Adsorptive Removal of Brilliant green dye from wastewater using activated CETP sludge

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Abstract

Brilliant Green, a synthetic and toxic dye, is used for dyeing various materials such as paper, leather, wool and silk. This study demonstrates the efficacy of an adsorbent derived from CETP sludge for the removal of Brilliant Green dye from wastewater. Activated sludge was characterised using SEM, XRF, FTIR and BET techniques. Several parameters including the contact time, pH, adsorbent dose, initial dye concentration and temperature were optimised to assess their impact on dye adsorption. The maximum removal efficiency of Brilliant green dye reached 98.50% within 120 minutes at a concentration of 20 mg/l, pH 5.0 and 0.1 g adsorbent dose at temperature 30°C.

Experimental data fitted well with the pseudo 2nd order kinetic model. Experimental isotherm study employing the Langmuir, Freundlich, Temkin and R-P isotherm models revealed that the Freundlich adsorption isotherm model best fitted the adsorption of Brilliant Green dye. The thermodynamic parameters such as ΔG°, ΔH° and ΔS° were studied and the adsorption was found to be spontaneous and endothermic in nature. These results suggested the significant potential of activated CETP sludge for the removal of dyes from wastewater.

Keywords: CETP sludge, Brilliant green dye, Pseudo 2nd order model, Freundlich isotherm, Wastewater treatment.

Introduction

In recent years, aquatic ecosystems have been severely affected by dyes which pose a potential health hazard to humans. The worldwide expansion of industrial activities has intensified the challenges working on wastewater management systems[16,30]. Water discoloration is primarily caused by dyes and pigments, which is the most noticeable indicator of water unsuitability for consumption. Research studies show that approximately one hundred thousand different types of dyes are manufactured, at a production rate of 7×10^5 annually[18,54]. Brilliant green is a synthetic and toxic dye that is currently being utilized for various purposes such as dyeing paper, leather, wool and silk[21]. The toxic nature of brilliant green dye affects aquatic life and results in environmental pollution. They also cause certain health hazards such as cancer, skin irritation and mutations[11,17,43,55]. Dyes in wastewater also prevent the passage of sunlight into the water, thus minimizing photosynthesis and causing environmental pollution. Therefore, removal of brilliant green dye from the waste water is necessary[56]. Low-cost materials focused on the application of reusable and biodegradable adsorbents made from natural sources like rice husk[39], wheat bran[10], waste apricot[45], bagasse fly ash[36]and powdered peanut hull[15]. Natural and modified clays like sepiolite[2], zeolite[5], perlite[12] and bentonite[46], sugar industry mud[34], palm-fruit bunch[44], jack fruit peel[25], peat[22], orange peel[42], sugar cane dust[29], peat[24] and neem leaf powder[7], acorns and olive sheds[31] and chemically treated guava leaf powder[51] which have been used for the removal of toxic substances from wastewater.

In India, many of the small-scale industries (SSI) are unable to put the treatment systems individually, so the concept of CETP's (Common Effluent Treatment Plant) is introduced to industries in treating its effluent before disposal in rivers and oceans[9]. The process of removing pollutants from municipal wastewater, which comprises of primarily household sewage and industrial wastewater, is referred to as sewage treatment. Physical, chemical and biological processes are used to remove contaminants and to produce treated effluent that is safe enough for release into the environment. A by-product of sewage treatment is a semi-solid waste or slurry, called sewage sludge. The sludge must undergo further treatment before being suitable for disposal or application to land[47].

The current study deals with the removal of hazardous brilliant green dye from wastewater using activated sludge as an adsorbent. Batch and kinetic studies were investigated to examine the feasibility of the prepared activated sludge for the adsorption of brilliant green dye from wastewater.

Material and Methods

Brilliant green (BG) is a cationic dye with a molecular formula of $C_{27}H_{34}N_2O_4S$ and molecular weight of 482.63 g mol^{-1}. The sludge was collected from Common Effluent Treatment Plant (CETP) in the Sanwer Road Industrial Area of Indore, Madhya Pradesh, India. It is composed of small, spherical, greyish-black particles. The collected sludge sample was filtered to achieve a particle size range (100 BSS). The sludge sample was then heated in a Muffle furnace at various temperatures (100-500°C) for different durations (15-120 minutes). The optimal scavenging efficiency was achieved by heating the sample to 300°C for 60 min, after which it was stored in a vacuum desiccator. A stock solution of 1000 mg/L was prepared by precisely weighing 0.1g of the brilliant green dye. Experimental solutions of the desired concentrations were obtained through the sequential dilution of the stock solution. The dye

concentration was determined using a UV-visible spectrophotometer.

