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Adsorption kinetics and dynamics of Brilliant Green dye on various low cost adsorbents: A comparative study

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ABSTRACT

In the present investigation shows the adsorption kinetics and dynamics for the removal of Brilliant Green (BG) dye on various low cost adsorbents derived from agricultural waste by bath experiment. Various experimental process parameters such as effect of initial concentration, contact time, dose of the adsorbents, pH of the solution and particles size of the adsorbents. Langmuir and Freundlich isotherm models indicate that the adsorption coverage is monolayer. Various kinetics models were also studied and the system obeyed first order kinetic model. The adsorption capacity of the various adsorbents is CAC>LPC>TSC>DSC>PSC. From the results of the present study it is concluded that the maximum percentage removal of BG dye is possible with low-cost adsorbents like LPC,TSC,DSC and PSC which are better alternate to CAC.

Keywords: Low cost adsorbents; Adsorption; Brilliant Green Dye, Adsorption Isotherms.

INTRODUCTION

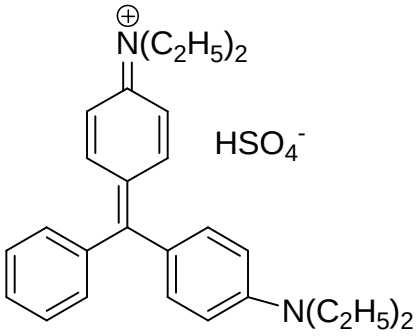
Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid [1,2]. Untreated disposal of this colored water into the receiving water body either causes damage to aquatic life or to human beings by their mutagenic and carcinogenic effect. As a matter of fact, the discharge of such effluents is worrying for both toxicological and environmental reasons [3,4].

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods, such as coagulation and flocculation, adsorption, ozonation, electrochemical techniques, and fungal decolorization [5,6]. Among these methods adsorption has gained favour in recent years due to proven efficiency in the removal of pollutants from effluents. Activated carbon, as an adsorbent has been widely investigated for the adsorption of dyes, but its high cost limits its commercial application. Studies indicated that many materials, such as chitosan, bagasse pith, peanut hull, peat, rice husk, fly ash, wood sawdust, natural clays such as sepiolite, zeolite, diatomite and hydrotalcite were used as adsorbents which could effectively remove the dyes from wastewaters [7-10].

In the present studies shows that the comparative studies of various adsorbents derived from agricultural waste on the removal of BG dye.

EXPERIMENTAL SECTION

The adsorbent materials are collected locally from shop and agricultural waste Sivakasi, Tamil Nadu, India. Brilliant Green (BG) dye (λ_{max} =628 nm) obtained from Merck used without any purification. The structure of BG dye is shown in Scheme.1. All the other chemicals are analytical grade used as received.



Scheme 1. Structure of BG

RESULTS AND DISCUSSION

3.1. Effect of change of initial concentration

The studies on the removal of dye by various low-cost adsorbents were carried out at different initial concentrations of dye (200-400ppm for LPC, 100-250 ppm for TSC, 75-225 ppm for DSC, and 40-180 ppm for PSC) at fixed dose of adsorbent ($2gL^{-1}$ for CAC, $20gL^{-1}$ for IPACs), particle size (90 min), contact time (30 min), agitation speed (200rpm) and pH (5.3). The data obtained are tabulated in Table.1.

