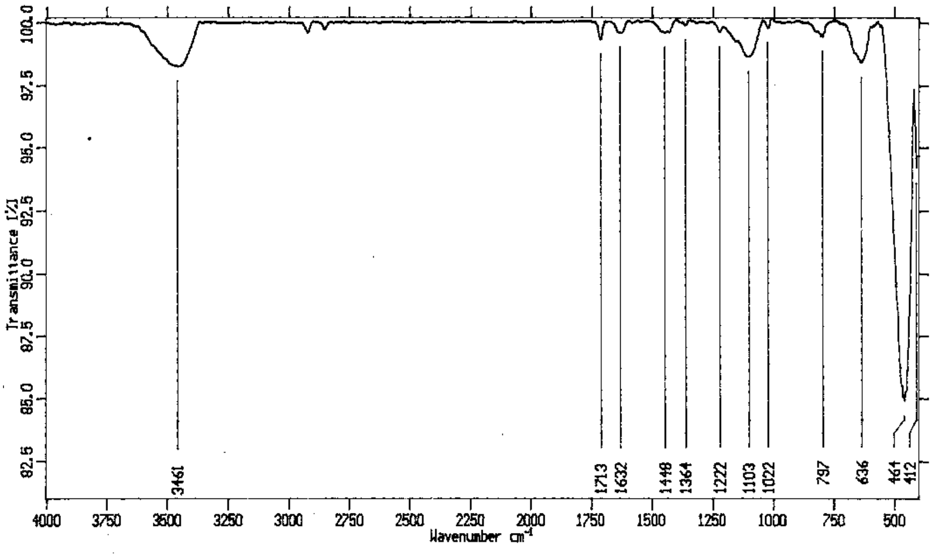
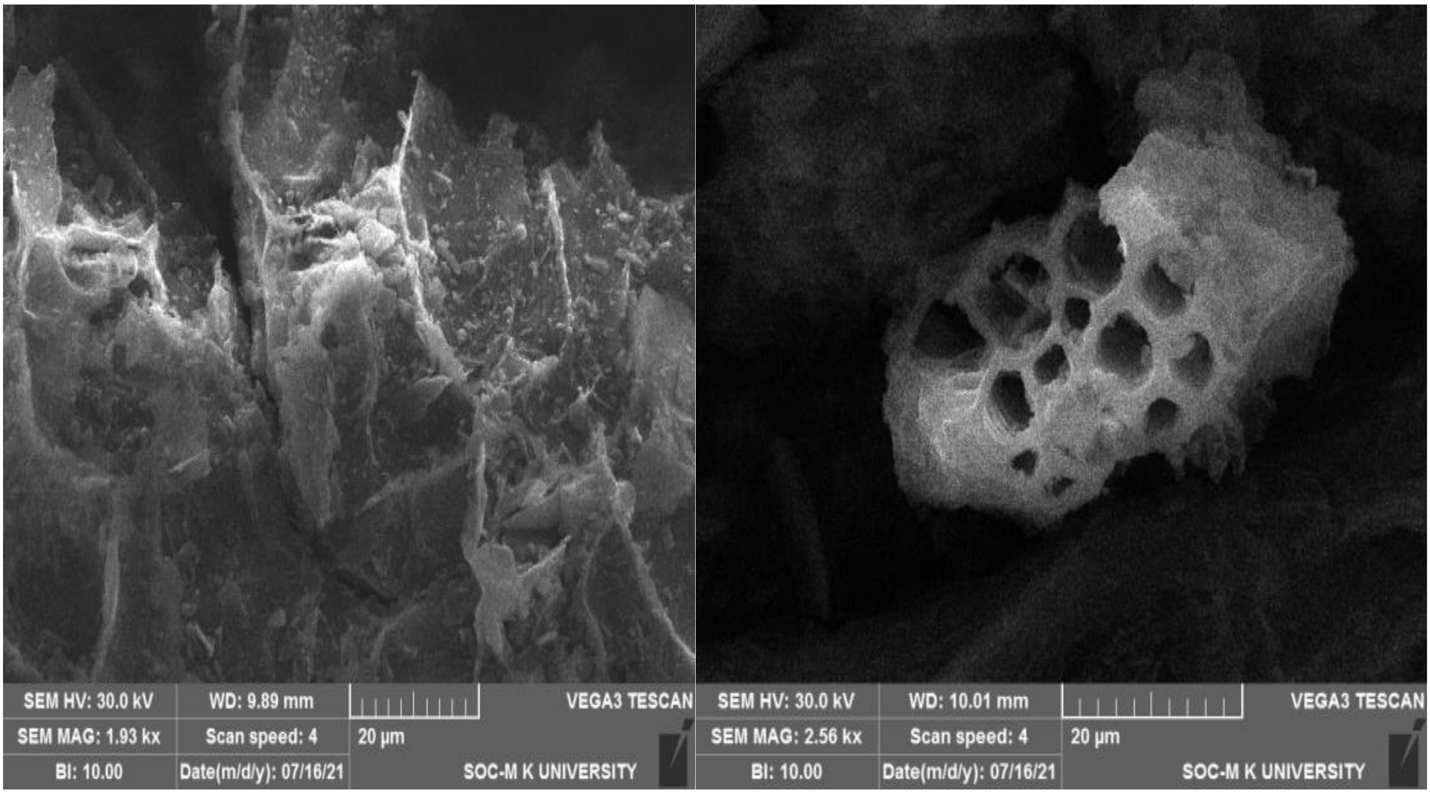
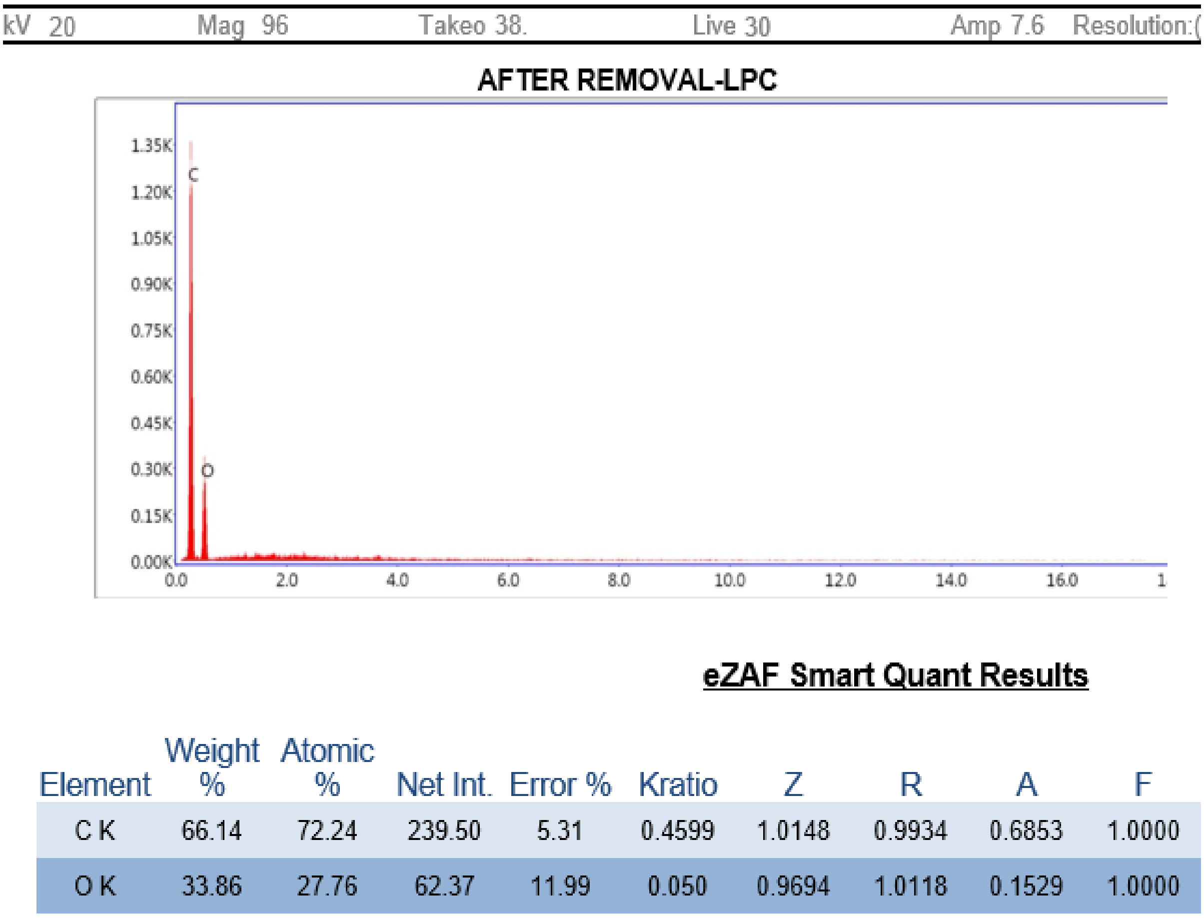