Adsorption studies: In a 100 mL volumetric flask, 20 mL solution of brilliant green dye solution with a known concentration was taken. The adsorption of BG onto the activated sludge was investigated using a batch technique at ambient temperature and specific pH levels. To adjust the pH values, solutions of NaOH (0.1 N) and HCl (0.1 N) were used. The investigation involved altering the adsorbent dose (0.1 to 0.5 gm), adsorbate concentration (5-50mg/L), pH (4-10) and contact time (240 mins). To assess the effect of temperature on dye adsorption, experiments were performed at 30°C, 40°C and 50°C. The solutions were filtered using Whatmann filter paper and dye uptake was examined spectrophotometrically at λ_{max} 623 nm.

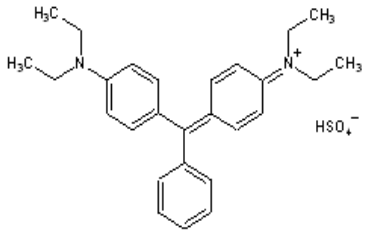


Fig. 1: Molecular structure of Brilliant green dye

Adsorption Isotherms
The Langmuir, Freundlich, Temkin and R-P isotherms are the most commonly utilized equilibrium models.

Freundlich Isotherm: The Freundlich isotherm model, introduced by Freundlich[13], said that adsorption occurs on heterogeneous surfaces[13].The nonlinear form of the Freundlich isotherm is expressed by eq. 1:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (1)$$

The equation may be linearized by taking the logarithm of both sides and is expressed as eq. 2:

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

where K_F is a constant indicative of the relative adsorption capacity of the adsorbent (m/g) and 1/n is a constant indicative of the intensity of adsorption.

Langmuir Isotherm: This is based on the assumption that maximum adsorption corresponds to a saturated solute monolayer on a homogenous adsorbent surface. It comprises of a finite number of identical sites with homogeneous adsorption energy. The following equation was developed by Langmuir[33]. The nonlinear Langmuir isotherm model is expressed in eq. 3:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (3)$$

The linearized form of Langmuir equation is represented in eq. 4:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{K_L q_m}\right)\left(\frac{1}{C_e}\right) \quad (4)$$

where C_e is the equilibrium concentration of dye (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g), q_m is the monolayer adsorption capacity (mg/g) and K_L is the constant related to the free energy of adsorption.

Separation Factor: For the study of separation factors under both fixed-bed systems and batch operation systems[48], Weber et al[57,58] investigated the effect of isotherm shape on favourable and unfavourable adsorption.

According to Hall et al[19], the main features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L which is specified by eq. 5.

$$R_L = \frac{1}{1 + b\, C_o} \quad (5)$$

R_L values were obtained by plotting the non-dimensional solid-phase concentration (Q), in contrast to the non-dimensional liquid phase concentration (X). The relationship between these terms is expressed as follows:

$$Q = \frac{X}{R_L (1 - X) + X} \quad (6)$$

$$X = \frac{C_e}{C_{ref}} \quad (7)$$

$$Q = \frac{Q_e}{Q_{ref}} \quad (8)$$

where C_{ref} is the highest concentration of the liquid phase measured and Q_{ref} is the concentrate of the solid-solid phase that stays with C_{ref}.

Equation 9 is formed by replacing equations 7 and 8 with equation 6.

$$R_L = \frac{C_e (Q_{ref} - Q_e)}{Q_e (C_{ref} - C_e)} \quad (9)$$

Substituting Q_e from equation 1 and then simplifying, equation 9 becomes:

$$R_L = \frac{1}{1 + b\, C_{ref}} \quad (10)$$

Since C_{ref} is highest fluid-phase concentration (i.e. $C_{ref} = C_o$), equations 5 and 10 are similar.

Temkin isotherm: The Temkin isotherm is based on the assumption that the reduction in sorption heat follows a linear pattern, rather than the logarithmic decrease predicted by the Freundlich equation. As surface coverage increases, the heat of sorption for all molecules in the layer would decrease linearly instead of logarithmically[27,52]. The

simplified linear form of this model is expressed by the following equation:

$$q_e = B \ln A_T + B \ln C_e \quad (11)$$

where A_T is the Temkin isotherm equilibrium binding constant (L/g) and B is the constant related to heat of adsorption (J/mol).