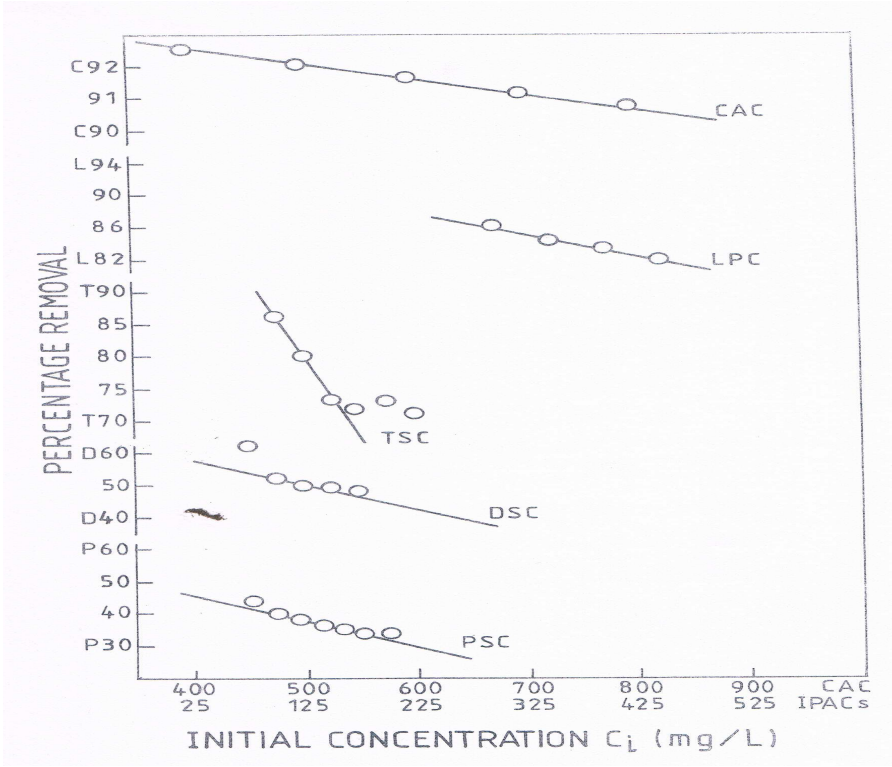


Figure 1. Effect of initial concentration of Brilliant Green on various low-cost adsorbents

The effect of initial concentration of Brilliant Green dye and the percentage removal of dye by various adsorbents are presented in Figure1.

The increase in the initial concentration of dye decreases exponentially with the extent of percentage removal of the dye. This indicates that there exists a reduction in immediate solute adsorption owing to the lack of available active sites required for the high initial concentration of dye. Similar results have been reported in literature [11,12].

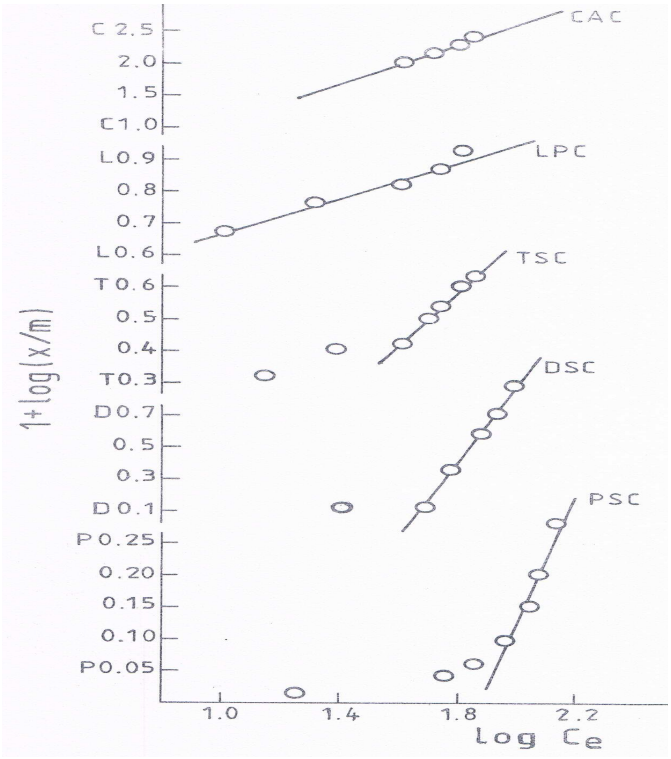
At an optimum initial concentration of dye (400 ppm for CAC, 300ppm for LPC, 125ppm for TSC, 75ppm for DSC and 60ppm for PSC), the maximum percentage removal was found. This may be due to maximum available active

sites. The experimental values indicate that the rate of removal of dye decreases with increase in initial concentration of dye and vice versa. This is due to the fact that after the formation of mono ionic layer at lower concentration over the adsorption surface, any further formation of layer is highly hindered. This is due to the interaction between dye in the surface and in the bulk of the solution.