Fig-3.1b. After dye adsorption FT-IR wave length on IPACs

SEM Studies



IVd) EDAX-Spectra

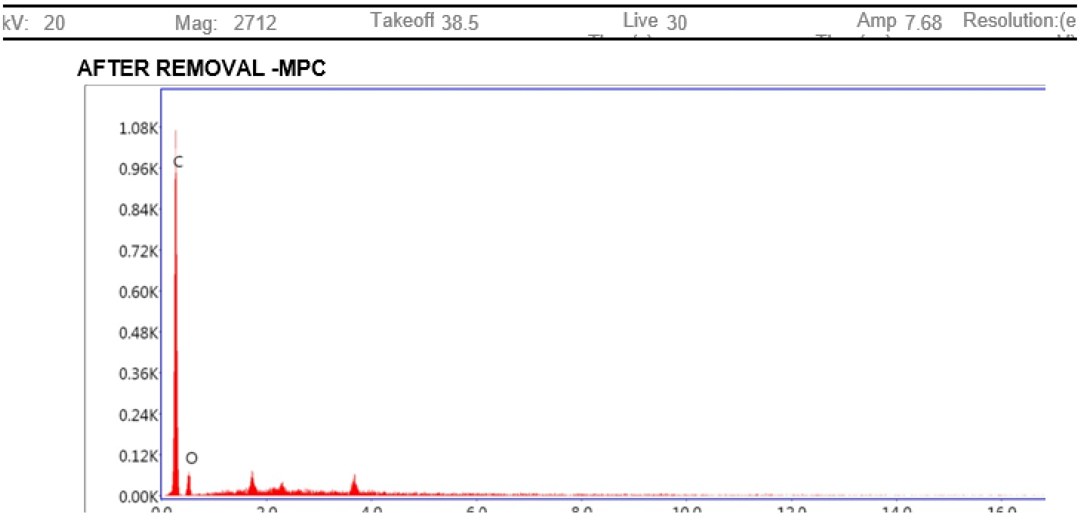


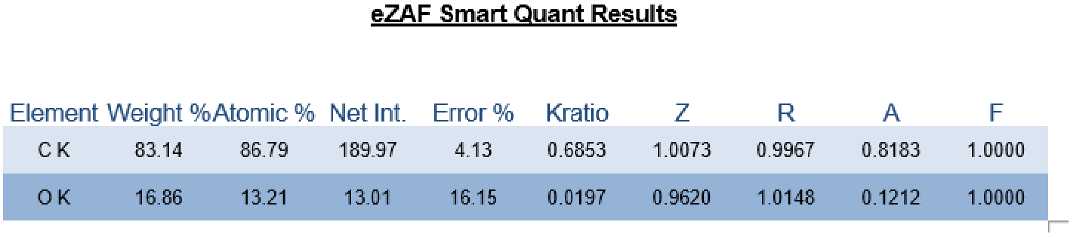
eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	66.14	72.24	239.50	5.31	0.4599	1.0148	0.9934	0.6853	1.0000
O K	33.86	27.76	62.37	11.99	0.050	0.9694	1.0118	0.1529	1.0000

Fig-3.1c-The SEM images of after adsorption AY on IPACs

EDAX-Spectra





eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	83.14	86.79	189.97	4.13	0.6853	1.0073	0.9967	0.8183	1.0000
O K	16.86	13.21	13.01	16.15	0.0197	0.9620	1.0148	0.1212	1.0000

Fig-3.1. d-Energy dispersive spectra on IPACs.

The Effect of Initial Concentration:

Batch adsorption experiments were carried out in order to study the effect of initial concentration of dyes (AY) on the extent of removal of dyes, in terms of percentage removal and amount adsorbed (in mgg $^{-1}$) by CAC and various indigenously prepared ACs such as LPC,MPC). The experiments were performed at 35 ±1^{o} C , with a fixed dose of adsorbent at constant contact time (40 min.) and particle size (90µ) at the pH of the solution itself [25] by varying the initial concentration (C_o) of dye (range of C_o , in ppm). The values of percentage removal of dye, initial concentration ($C_o$in ppm) and the equilibrium concentration (C_e in ppm) of dye for the adsorption of dye by CAC and various indigenously prepared ACs are given in Tables-4.1.

TABLE 4.1 a–: Effect of initial concentration of on the percentage removal and the amount adsorbed AY dye by adsorption on ACs at 35 ± 1 °C

Temperature : 35^{o}C Contact Time : 40 min

Dose of adsorbent : 20 g L^{-1} pH : 7.2

Conc. (ppm)	CAC		Conc. (ppm)	LBC		MPC	
	% removal	Amount adsorbed		% removal	Amount adsorbed	% removal	Amount adsorbed
48	99.16	2.38	48	94.58	2.27	92.91	2.21
50	98.42	2.46	50	93.80	2.34	92.00	2.30
52	97.88	2.54	52	93.07	2.42	91.73	2.38
54	97.03	2.62	54	92.77	2.50	90.92	2.45
56	96.03	2.70	56	91.96	2.57	89.82	2.51
58	95.86	2.78	58	90.68	2.63	88.62	2.57
60	94.83	2.84	60	89.83	2.69	87.83	2.63
62	93.87	2.91	62	88.87	2.75	87.09	2.70