Redlich-Peterson Isotherm: Redlich isotherm is proposed by Redlich and Peterson which is a mixture of Langmuir and Freundlich isotherms[49]. This model is defined as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (12)$$

Further, this nonlinear form (Equation 12) can be converted into a linear form by taking the logarithm of the above equation:

$$\ln = (A\frac{C_e}{q_e} - 1) = g \ln (Ce) + \ln (B) \quad (13)$$

where *A* (L/g) and B (L/mg) are Redlich-Peterson isotherm constant, g is an exponent ranging from 0 to 1, C_e is equilibrium liquid-phase concentration of the adsorbent (mg/L) and q_e is equilibrium adsorbate loading on the adsorbent (mg/g).

Thermodynamic Studies: Experiments on dye adsorption were conducted at temperature 30°C, 40°C and 50°C. Thermodynamic parameters were studied including Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption. In endothermic processes, the adsorbate molecules displace multiple water molecules from the surface during adsorption. Conversely, in exothermic processes, the energy released from bond formation between adsorbate and adsorbent surpasses that of bond breaking, resulting in a negative ΔH° value[6,14]. The ΔH° magnitude serves as a reliable indicator of the adsorption type.

A positive ΔS° value suggests increased disorder at the solid-liquid interface and structural alterations in both adsorbate and adsorbent. A low ΔS° value implies minimal changes in the adsorbent's internal structure during adsorption. Adsorption is feasible and spontaneous when the Gibbs free energy (G°) is negative. The Gibbs free energy, enthalpy and entropy of adsorption can be determined using the following equation:

$$\log \frac{b_2}{b_1} = \frac{\Delta H^o}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad (14)$$

$$\Delta G° = -2.303 \, RT \log b \quad (15)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (16)$$

where b_1 and b_2 are the Langmuir constants and T_1 and T_2 are the temperatures at 30°C and 40°C respectively. R (8.314 J/ (mol K)) is the ideal gas constant.

Specific rate constant of adsorption - Pseudo First Order: The pseudo first order model proposed by Lagergren[32] was used to investigate the rate constant of dye adsorption onto sewage sludge. The nonlinear form of the pseudo first order model is given in equation 17:

$$q_t = q_e \, (1 - e^{-K_{ad} \, t}) \quad (17)$$

The logarithm of both sides is taken to linearize the equation:

$$\log (q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} t \quad (18)$$

where q_e is the amount of dye adsorbed at equilibrium and q_t is the amount of dye adsorbed at time t (both in mg/g).

Pseudo Second Order: Ho and McKay[22-24] proposed a second-order kinetic model, which assumes that adsorption follows second-rate chemisorption. Pseudo second order kinetic in its nonlinear form is expressed as equation 19:

$$qt = \frac{K_2 \, q_e^2 \, t}{1 + K_2 q_e \, t} \quad (19)$$

The linear form of this equation is expressed as follows:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (20)$$

where q_e represents the amount of adsorption at equilibrium (mg/g), q_t represents the amount of adsorption at time t (mg/g) and K_2 represents the pseudo-second-order rate constant (g/mg/min).

Intraparticle Diffusion Model: The model proposed by Weber and Morris[58] is the most common technique used to identify the mechanism involved in the adsorption process. This equation is expressed as:

$$q_t = K_i \sqrt{t} + C \quad (21)$$

where K_i is the intra-particle diffusion rate constant [(mg/g $min^{1/2}$] and *C* is the intra-particle diffusion constant.

Non-linear regression analysis and error function analysis: Determining the isotherm parameters using the linearized models has a major disadvantage because the inherent bias resulting from linearization may cause the R^2 not able to provide the best isotherm constants to correlate with the original isotherm[59].The solver add-in under Microsoft Excel was used to determine the isotherm parameters as well its coefficient of determination (R^2) between experimental data and isotherms.

The nonlinear form was a good alternative parameter that provided an accurate technique to determine isotherm and kinetic parameters from the original equation forms[28]. The error function is required to evaluate the best fit of nonlinear models[35]. Statistical error functions used to validate the best-

fitting sorption kinetic and equilibrium isotherm models are: chi-square($\chi 2$), log-likelihood test(G^2), hybrid fractional error (HYBRID), Marquardt's percent standard deviation (MPSD), root mean square error (RMSE) and mean square error (MSE)[3,4,8,20,41,53].

Results and Discussion

Sewage sludge samples (Raw and activated) collected from common effluent treatment plant were characterized using X-ray fluorescence spectroscopy (XRF), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and BET analysis.