Table 1. Effect of initial concentration of Brilliant Green on various low-cost adsorbents

Contact time: 30 min;
Particle size : 90 mic.
pH: 5.3
Dose CAC : 2gL^{-1}
IPACS 20gL^{-1}

Initial Concentration (ppm)					% Removal				
CAC	**LPC**	**TSC**	**DSC**	**PSC**	**CAC**	**LPC**	**TSC**	**DSC**	**PSC**
400	200	100	75	40	92.5	94	86.0	62.66	97.5
500	250	125	100	60	92.0	92.0	80.8	52.00	68.33
600	300	150	125	80	91.6	86.66	73.33	49.33	40.0
700	350	175	150	100	91.14	84.66	72.57	51.42	44
800	400	200	175	120	90.75	84.57	73.0	54.00	38.33
	450	225	200	140		84.5	71.55		36.42
		250	225	160		85.33	73.6		35.62
				180					35.55



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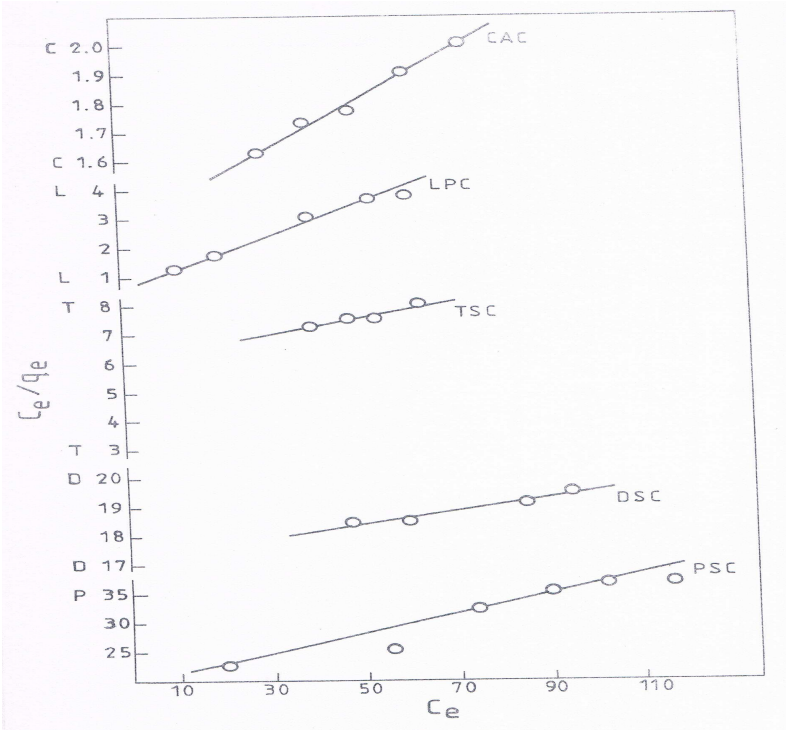


Figure 2. Freundlich (A) and Langmuir (B) Isotherms

The results of correlation analysis of adsorption isotherms for the removal of dye by adsorption on various adsorbents and the value of Q_0, b and RL are given in Table 4. The statistical analysis of data reveals that both the isotherms are applicable and the correlations are statistically significant. Further, the essential characteristic of the Langmuir isotherm and the feasibility of the process is expressed in terms of the dimensionless constant described by the separation factor [14].

The separation factor or equilibrium parameter RL which is defined by the equation RL=1/1+bCi, Where b is the Langmuir constant and C_i is the initial concentration of Brilliant Green.

Table – 2.Effect of initial concentration of Brilliant Green dye on various low-cost adsorbents

Contact time : 30 min
Particle size : 90 mic.
pH : 5.3
Dose CAC : 2gL^{-1}
IPACS : 20gL^{-1}

Initial Concentration					Logx/m				
CAC	**LPC**	**TSC**	**DSC**	**PSC**	**CAC**	**LPC**	**TSC**	**DSC**	**PSC**
400	200	100	75	40	1.9661	0.6721	0.3325	0.0701	1.6812
500	250	125	100	60	2.0606	0.7597	0.4023	0.1140	1.7481
600	300	150	125	80	2.1538	0.8130	0.4394	0.3522	1.8692
700	350	175	150	100	2.2027	0.8693	0.5018	0.5798	1.9493
800	400	200	175	120	2.2588	0.9269	0.5623	0.7251	2.0128
	450	225	200	140		0.9821	0.6048	0.8389	2.0644

Table – 3. Effect of initial concentration of Brilliant Green dye on various low-cost adsorbents

Contact time: 30 min
Particle size: 90 mic.
pH: 5.3
Dose CAC : 2gL^{-1}
IPACS: 20gL^{-1}