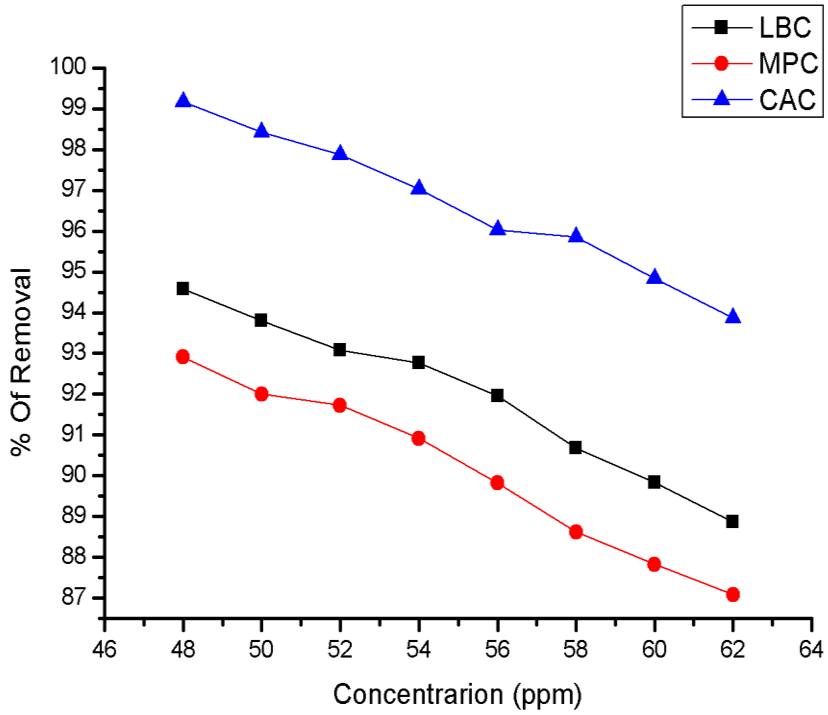


Fig-4a-The Effect of Concentration removal of AY on IPACs

The values of amount of dye adsorbed (q in mgg^{-1}) in the case of all the dye-AC systems were found to increase with the increase in initial concentration of dye. The percentage removal of dye decreases with the increase in initial concentration of dye. The plots of percentage removal of dye as a function of initial concentration of AY are given in Figures-4a respectively. The decrease in the percentage removal of dye (or increase in the amount of adsorbed) with the increase in the initial concentration of dye, may be due to the reduction in the immediate solute / adsorbate (dye), adsorption owing to the lack of available active sites on the surface of the adsorbent (AC), compared to the relatively large number of active sites required for the high initial concentration of dye. This is probably be due to the formation of unimolecular layer with a thickness of a layer which is only one molecule [110] thick on the surface of the adsorbents (ACs), at low initial concentration of dye, any further formation of layers of dye molecules (i.e., multilayers) on the surface of the adsorbent is highly hindered at the high initial concentration of dye, due to the repulsive interaction (forces) between the adsorbate species (dye molecules) on the surface of the adsorbent and the dye species in the bulk of the solution.

The Effect of Contact Time:

In the adsorption system, contact time plays a vital role, irrespective of the other experimental parameters affecting the adsorption kinetics. In order to study the kinetics / dynamics of adsorption of dye on CAC and various other indigenously prepared ACs and to find out the effect of contact time on the extent of the removal of dyes, the batch adsorption experiments were carried out at the optimum initial concentration of dye (Table – 4.1), with a fixed dose of adsorbent (ACs = gL^{-1}; Dose of CAC (in gL^{-1}) for dyes : AY) and particle size (90µ) at 35±1^{o} C and at the solution pH itself [109] by varying the contact time (range : 5-40 min.). The effect of contact time on the amount of dye adsorbed for different dye by various adsorbents (ACs) are presented in Tables 4.2a.

The extent of removal of dye (both in terms of % removal and q) by these ACs increases exponentially with the increase in contact time for all the dye. The representative plots are shown in Figures-4b as percentage removal of AY respectively as a function of contact time. The extent of removal of dye (both in terms of % removal and q) increases exponentially with the increase in contact time and then levels off at a particular contact time, which is fixed as optimum contact time. A decrease in the extent of removal of dye is noted in some cases, after the optimum contact time, which may be due to ‘desorption process’.The relative increase in the extent of removal of dyes by ACs is found to be substantially low after 40 min. of contact time in all the cases, which is fixed as the optimum contact time.

Table 4.2 a -:Effect of contact time on the percentage removal and the amount adsorbed AY dye by adsorption on ACs at 35± 1°C

Particle size : 90µ Concentration : 54 ppm for LBC

Dose of adsorbent : 20g L^{-1} 52 ppm for MPC

pH : 7.2 54 ppm for CAC

Temperature :35^{o}C

Contact time (min.)	**CAC**		**LBC**		**MPC**	
	% removal	**Amount adsorbed**	**% removal**	**Amount adsorbed**	**% removal**	**Amount adsorbed**
5	90.74	2.45	86.85	2.34	85.96	2.23
10	91.85	2.48	87.77	2.37	86.92	2.26
15	92.77	2.50	88.70	2.39	87.88	2.28
20	93.70	2.53	89.25	2.41	88.46	2.30
25	94.44	2.55	89.81	2.42	89.03	2.31
30	95.18	2.57	90.92	2.45	89.80	2.33
35	95.72	2.59	91.66	2.47	90.57	2.35
40	96.85	2.65	92.03	2.48	91.11	2.37

The rate of removal of dye (AY) on various ACs is rapid at the initial period of contact time, becomes slow, stagnates and then decreases with the increase in contact time. This indicates that the rate of removal of dye is higher only during the initial periods of contact time, owing to the greater availability of adequate active sites on the surface of the adsorbent (AC). The lower rate of adsorption of dye at the latter periods of contact time (with the increase in contact time) may be due to the decrease in the availability of the effective surface area and active sites for the adsorption of dye, owing to the increase in the surface coverage by the dye molecules (adsorbates) by adsorption on the surface of the adsorbent (AC).

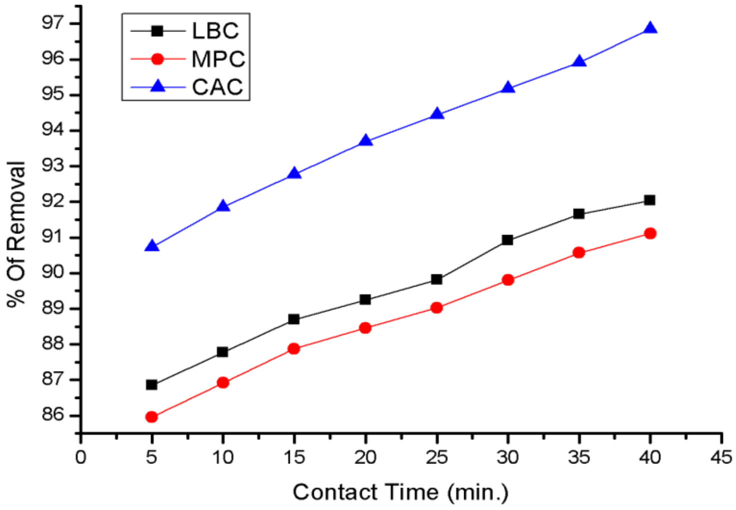


Fig -4b-The Effect of Contact time removal of AY on IPACs

The Effect of Dose Of Adsorbent:

The experiments for the removal of dyes by adsorption on CAC and various indigenously prepared ACs (viz.CAC, LBC, and MPC) with different doses of adsorbent (Dose of CAC (in g L^{-1}) dose of ACs = 4.0 – 32.0 gL^{-1}) at the optimum initial concentration (C_o) of dye (Table 4.3) and 40 min. of contact time and 90µ particle size at solution pH itself were carried out at 35±1°C. The results obtained on the extent of removal of dye by CAC and various other indigenously prepared ACs are presented in Tables 4.3 a and in Figures-4c.