X-ray fluorescence analysis: XRF spectrometer Rigaku (ZSX,Primus IV) model, IIT Roorkee was used for the determination of elemental composition of sludge sample using X-ray fluorescence analysis (Fig. 2). Elements such as sodium, magnesium, calcium, titanium, cobalt, chromium and copper showed increased concentrations in the activated sludge, indicating a retention or adsorption process. The decrease in concentrations of some other elements such as silicon, iron and nickel suggests that they could have undergone leaching during activation. The compositional changes in this regard indicate a shift in the sludge structure which makes it more effective.

SEM analysis: Scanning electron microscopy (SEM) helps to explain the surface morphology, texture and sizes of the particles. Raw CETP sludge consists of fine particles of irregular shape and the microsporus structure of the heterogeneous rough surface with different levels of porous surface is seen in fig. 3(a). Activated CETP sludge showed a surface morphology with a rough, spherical and microspores in shape which promotes increased adsorption of dyes as seen in fig. 3(b). SEM analysis was performed at IIT Indore,India, using FE-SEM Supra 55 (Carl Zeiss, Germany).

FTIR analysis: FTIR spectra were obtained using a Bruker Vertex FTIR- 7600 spectrometer (4,000 – 400 cm^{-1}) (Fig. 4). The presence of alcohols in collected sewage sludge was detected due to hydroxyl group (O–H) stretching vibrations at 3415 cm^{-1}. This band shifted to 3422 cm^{-1} in activated sludge and 3432 cm^{-1} in brilliant green dye treated sludge. The peak's broadening could be related to the activation of sewage sludge at high temperatures. The FTIR measurement of CETP after activation showed a structure that was significantly altered. The existence of the –COOH group was detected by the O–C=O linkage at 1412–1426 cm^{-1} in collected and activated sewage sludge, however this band shifted to 1431 cm^{-1} in dye treated sludge. Asymmetric C–H stretching vibrations could be responsible for the absorption band at 2924 cm^{-1}. The bands that appeared at 1628–1637 cm^{-1} represented the aromatic ring's C=C stretching vibration. Distinctive peaks for C–X halogen stretching vibration were found at 1025 and 1027 cm^{-1} for raw and activated sludge samples respectively.

BET analysis: The sludge was texturally characterised using an ASAP 2010 micro pore analyser. N_2 (g) adsorption at 77 K and BET surface area, pore volume, pore size were calculated (Table 2).

Batch studies

Influence of contact time: The percentage adsorption of Brilliant green (BG) dye on activated sludge steadily increased with increasing contact time and showed a constant percentage adsorption at 120 min contact time.

Table 1
Characteristic EDXRF of elements (%).

S.N.	Elements	Raw Sludge	Activated sludge
1	Na	0.4088	0.673
2	Mg	1.5483	2.3982
3	Al	4.3388	4.8862
4	Si	30.857	27.5241
5	P	2.8083	2.8871
6	S	3.3285	3.3285
7	Cl	0.9963	2.024
8	K	0.8349	1.0458
9	Ca	17.8818	23.8514
10	Ti	0.8749	1.2503
11	V	0.021	-
12	Cr	0.275	0.3969
13	Mn	0.4446	0.5276
14	Fe	32.7574	20.4066
15	Co	0.0338	0.0716
16	Ni	0.0637	0.0469
17	Cu	0.0778	0.098
18	Zn	1.0778	1.2016