Initial Concentration (ppm)					Ce/qe				
CAC	**LPC**	**TSC**	**DSC**	**PSC**	**CAC**	**LPC**	**TSC**	**DSC**	**PSC**
400	200	100	75	40	1.6216	1.276	3.255	11.91	0.5128
500	250	125	100	60	1.7391	1.739	4.752	18.46	9.2682
600	300	150	125	80	1.7543	3.076	7.272	18.46	25.4545
700	350	175	150	100	1.9435	3.648	7.557	20.50	32.1739
800	400	200	175	120	2.0385	3.668	7.397	18.88	34.9019
	450	225	200	140		3.439	7.950	17.03	36.1403

The separation factor RL indicates the feasibility of that process as unfavourable(RL>1), linear (RL=1, favourable (0<RL<C1) and irreversible (RL=0). In the present study, the values of RL being for CAC, LPC, TSC, DSC, and PSC indicate that the adsorption for dye BG is favourable [16].

Table -4. Result and correlation analysis for the adsorption isotherms for the removal of Brilliant Green by various adsorbents

Parameters	Adsorbents				
Freundlich Isotherm	**CAC**	**LPC**	**TSC**	**DSC**	**PSC**
Slope (1/n)	0.7493	0.3602	0.4421	1.5281	0.0916
Intercept (log K)	0.1363	0.7227	1.2045	3.2734	0.9258
Correlation coeffiecient (r)	0.9965	0.9566	0.9342	0.9244	0.9533
Langmuir Isotherm					
Slope($1/Q_0$)	0.0094	0.0509	0.0980	0.1715	0.1591
Intercept ($1/Q_0b$)	1.3336	0.7670	2.4313	8.2400	11.77
Correlation coeffiecient (r)	0.9891	0.9826	0.9419	0.9278	0.9301
Q_o (mg g-1)	105.48	19.6463	10.2040	5.830	6.2853
b(gL-1)	140.67	15.068	24.809	48.04	74.005
R_L	0.0174	0.1760	0.2439	0.2173	0.1838

The adsorption capacity Q_0 of these adsorbents for Brilliant Green is found to be mgg^{-1} respectively for CAC, LPC, TSC, DSC, and PSC.The increasing order of the adsorption capacity (Q_0) is CAC > LPC > TSC > DSC > PSC

Effect of Contact Time

To study the effect of contact time on the removal of Brilliant Green dye by adsorption, adsorption experiments were carried out at constant dose of adsorbent and initial concentration.

The percentage removal of dye on various adsorbents at 90 min of contact time (Table-5) reveals that maximum removal efficiencies of the adsorbents CAC, LPC, TSC,DSC and PSC are 92.5%,92.0%,80.80, 62.66%, and 68.30% respectively. The percentage removal of BG dye increases with increase in contact time, reaches a maximum value (Figure-3).

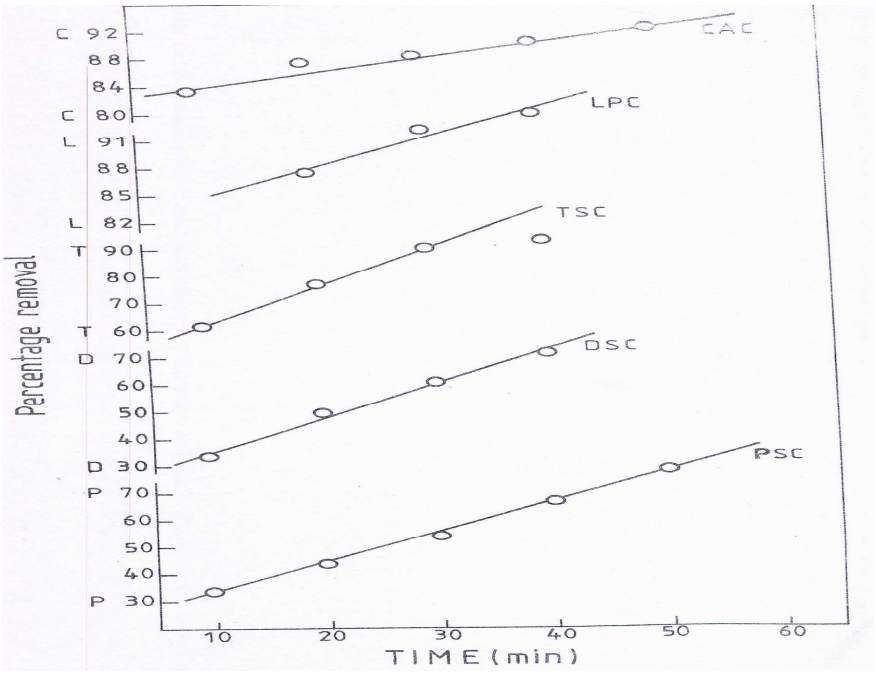


Figure 3. Effect of contact time on the extent of removal of Brilliant Green dye by various adsorbents