The values of percentage removal of dyes by adsorption onto various ACs are found to increase exponentially with the increase in dose of the adsorbent and then level-off at higher doses of adsorbents (ACs). As the dose of adsorbent (AC) increases, the surface area proportionally increases (as the particle size of AC remains almost constant; 90µ), which has resulted in an increase in the percentage removal of dye, owing to greater availability of surface active sites. The increase in the extent of removal of dye in terms of percentage removal is thus probably be due to the increase in the availability of surface active sites, due to the increase in the effective surface area resulting.

Table-4.3-:Effect of Dose of adsorbent on the percentage removal and the amount adsorbed AY dye by adsorption on ACs at 35± 1 °C

Particle size : 90µ Concentration : 54 ppm for LBC

Contact time :40 min. 52 ppm for MPC

pH : 7.2 54 ppm for CAC

Temperature :35°C

Amount of adsorbent (gm)	**CAC**		**LBC**		**MPC**	
	% removal	**Amount adsorbed**	**% removal**	**Amount adsorbed**	**% removal**	**Amount adsorbed**
0.2	94.44	2.55	89.81	2.42	89.42	2.32
0.4	95.18	2.57	90.74	2.45	90.00	2.34
0.6	95.92	2.59	91.66	2.47	90.96	2.36
0.8	96.66	2.61	92.03	2.48	91.34	2.37
1.0	97.22	2.63	92.59	2.50	92.30	2.40
1.2	98.14	2.65	93.14	2.51	93.26	2.42
1.4	98.70	2.66	94.25	2.54	94.03	2.44
1.6	99.07	2.67	95.18	2.57	95.00	2.47

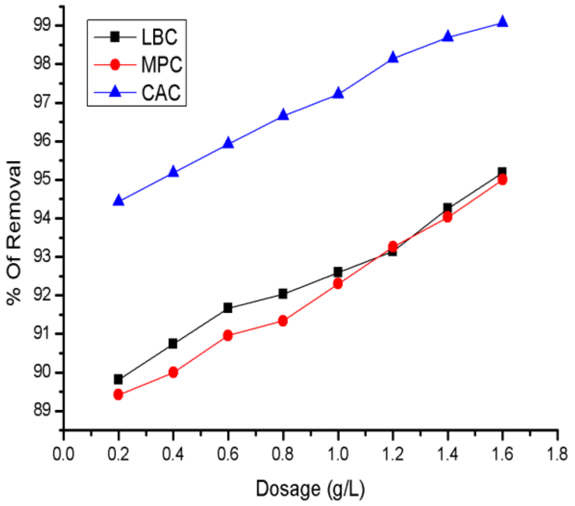


Fig-4c-The Effect of Dose of adsorbent removal of AY on IPACs

These results are found to be in harmony with the available reports in literature on the study of the effect of dose of various adsorbents on the removal of dye by adsorption[26,27]. Similar results on the effect of dose of adsorbent have also been reported in literature based on the studies on the removal of metal ions[28,29] by various adsorbents.

The extent of removal of dye is found to be insignificant beyond a dose 1gL^{-1} for various indigenously prepared ACs, which is fixed as the optimum dose of adsorbent (AC) (for CAC, the optimum dose (in gL^{-1})). The values of amount of dye adsorbed are found to vary exponentially with the fractional power term of the dose of adsorbent [30] according to the following model (eqn. 3.1)

q_e = [dose]$^{-n}$ + C' .... (3.1)

On taking logarithm, the above equation (eqn.3.1) becomes eqn. 3.2

Log q_e = -n log [dose] + C .... (3.2)

The Effect of Temperature:

Low Temperature favors adsorption studies. Temperature increases rate of adsorption process decreases because of due to **desorption**.

Table 4.4-:Effect of Temperature on the percentage removal and the amount adsorbed dye AY by adsorption on ACs at 35± 1 °C

Particle size : 90µ Concentration : 54 ppm for LBC

Dose of adsorbent : 20g L^{-1} 52 ppm for MPC

pH : 7.2 54 ppm for CAC

Contact time : 40 min.

Temp. (ºC)	**CAC**		**LBC**		**MPC**	
	% removal	**Amount adsorbed**	**% removal**	**Amount adsorbed**	**% removal**	**Amount adsorbed**
35	96.29	2.60	91.11	2.46	90.76	2.36
40	95.55	2.58	89.81	2.42	88.65	2.30
45	94.62	2.55	87.59	2.36	86.92	2.26
50	93.88	2.53	86.29	2.33	85.76	2.23

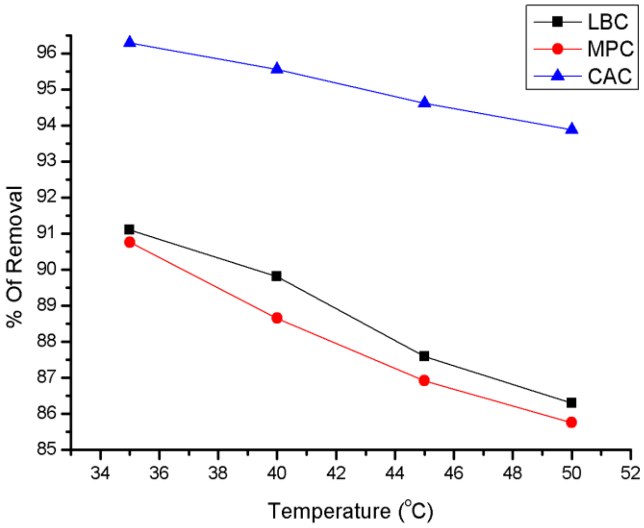


Fig -4d-Temperature Variation removal of AY on IPACs

The Effect of pH:

The dye adsorption has been reported to be significantly affected by the variation of solution pH[31,32]. The effect of pH on the adsorption process of dyes by ACs was studied (Table-4.5) at different pH values (range:2 – 10), at the constant optimum experimental conditions of initial concentration (C_i), conduct time, dose of adsorbent and particle size at 35± 1^o C. The experimental results indicate that the adsorption of dye is highly pH sensitive and the adsorption behavior is different for acidic, neutral and basic dyes. The extent of removal of dye increases with the increase in pH value in the dyes (AY). The observed results are noted to be similar to that found in literature[33,34] especially for the removal of dye [35,36.]by various adsorbents.

Table 4.5 -: Effect of pH variation on the extent of removal of dye by adsorption on ACs at 35± 1° C

Initial Conc. = Optimum Dose : ACs = 20 gL^{-1}

Particle size = 90µ Contact time = 40 min.

pH range = 2 – 10

AC	Extent of removal*	AY
CAC	Q	2.60
	%R	96.48
LBC	Q	2.44
	%R	90.37
MPC	Q	2.33
	%R	89.80

*q = amount adsorbed (in mg g^{-1}); %R = % removal.

The max-min values of q and % removal are given.

To sum up the extent of removal of dye :

Increases with the increase in pH in the case of AY(Basic dyes).