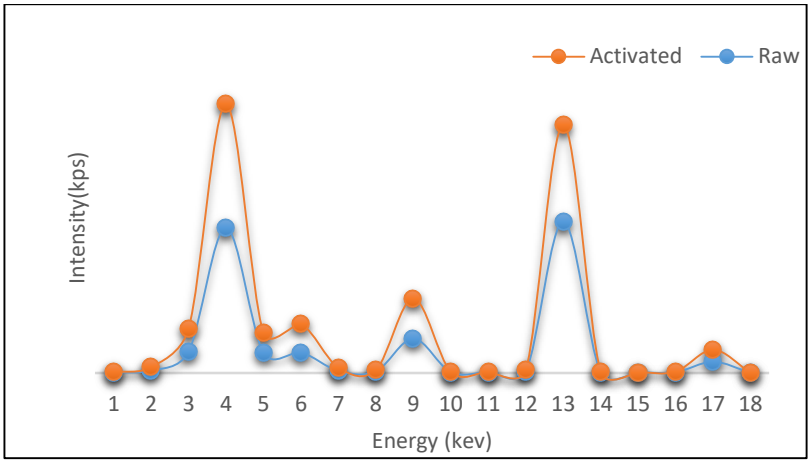
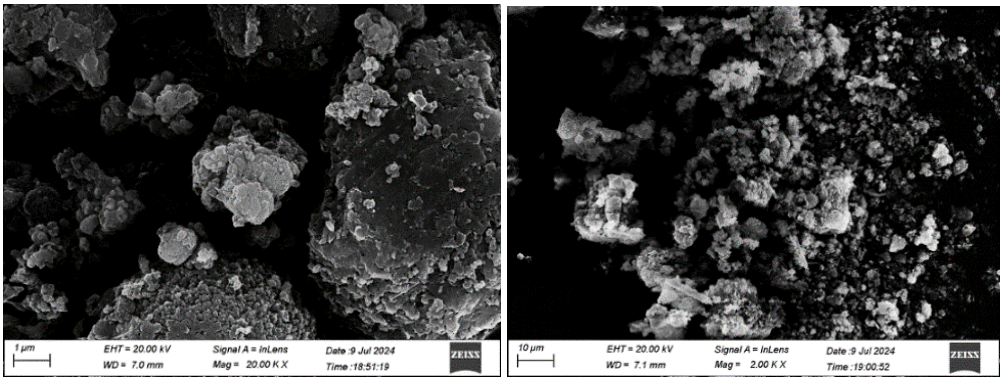
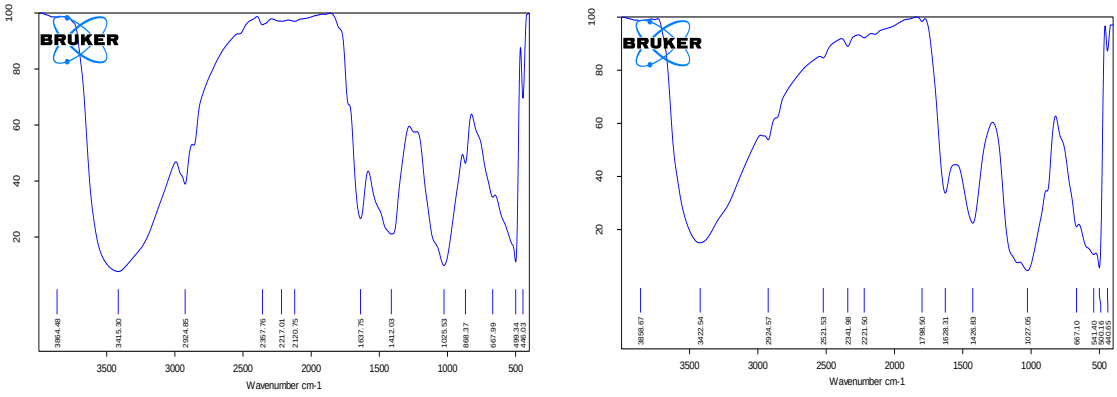


Fig. 2: XRF spectra of Raw and Activated sludge

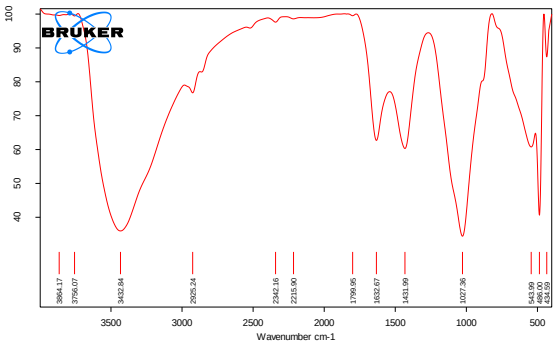


(a) **(b)**

Fig. 3: SEM analysis (a) Raw sludge (b) Activated sludge



(a) **(b)**



(c)

Fig. 4: FTIR Spectra of a) Raw sludge b) Activated sludge (c) Brilliant green dye

Table 2
BET parameters of Raw and Activated sludge.

Parameters	Raw sludge	Activated sludge
BET surface area (m^2g)	3.608	38.279
Pore volume (cm^3g)	0.017	0.103
Pore size (nm)	19.938	10.797

The adsorption efficiency at a case of the 10ppm concentration was 98.10%. Upon increasing the concentration to 20 ppm, the adsorption efficiency increased further to 98.50%. The maximum dye removal occurs during the initial phase owing to the availability of maximum sites that are active for dye adsorption and as time increases, the dye removal increases slowly owing to the lower number of active sites left for adsorption[26].