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 and dynamics of adsorption of Brilliant Green dye, adsorption experiments were carried out at different contact time (10,20,30,40,50,60,70 and 80 min) at constant optimum initial concentration of dye (400ppm for CAC, 300ppm for LPC, 125ppm for TSC, 75ppm for DSC and 60ppm for PSC). Relevant experimental data are given in Table-5

Table – 5. Effect of contact time on the extent of removal of Brilliant Green dye by various adsorbents

Initial Concentration : 300,100 ppm
Particle size : 90 mic
pH: 5.3
Dose : CAC : 2gL^{-1}
IPACS : 20gL^{-1}

Contact time (min)	% removal				
	CAC	LPC	TSC	DSC	PSC
10	84.75	81.33	61.6	33.33	41.66
20	89.0	87.33	77.6	49.33	50
30	90.0	92.00	90.4	60.00	80
40	91.75	93.33	92.0	70.66	71.6
50	93.0	91.66	87.2	68	60
60	89.5	88.00	-	60	48.33
70	89.0	-	-	46.66	35

The contact time at which the maximum percentage removal of Brilliant Green occurs is fixed as the optimum contact time. The decrease in the percentage removal of Brilliant Green dye, after reaching the optimum contact time, may be due to the desorption process. The removal of Brilliant Green dye by adsorption on various low-cost adsorbents was found to be rapid at the initial period of contact time and then become slow and stagnant with increase in contact time.

The boundary layer resistance will be affected by the rate of adsorption and increase in contact time will reduce the resistance and will increase the mobility of the adsorption in the adsorption system. Since the uptake of dye at the active sites of adsorbents is rapid process the rate of adsorption is governed by either liquid phase mass transfer rate or intra-particle mass transfer rate.

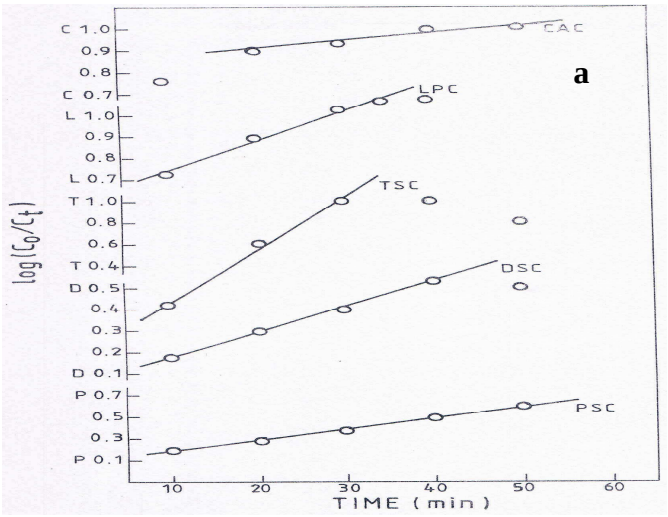
The following equations were used to study the kinetics and dynamics of adsorption under the conditions of first order kinetics [17,18]:

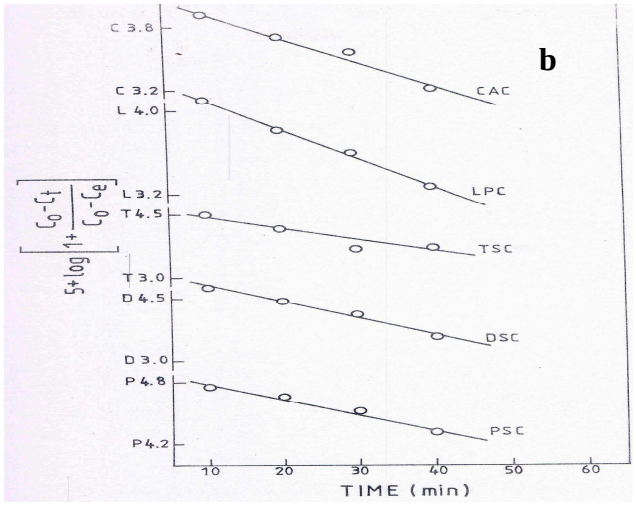
Natarajan and Khalaf model : $K=(2.303/t)\log(C_i/C_t)$