Adsorption Isotherms

The applicability of adsorption isotherm has been of importance and significance in water and wastewater treatment process employing the batch adsorption technique, as it provides an approximate estimate of the monolayer / saturation adsorption capacity of the various adsorbents [37].The equilibrium adsorption data (Table-5.1a)obtained in the batch type adsorption experiments carried out at 35^o C, to study the effect of initial concentration of dyes on the extent of removal of dyes by adsorption on CAC and ACs were employed to test the applicability of the adsorption isotherms like Freundlich, Langmuir and Temkin isotherms [38,39].

Freundlich Isotherm:

Freundlich isotherm [40,41] – as cited by Freundlich [42], Giles and his co-workers [43], Adamson [44], Barrow [45], , Gupta et al.[46],[47] and Allen et al.[48], has been a special case of heterogeneous surface energies and it could easily be extended to the present case. Freundlich isotherm incorporating all the factors affecting the adsorption process may be represented as:

$$(X / m) = q_e = K C_e^{1/n} \qquad \ldots\ldots\ldots\ldots\ldots(3.3)$$

which may also be expressed by the linearised logarithmic relationship as :

$$\text{Log } q_e = \log K + (1/n) \log C_e \qquad \ldots\ldots\ldots\ldots\ (3.4)$$

Where,

q_e = amount of dye adsorbed at equilibrium, in mg g^{-1}

X = extent of dye adsorbed (in ppm); X = (C_o – C_e)

m = mass of adsorbent, in gL^{-1}

C_o= initial concentration of dye, in ppm

C_e = dye concentration in solution at equilibrium, in mg L^{-1}

K = Freundlich constant, a measure of adsorption capacity and

1/n = Freundlich constant, a measure of adsorption intensity

to Adamson [49] and Barrow [50]the value of 1/n in the Freudlich adsorption isotherm equations (eqns3.3&3.4) should be a fraction or less than unity $[0 < (1/n) < 1]$ and hence the order of adsorption (n) is greater than unity(n >1).The adsorption data were fitted with the linearised Freundlich adsorption isotherm equation. The plots of log q_e vs log C_e are found to be linear in all the cases. Freundlich isotherm plots for AY respectively shown in Figures-5a.

The values of K (given as log K) and 1/n of the linearised Freundlich isotherm give an idea about the adsorption capacity and intensity of adsorption, respectively. The magnitude of K represents adsorption capacity (in mgg^{-1}) of the various adsorbents. The adsorption capacity of adsorbent depends on the nature of the adsorbent material and the adsorbate (dye). CAC and LBC show maximum adsorption capacity for AY. The Log K values give an idea about the adsorption capacity.The increasing order of adsorption capacity of ACs for any given dye is:

MPC < LBC< CAC

The observed values of 1/n for the dye indicate an adsorption mechanism with an intra-particle diffusion or mass transfer as the rate limiting step as suggested by Weber and Morris [51].

TABLE:5.1a.Freundlich Adsorption Isotherm for the removal of AY:

Conc. (ppm)	CAC			Conc. (ppm)	LBC			MPC		
	C_e	LogC_e	Logq_e		C_e	LogC_e	Logq_e	C_e	LogC_e	Logq_e
48	0.4	-0.39	0.37	48	2.6	0.41	0.35	3.4	0.53	0.34
50	0.8	-0.09	0.39	50	3.1	0.49	0.36	4.0	0.60	0.36
52	1.1	0.04	0.40	52	3.6	0.55	0.38	4.3	0.63	0.37
54	1.6	0.20	0.41	54	3.9	0.59	0.39	4.9	0.69	0.39
56	2.0	0.30	0.43	56	4.5	0.65	0.40	5.7	0.75	0.40
58	2.4	0.38	0.44	58	5.4	0.73	0.41	6.6	0.81	0.40
60	3.1	0.49	0.45	60	6.1	0.78	0.42	7.3	0.86	0.42
62	3.8	0.57	0.46	62	6.9	0.83	0.43	8.0	0.90	0.43

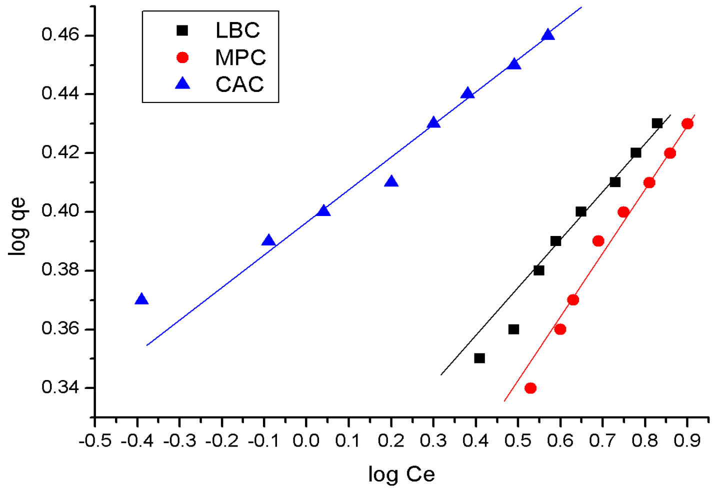


Fig-5a-Freundlich isotherms for the removal of AY on IPACs

Langmuir Isotherm:

Langmuir isotherm [52-54] is valid for monolayer adsorption of adsorbates (dye) onto an adsorbent (AC) surface containing a finite number of identical active sites. This also assumes uniform energies of adsorption onto the surface and nontrans-migration of the adsorbate species in the plane of adsorbent surface.Langmuir isotherm is applicable to a wide range of initial concentration of adsorbates, however Freundlich isotherm is applicable only to a limited range of initial concentration.The distribution of dye between solid-liquid (solution) interface at equilibrium has been described by Langmuir [55-57] in the form of Langmuir isotherm as follows:

$(C_e/q_e) = (1 / ab) + (C_e / a)$ ……….. (3.5)

Where,

C_e = dye concentration in solution at equilibrium, in mgL^{-1}

q_e = amount of dye adsorbed on solid phase at equilibrium, in $mg\ g^{-1}$

a =Langmuir constant related to the saturation / monolayer adsorption capacity, in $mg\ g^{-1}$ and

b = Langmuir constant related to the energy of adsorption, in $l\ mg^{-1}$

The plots of (C_e/q_e) versus C_e are found to be linear for all the adsorbent-adsorbate systems. Typical liner plots of Langmuir isotherms are shown in Figures-5b, respectively for the adsorption of various dyes viz, AY on CAC and indigenously prepared ACs. The values of (C_e / q_e) are linearly correlated with q_e values for all the adsorbent-adsorbate systems The computed correlation coefficients (r – values) are found to be the applicability of Langmuir isotherm model indicates the formation of monolayer coverage of adsorbate (dye) on the surface of the adsorbent –AC [58-60]. The adsorption capacity (for monolayer coverage) depends on the nature of the adsorbate and adsorbent. Among the indigenously prepared ACs, AY dye has the higher adsorption capacity for monolayer coverage of dye. The increasing order of adsorption capacity of various ACs for dye, as given by the a values is : MPC < LBC < CAC

Further, the essential characteristics of the Langmuir isotherm is expressed in terms of equilibrium parameter (R_L), which is also termed as a dimensionless separation factor[61]. According to Hall et al. (1986), the equilibrium parameter, R_L, is defined by the equation:

$R_L = 1 / (1 + b\ C_i)$ ………………. (3.6)

Where, b = Langmuir constant related to energy of adsorption, in $l\ mg^{-1}$

C_i = optimum (fluid phase) initial concentration of dye, in mgL^{-1} (or in ppm)

It may be of interest to note that, the value of separation factor, R_L indicates the shape of isotherm and the nature of the adsorption process [145,146] as :

Separation factor (R_L)	Nature of adsorption and shape of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

TABLE: 5.1bLangmuir Adsorption isotherm for the removal of AY:

Conc. (ppm)	CAC			Conc. (ppm)	LBC			MPC		
	C_e		C_e/q_e		C_e		C_e/q_e	C_e		C_e/q_e
48	0.4		0.16	48	2.6		1.14	3.4		1.53
50	0.8		0.32	50	3.1		1.32	4.0		1.73
52	1.1		0.43	52	3.6		1.48	4.3		1.79
54	1.6		0.61	54	3.9		1.56	4.9		2.04
56	2.0		0.74	56	4.5		1.75	5.7		2.26
58	2.4		0.86	58	5.4		2.05	6.6		2.56
60	3.1		1.08	60	6.1		2.26	7.3		2.76
62	3.8		1.30	62	6.9		2.50	8.0		2.96

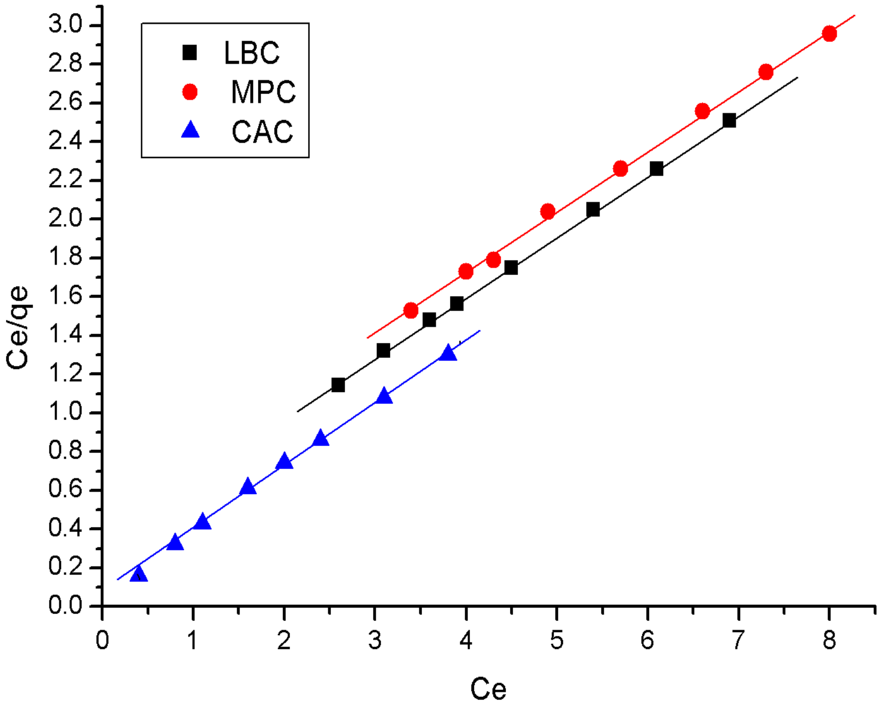


Fig-5b-Langmuir Isotherm for the removal of AY on IPACs

Temkin Isotherm

TABLE : 5.1c.Temkin Adsorption Isotherm for the removal of AY:

Conc. (ppm)	CAC			Conc. (ppm)	LBC			MPC		
	C_e	$LogC_e$	q_e		C_e	$LogC_e$	q_e	C_e	$LogC_e$	q_e
48	0.4	-0.39	2.38	48	2.6	0.41	2.27	3.4	0.53	2.21
50	0.8	-0.09	2.46	50	3.1	0.49	2.34	4.0	0.60	2.30
52	1.1	0.04	2.55	52	3.6	0.55	2.42	4.3	0.63	2.39
54	1.6	0.20	2.62	54	3.9	0.59	2.50	4.9	0.69	2.46
56	2.0	0.30	2.70	56	4.5	0.65	2.57	5.7	0.75	2.52
58	2.4	0.38	2.78	58	5.4	0.73	2.63	6.6	0.81	2.57
60	3.1	0.49	2.85	60	6.1	0.78	2.69	7.3	0.86	2.64
62	3.8	0.57	2.91	62	6.9	0.83	2.75	8.0	0.90	2.70

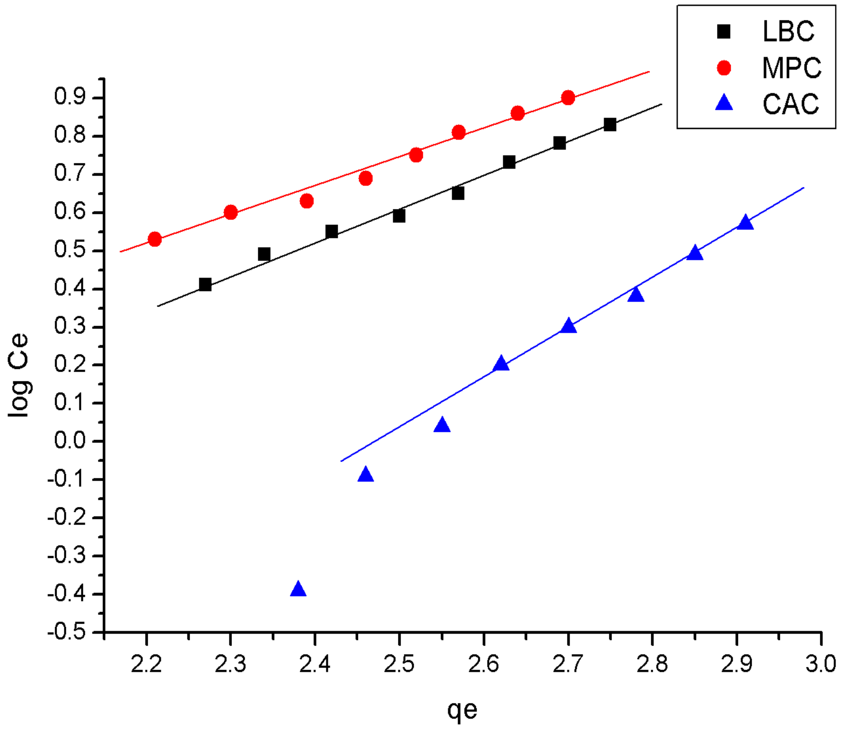


Fig-5c-Timken Isotherm for the removal of AY on IPACs

KINETICS OF ADSORPTION: The adsorption data obtained from the batch type adsorption experiments to study the effect of contact time were used to test the following kinetic equations/models.

GENERALISED FIRST ORDER KINETIC EQUATION:

The kinetics of adsorption process was studied by using the following generalized first order kinetic equation, proposed by Annadurai and Krishnan [62,] :

$(1 / q_t) = (k / q_{max}) (1 / t) + (1/ q_{max})$……………………….(3.7)

where, q_{max} = the maximum adsorption capacity (in mg g^{-1})

q_t = amount adsorbed at time, t (in mg g^{-1})

t = time (in min) and

k = first order rate constant for adsorption, (in min^{-1})

The plots of q_t versus time were found to be exponential, while the plots of $(1/q_t)$ against (1/t) were found to be linear.