Influence of adsorbent dosage: Figure 5b shows the extent of BG dye removal with a change in adsorbent dosage. The adsorbent surface area and availability of more adsorption sites play a key role in the increase in adsorption with increasing adsorbent dosage. As the adsorbent pore size and vacant sites match the adsorbate, the amount of adsorbed dye molecules on the adsorbent surface increases; otherwise, it limits the rate of adsorption[1].The adsorption efficiency corresponding to a 10ppm concentration was observed to be 98.5%. Upon further increasing this concentration to 20ppm, the adsorption efficiency increased to 99.7%. The tendency for the adsorption of dye molecules is very high due to the high surface area and small particle size of the activated sludge.

Effect of pH: The effect of pH on the dye activated sludge was observed in the pH range of 4-12. The structural stability and colour intensity of the BG molecule are pH dependent[40,50]. The surface charge and degree of ionization of the adsorbent in the solution were highly affected by the pH parameter. The maximum % age removal of the dye was obtained at pH 6. The extent of adsorption at pH 6 was 98.30 % at 10 ppm and 98.79 % at 20 ppm. (Fig. 5c).

Effect of temperature and initial dye concentrations: To investigate the influence of temperature on the adsorption of BG on the sludge, the temperature was varied from 30°C to 50°C. The influence of temperature on brilliant green adsorption on sludge is shown in fig. 5d. The maximum adsorption values were obtained at 30°C, using sludge as the adsorbent. The results reveal that the percentage removal of BG increases with increasing temperature which indicates the endothermic nature of dye removal on the prepared adsorbent.

Adsorption isotherms: The Langmuir isotherm elucidates the process of single-layer adsorption when an adsorbent removes an adsorbate. Linear plots $1/q_e$ vs $1/C_e$. were obtained from Langmuir isotherms at different temperatures (Fig. 6). The Langmuir parameters q_m, R_L, K_L were calculated and are shown in table 3. Similarly, Freundlich isotherm plots (Log q_e Vs Log C_e) at varying temperatures yielded straight lines (Fig. 7). Slopes and intercepts were employed to determine the Freundlich parameters 1/n and K_f (Table 3). The value of 1/n was found between 0 and 1 which showed the favourable adsorption of brilliant green dye.

Temkin isotherm plots (Fig. 8) showed moderate B_T values representing a reasonable adsorptive ability whereas its K_T higher values suggest better affinity bonding at 30°C as given in table 3. Fig. 9 showed the graph plotted between ln $(A\ (C_e/q_e)^{-1})$ v/s ln C_e at temperatures 30°C, 40°C and 50° C. Redlich Peterson constants B and g were calculated from the linear plot and are given in table 3.

The result shows that BG initially forms a monolayer on the adsorbent's active sites, followed by multilayer adsorption, once the monolayer is saturated on the outer surface of adsorbent, which showed the fitness of Freundlich model.

Thermodynamic parameters: Thermodynamic parameters such as ΔG°, ΔH° and ΔS° were calculated and are shown in table 5. The adsorption was found to be spontaneous and endothermic in nature.

Kinetic studies: The pseudo first order plot of log $(q_e - q_t)$ v/s t is linear for brilliant green dye at temperature 30°C, 40°C and 50° C (Fig. 10). The parameters obtained are shown in table 4. The values of the rate constant of adsorption (k_{ad}) determined from the slope showed the applicability of the first-order rate expression equation.

Pseudo second order graph was plotted between t/q_t Vs t (Fig. 11). The slope and intercept of the graph were used to compute the values of K_2 and q_e which are listed in table 4.

Intraparticle diffusion-The graph between the amount absorbed (q_t) and the square root of time ($\sqrt{t}$) was plotted (Fig. 12). It is clear from the graph that both intraparticle diffusion and film diffusion mechanisms took place at the same time during adsorption. Parameters obtained are shown in table 4.

Non-linear regression analysis and error function analysis: Non-linear analysis and error function analysis for the isotherms of the sorption of Brilliant green dye were calculated with the help of Solver add-in function in

Microsoft Excel. Predicted curves for the various adsorption isotherms such as Freundlich, Langmuir, Freundlich, Temkin and Redlich were fitted for brilliant green dye at 30°C, 40°C and 50°C as shown in fig. 13(a-c).

Results are summarized in table 6. It was found that Freundlich model fitted well with a higher correlation coefficient (R^2-0.999). It showed that distribution of active sites of the adsorbent was exponential and the adsorption process occurred on a heterogeneous surface of the adsorbent. The value of 1/*n* (0.397) was found less than 1 which showed the favourable adsorption of BG on the activated sludge. Error function analysis for adsorption isotherms and kinetics of the sorption of Brilliant green dye were calculated with the help of Solver add-in function in Microsoft Excel and results are summarized in table 7.