Lagergran's model : $\text{Log}(q_e-q_t)=\log q_e-(K_{ad}/2.303)t$

Bhattacharya and Venkobachar model : $\text{Log}(1-((C_i-C_t)/(C_i-C_e)) = (K_{ad}/2.303)t$

The plots of Log (C_i/C_t), log (q_e-q_t) and $\text{Log}(1-((C_i-C_t)/(C_i-C_e))$ against t were found to be linear (figure 4). The applicability of these equations (Table 6) indicates the first order nature of the adsorption kinetics of dye on various carbons.





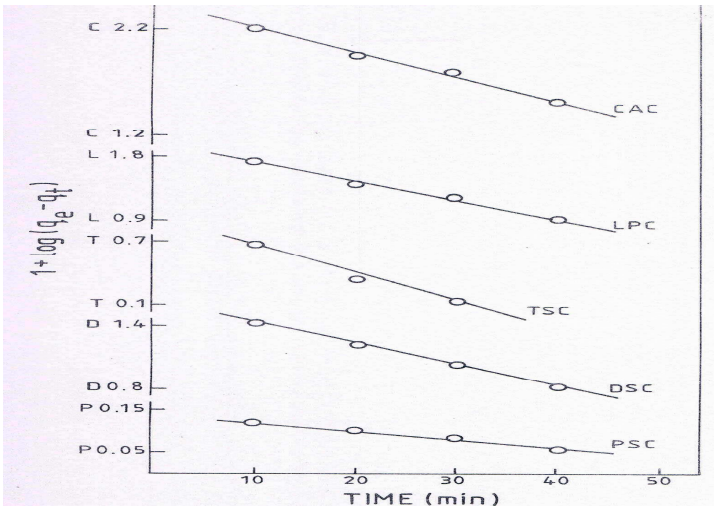


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Figure 4. Natarajan and khalaf (a); Lagergren (b) and Bhattacharya and Venkobachar (c) equations for Brilliant Green dye adsorption on various adsorbents

Intra-Particle Diffusion Model

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through intra-particle diffusion process, which is often the limiting step in many adsorption process, especially in a rapidly stirred batch reactor.

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model.

$q_t=K_pt^{1/2}+C$

Where q_t is the amount of dye adsorbed at time t, C is the intercept and K_p is the intra-particle diffusion rate constant (in mg $min^{1/2}g^{-1}$). The values of q_t were found to be linearly correlated with the values of $t^{1/2}$. The K_p values were calculated by using correlation analysis (Table -6). The r-values are close to unity indicating the applicability of this model.

This reveals the presence of intra-particle diffusion process. The values of intercept give an idea about the boundary layer thickness i.e, the larger the intercept, the greater is boundary layer effect [19, 20].

Table 6. Kinetics and dynamics of adsorption of Brilliant Green dye by adsorption on various adsorbents

Parameters	CAC	LPC	TSC	DSC	PSC
Natarajan and khalaf equation					
Correlation coefficient(r)	0.9859	0.9870	0.9758	0.9457	0.9788
10^2 K(min^{-1})	9.200	8.4600	14.100	2.6042	3.0400
Lagergren equation					
Correlation coefficient(r)	0.9816	0.9963	0.9612	0.9890	0.9649
10^2 K(min^{-1})	14.880	11.900	5.8200	3.000	4.5300
Bhattacharya and Venkobachar equation					
Correlation coefficient(r)	0.9819	0.9817	0.9618	0.9758	0.9657
10^2 K(min^{-1})	63.590	63.490	49.280	33.240	22.090
Intra - particle diffusion model					
Kp	4.3982	0.5898	0.6315	0.4385	0.3450
Correlation coefficient(r)	0.9842	0.9864	0.9759	0.9995	0.9860
Intercept	153.28	10.4089	7.9565	0.1309	0.1792

Effect of Dose of Adsorbent

The data on the removal of Brilliant Green dye by adsorption on various adsorbents viz., CAC, LPC, TSC, DSC, and PSC at different dose of adsorbent at constant initial concentration of dye and contact time are presented in Table-7.