Natarajan and Khalaf eqn: -

$\text{Log} (C_i / C_t) = (k / 2.303) t$……………………..(3.8)

Lagergren eqn:-

$\text{Log} (q_e /q_t) = \log q_e - (k_{ad} / 2.303)t$…………..(3.9)

Elovichequation:

$(dqt/ dt) = a \exp(-bqt)$……………………..(4.0) where, C_i = initial concentration of dye, in mg L^{-1}

C_t = concentration of dye at time, ‘t’, in mg L^{-1}

q_e = amount of dye adsorbed (in mgg^{-1}) at equilibrium time

q_t = amount of dye adsorbed (in mgg^{-1}) at time ‘t’

t = contact time, ‘t’, in min

k and k_{ad} = first order rate constant for adsorption, in min $^{-1}$

Plots of log (C_i/C_t) against time were found to be linear for all the adsorbent – adsorbate systems studied. The values of rate constant (k) are computed from the linear regression analysis of values of log (C_i/C_t) with time and presented in Table. In all the adsorbent-adsorbate systems indicate the applicability of Natarajan and Khalaf equation (eqn. 3.8) and also the first order nature of adsorption kinetics of dyes by CAC and ACs. Plots of log [q_e/q_t] versus time (t) are found to be linear. Lagergren plots are shown in Figures 6.1b respectively for the dyes AY.The values of q_t are plotted against time Ln (T) for the adsorption of dyes on the various adsorbents (ACs). Elovich plots are shown in Figures 6.1c respectively for AY. Reports are also available in literature regarding the applicability of all these kinetic equations in various adsorption studies.

TABLE :6.1a)Natarajan & Khalaf equations used for the removal of AY dye

Time (min)	**CAC**			**LBC**			**MPC**		
	Ce	**Co/Ce**	**Log Co/Ce**	**Ce**	**Co/Ce**	**Log Co/Ce**	**Ce**	**Co/Ce**	**Log Co/Ce**
5	5.0	10.8	1.03	7.1	7.60	0.88	7.3	7.12	0.85
10	4.4	12.27	1.08	6.6	8.18	0.91	6.8	7.64	0.88
15	3.9	13.84	1.14	6.1	8.85	0.94	6.3	8.25	0.91
20	3.4	15.88	1.20	5.8	9.31	0.96	6.0	8.66	0.93
25	3.0	18.00	1.25	5.5	9.81	0.99	5.7	9.12	0.95
30	2.6	20.76	1.31	4.9	11.02	1.04	5.3	9.18	0.99
35	2.2	24.54	1.38	4.5	12.00	1.07	4.9	10.61	1.02
40	1.7	31.76	1.50	4.3	12.55	1.09	4.6	11.30	1.05

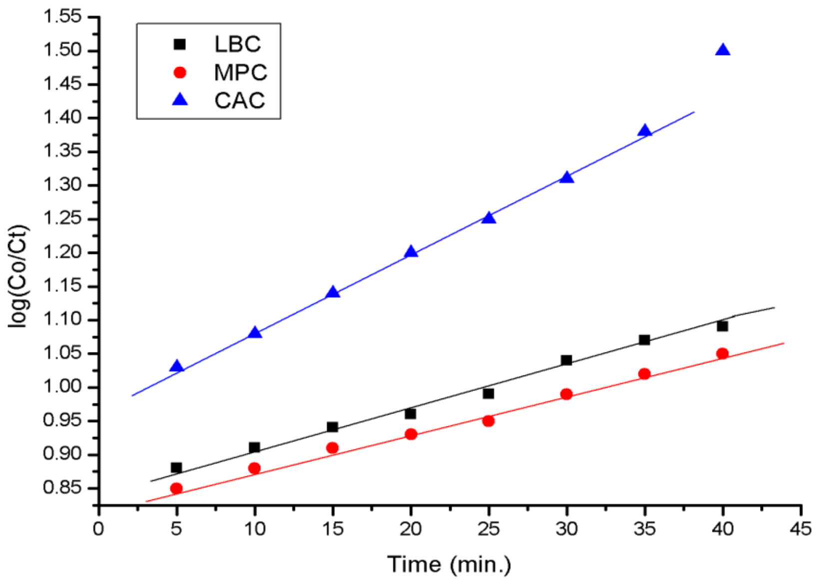


Fig-6a-Natarajan and Khalaf kinetic plot for the removal of AY on IPACs

TABLE: 6.1b. Lagergran equations used for the removal of AY dye:

Time (min)	**CAC**			**LBC**			**MPC**		
	q_t	**q_e/q_t**	**Log (q_e/q_t)**	**q_t**	**q_e/q_t**	**Log (q_e/q_t)**	**q_t**	**q_e/q_t**	**Log (q_e/q_t)**
5	2.45	1.06	0.0028	2.34	1.05	0.025	2.23	1.06	0.025
10	2.48	1.05	0.022	2.37	1.04	0.020	2.26	1.04	0.020
15	2.50	1.04	0.018	2.39	1.03	0.015	2.28	1.03	0.015
20	2.53	1.03	0.014	2.41	1.03	0.013	2.30	1.03	0.013
25	2.55	0.02	0.010	2.42	1.02	0.010	2.31	1.02	0.010
30	2.57	1.01	0.007	2.45	1.01	0.005	2.33	1.01	0.006
35	2.59	1.00	0.003	2.47	1.00	0.001	2.35	1.00	0.002

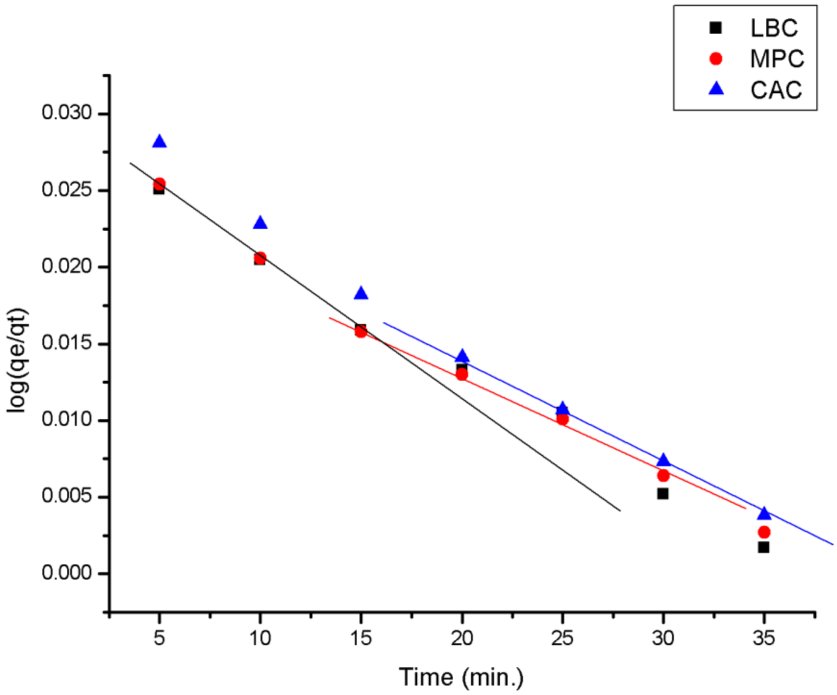


Fig-6b-Lagergran kinetic plot for the removal of AY on IPACs

TABLE:6.1c Elovich equations used for the removal of AYdye

Contact time (min.)	**CAC**		**LBC**		**MPC**	
	ln T	**q_t**	**ln T**	**q_t**	**ln T**	**q_t**
5	1.60	2.45	1.60	2.35	1.60	2.23
10	2.30	2.48	2.30	2.37	2.30	2.26
15	2.70	2.51	2.70	2.39	2.70	2.28
20	2.99	2.53	2.99	2.41	2.99	2.30
25	3.21	2.55	3.21	2.42	3.21	2.31
30	3.40	2.57	3.40	2.45	3.40	2.33
35	3.55	2.59	3.55	2.47	3.55	2.35
40	3.68	2.62	3.68	2.48	3.68	2.37