The results showed that adsorption process follows Freundlich isotherm model (lowest χ^2value 0.5338) and pseudo second order kinetics (lowest χ^2value 0.0015).

Table 3
Adsorption constants for the uptake of Brilliant green dye onto sludge at 30°C, 40°C and 50°C.

Isotherms	Parameters	30°C	40°C	50°C
Langmuir	q_{max}(mg/g)	8.216	17.534	18.348
	K_L(L/mg)	2.468	0.524	0.506
	R_L	0.038	0.160	0.164
	R^2	0.919	0.912	0.911
Freundlich	K_f (mg/g)	5.223	5.822	6.367
	1/n	0.349	0.595	0.660
	R^2	0.951	0.950	0.913
Temkin	B_T	1.989	3.317	3.654
	K_T	16.083	6.776	6.332
	R^2	0.936	0.892	0.853
R-P	A (L g^{-1})	20	20	20
	B (L mg^{-1})	0.522	0.522	0.698
	g	0.688	0.899	0.982
	R^2	0.939	0.810	0.885

Table 4
Kinetic plots for adsorption of Brilliant Green dye onto sludge at 30°C, 40°C and 50°C.

Kinetic models	Parameters	30°C	40°C	50°C
Pseudo first order	q_e (mg/g)	0.840	0.804	0.919
	K_1 (min^{-1})	0.016	0.023	0.013
	R^2	0.800	0.883	0.801
Pseudo second order	q_e (mg/g)	5.763	5.959	5.970
	K_2 (g/mg)	0.063	0.064	0.065
	R_2	0.999	0.999	0.999
Intraparticle diffusion	C (mg g)	4.580	4.754	4.933
	K_{diff}	0.110	0.106	0.091
	R^2	0.850	0.841	0.847

Table 5
Thermodynamic parameters for the uptake of Brilliant green dye onto sludge

Temp	-ΔG° [KJ $mole^{-1}$]	ΔH° [KJ $mole^{-1}$]	ΔS° [KJ $mole^{-1}$]
30°C	-1.264	48.603	157.675
40°C	1.681		
50°C	1.829		

Table 6
Parameters of adsorption isotherms and kinetic models of Brilliant Green dye onto sludge

Isotherms	Parameters	30°C	40°C	50°C
Langmuir	q_{max} (mg/g)	9.535	19.800	24.380
	K_L (L/mg)	1.435	0.438	0.364
	R^2	0.998	0.999	0.969
Freundlich	1/n	0.397	0.665	0.699
	K_F (mg/g)	5.021	5.890	6.374
	R^2	0.999	0.995	0.997
Temkin	B_T	1.989	3.318	3.660
	A_T	16.08	6.777	6.000
	R^2	0.998	0.998	0.971
R-P	A (L g^{-1})	146.9	9.304	725.30
	B (L mg^{-1})	27.828	60.831	111.57
	G	0.625	0.362	0.292
	R^2	0.998	0.999	0.996

Kinetics	Parameters	30°C	40°C	50°C
Pseudo first order	K_1(min^{-1})	0.131	0.145	0.153
	q_e(mg/g)	5.320	5.636	5.697
	R^2	0.842	0.999	0.999
Pseudo second order	K_2 (g/mg min^{-1})	0.053	0.062	0.072
	q_e	5.831	5.917	5.940
	R^2	0.999	0.999	0.999
Intraparticle diffusion	K_{diff}	0.110	0.107	0.095
	C	4.5794	4.855	4.957
	R^2	0.999	0.903	0.958