The percentage removal of BG dye by adsorption on various adsorbents were found to be increasing with increase of dose of adsorbent (Figure 5).

The extent of removal of BG dye increases with increase in dose of adsorbent due to increase in availability of surface active sites. This may also be due to the increase in effective surface area resulting from the conglomeration of the adsorbents especially at the higher adsorbent dose. A similar report is available in literature [21, 22].

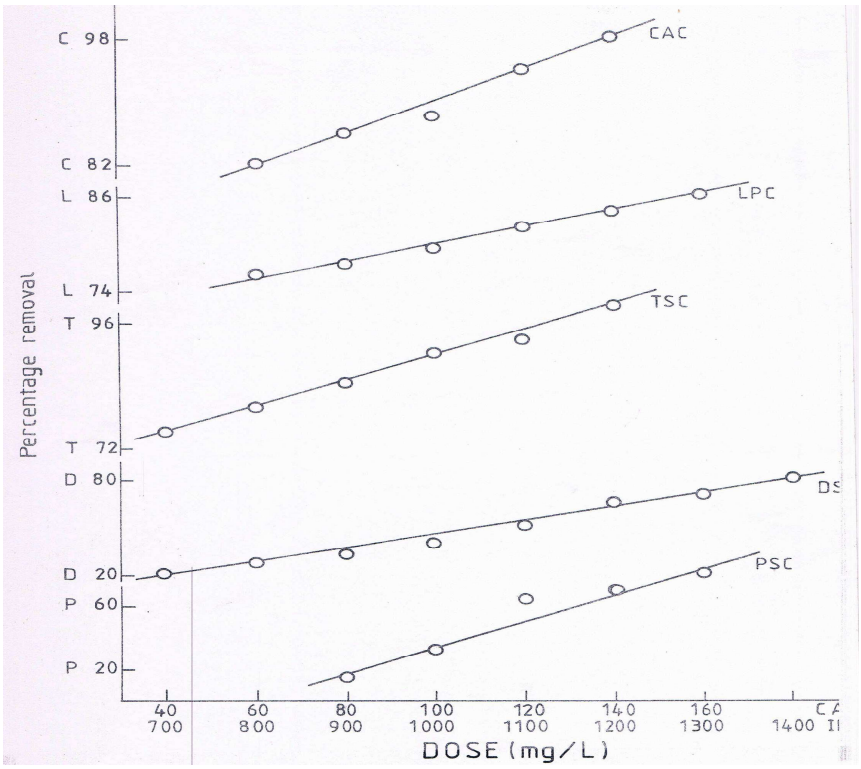

Figure 5. Effect of dose of adsorbents on the removal of Brilliant Green dye by adsorption on various adsorbents

The plots of percentage removal of dye versus dose of adsorbent was found to be exponential for the dye (Figure 5) and hence the amount of dye adsorbed on these two adsorbents varied in accordance with the fractional of adsorbent power term of the dose of adsorbents as $(Dose)^n$, Where n=fraction. This suggests that the adsorbed dyes either block the access to internal pores or cause particles to aggregate thereby reducing the availability of active sites. The optimum dose was $2gL^{-1}$ for CAC and$20gL^{-1}$ for IPACS.

Table – 7.Effect of dose of adsorbents on the removal of Brilliant Green dye by adsorption on various adsorbents

Initial Concentration : 300,100 ppm
Particle size : 90 mic;
pH:5.3;
Dose : CAC : $2gL^{-1}$
IPACS: $20gL^{-1}$

Dose of CAC (mg/L)	% of removal	Dose of IPACS (mg/L)	% of removal			
			LPC	TSC	DSC	PSC
40	75.25	700	75.33	74.4	20	
60	80.5	800	76.66	80.8	25.33	6.0%
80	86.5	900	77.33	90.4	30.66	33.83
100	88.0	1000	79.33	90.4	38.66	33.83
120	94.5	1100	82.00	93.6	49.33	63.33
140	98.0	1200	84.66	96.8	66.66	73.33
160	-	1300	-	-	70.66	81.66
180	-	1400	-	-	78.66	-

Effect of pH

The adsorption of Brilliant Green on these adsorbents namely CAC, LPC, TSC, DSC, and PSC (pH: 2-10) with constant optimum initial concentration ($2gL^{-1}$ for CAC and $20gL^{-1}$ for IPACS) of Brilliant Green, contact time (30 min) and optimum dose of adsorbents were also studied in order to find out the variation on adsorption potential of these adsorbents as a function of pH in adsorbing BG. The results are presented in Table 8. The adsorption of BG on various adsorbents are found to be highly pH dependent. The variation in amount adsorbed with pH is shown in Figure 6.