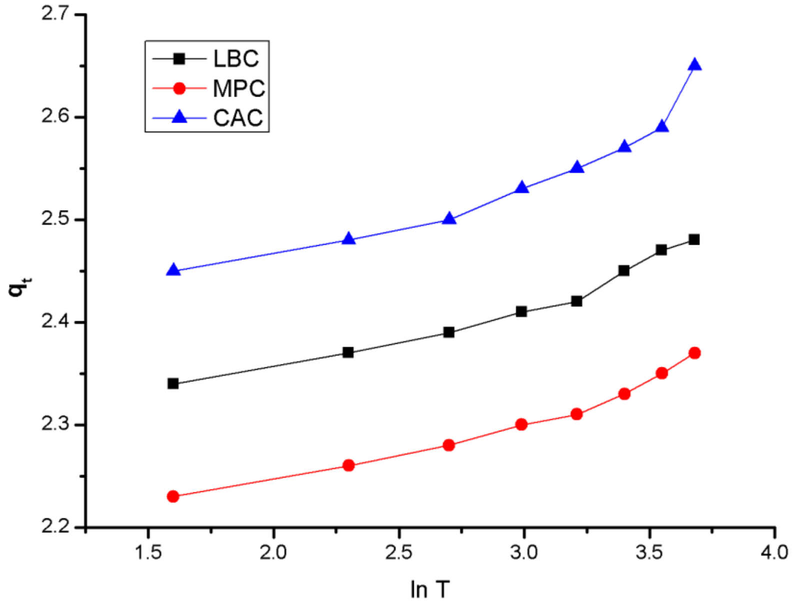


Fig-6c-Modified Elovich kinetic plot for the removal of AY on IPACs

TABLE:6.1d.Pseudo first order equations used for the removal of AY dye

Time (min)	**CAC**			**LBC**			**MPC**		
	q_t	**$q_e - q_t$**	**Ln (q_e-q_t)**	**q_t**	**q_e-q_t**	**Ln (q_e-q_t)**	**q_t**	**$q_e - q_t$**	**Ln (q_e-q_t)**
5	2.45	0.16	-1.80	2.34	0.14	-1.96	2.23	0.13	-2.00
10	2.48	0.13	-2.00	2.37	0.11	-2.16	2.26	0.11	-2.20
15	2.50	0.11	-2.20	2.39	0.09	-2.40	2.28	0.08	-2.46
20	2.53	0.08	-2.46	2.41	0.07	-2.59	2.30	0.07	-2.65
25	2.55	0.06	-2.73	2.42	0.06	-2.81	2.31	0.05	-2.90
30	2.57	0.04	-3.10	2.45	0.03	-3.50	2.33	0.03	-3.35
35	2.59	0.02	-3.68	2.47	0.01	-4.60	2.35	0.01	-4.19

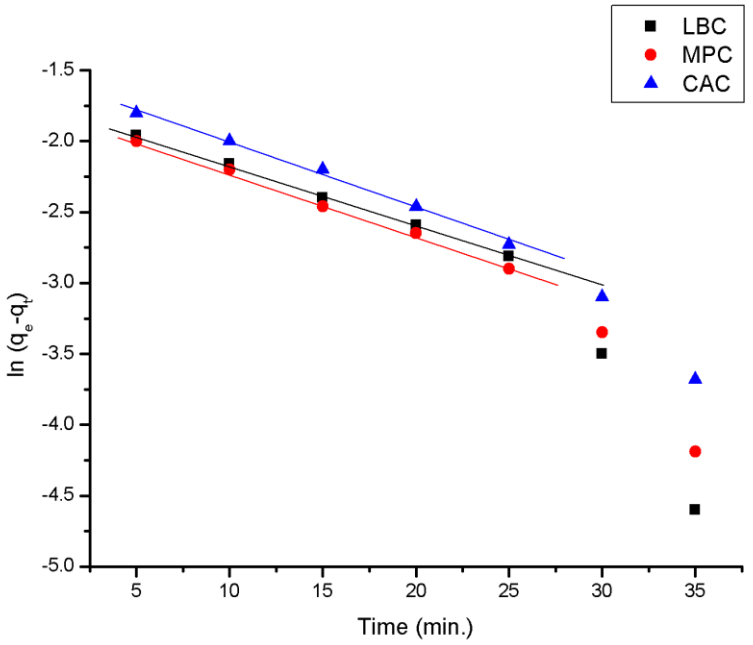


Fig-6d.Pseudo first order kinetic plot for the removal of AY on IPACs

RESULTS

ACs have been indigenously prepared from agricultural wastes like Lima Beans and Musa Paradisiac. CAC and indigenously prepared ACs have been used for adsorption of AY dyes. Studies on the physio-chemical, textural, spectral and thermal degradation characteristics of AC and dye-AC samples have been determined. The preliminary studies on the removal of dye by adsorption on ACs revealed that these ACs could be used as alternate adsorbent for CAC. The ACs and dye loaded ACs are found to be thermally stable and hence dye could not be desorbed thermally. The dyes are strongly bonded to ACs, probably by chemisorption. The increasing order of the adsorption capacity of ACs is :

The increasing order of the extent of removal of dye by any one of the ACs is :-

MPC < LBC < CAC

The percentage removal of dye by adsorption on ACs increased with the decrease in initial concentration of dye, in temperature increases, particle size and increased with increase in contact time and dose of adsorbent. The increase in pH increases the extent of removal of basic dyes (AY) and the increase in pH decreases. SC possess the maximum adsorption potential for dye among the indigenously prepared ACs.The adsorption process followed first order kinetics with intra-particle diffusion as one of the rate determining steps. Freundlich, Laugmuir, and Temkin isotherms are found to be applicable for the adsorption of dye on ACs. The adsorption data were modelled with kinetic equations such as generalized Pseudo first order, Natarajan and Khalaf, Lagergren and Elovich equations. Equilibrium studies have been made to calculate the thermodynamics parameters. The adsorption process is found to be spontaneous, endothermic and the randomness increases at solid / liquid interface. The extent of desorption is noted to be very less in all the cases indicating that the dye undergo chemisorption on ACs with a strong binding. The results of the study will be highly useful in designing water and wastewater treatment plant for the efficient and economic removal of dye by adsorption on indigenously prepared ACs. Indigenously prepared ACs could be used as low-cost adsorbents as alternates to CAC for the removal of pollutants, in general and dye/colour, in particular

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