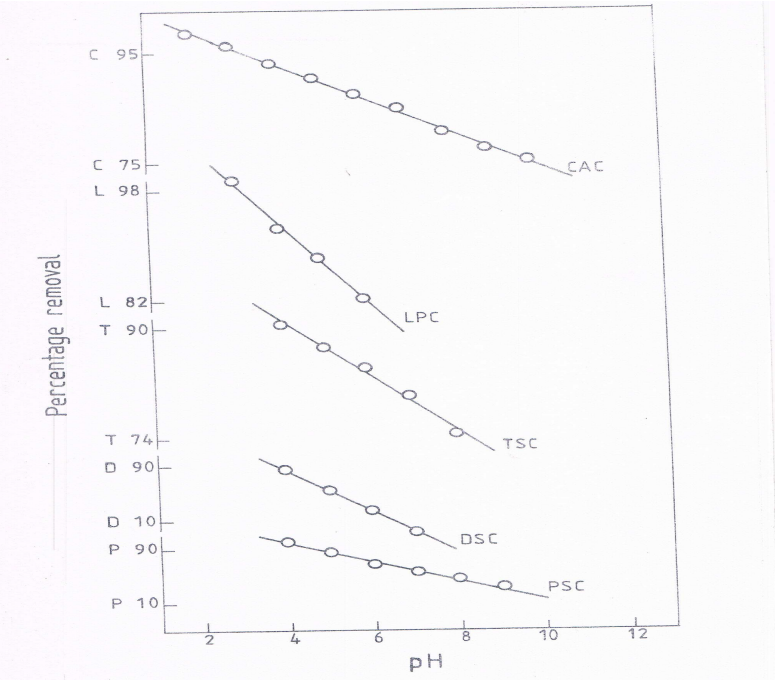

Figure 6. Effect of pH on the removal of Brilliant Green dye by various adsorbents

The data reveals that the removal of BG is maximum (CAC, LPC, TSC,DSC and PSC are 92.5%,92.0%,80.80 62.66%, and 68.30% respectively) at high pH. The pH affects the change on the surface of the adsorbents altering its capacity to adsorb materials [19-22].

Table -8. Effect of pH on the removal of Brilliant Green dye by various adsorbents

Initial Concentration : 300,100 ppm
Dose : CAC : 2gL^{-1}
Contact time : 30 min
IPACS : 20gL^{-1}

pH	% removal				
	CAC	**LPC**	**TSC**	**DSC**	**PSC**
2	98	-			
3	96	100			
4	93.75	92.66	92.0	86.66	98.33
5	90.5	88.66	87.2	54.66	83.33
6	87.5	82.66	84.00	20.00	66.66
7	84.0	93.33	80.8	12.00	53.33
8	80.5	96.66	74.4	81.33	43.33
9	77.75	97.33	69.6	86.66	26.66
10	75.25	-	-	-	3.33

CONCLUSION

The present study deals with the removal of Brillian Green dye on various adsorbents viz, CAC, LPC,TSC,DSC and PSC.

The percentage removal of dye on various adsorbents is found to decrease with increase in initial concentration of dye. The kinetic equations such as Natarajan and Khalaf, Bhattacharya and Venkobachar, Lagergren and Intra-paraticle diffusion model were found to be applicable in our system to get linearity. The system obeyed first order kinetics. Langmuir and Freundlich modles were tested. The system covered monolayer adsorption system. The percentage removal of dye by adsorption exponentially increases with increase in dose of adsorbent and decrease in particle size of the adsorbent. The order of adsorption capacity of these adsorbents is CAC>LPC>TSC>DSC>PSC. From the results of the present study it is concluded that the maximum percentage removal of Brillian Green dye is possible with low-cost adsorbents like LPC,TSC,DSC and PSC which are better alternate to CAC.

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