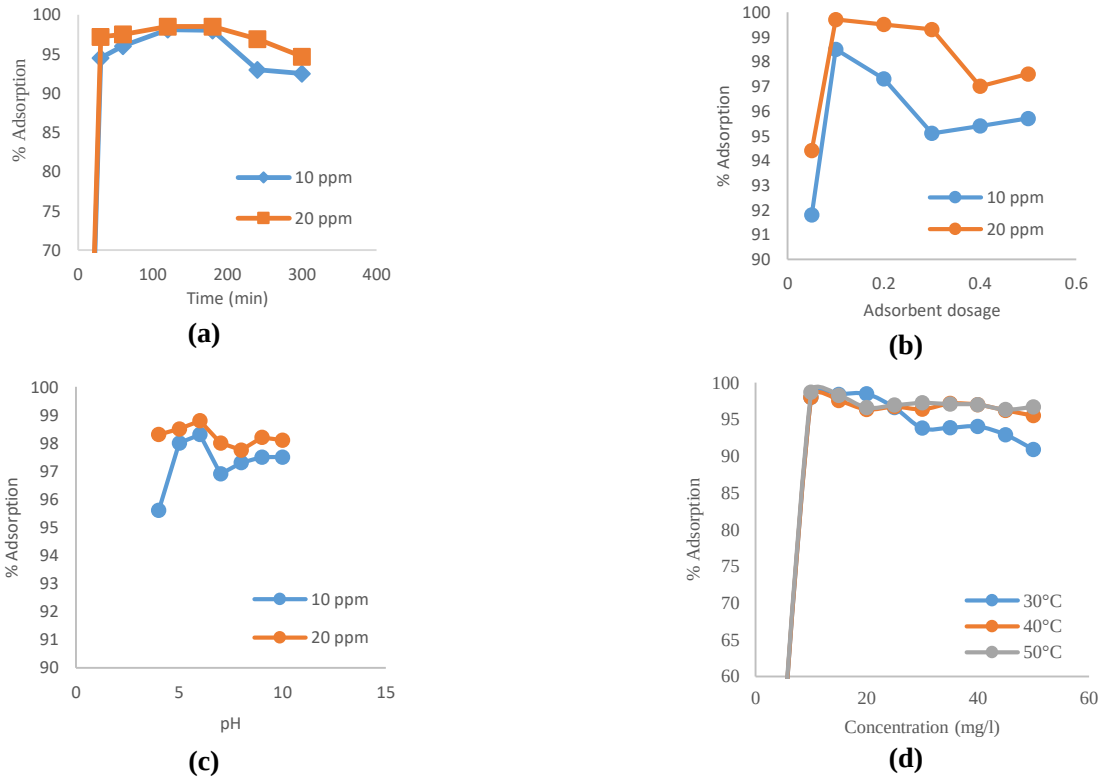


Fig. 5: Batch studies of BG dye onto sludge (a) Influence of contact time (b) Influence of adsorbent dose (c) Influence of pH and (d) Effect of Initial adsorbate concentration and temperature

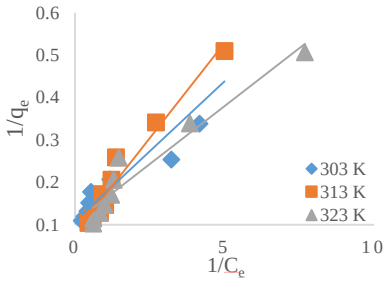


Fig. 6: Langmuir constants of BG dye

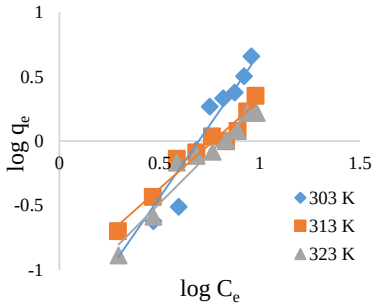


Fig. 7: Freundlich constants of BG dye

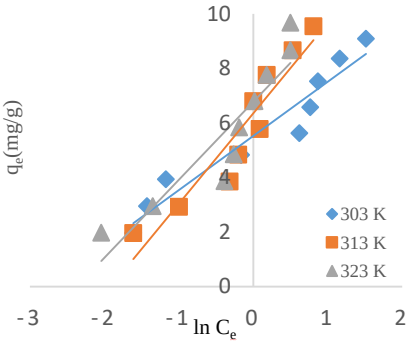


Fig. 8: Temkin constants of BG dy

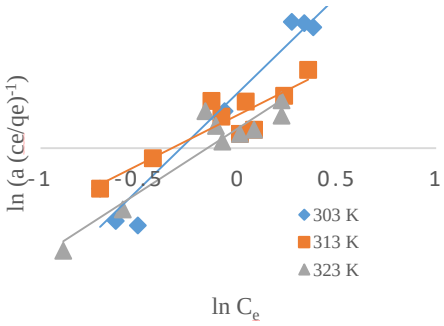


Fig. 9: R-P constants of BG dye

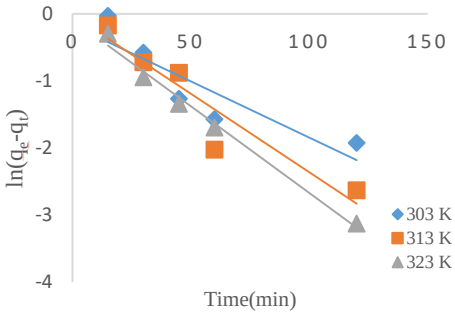


Fig. 10: Pseudo first order plots of BG dye

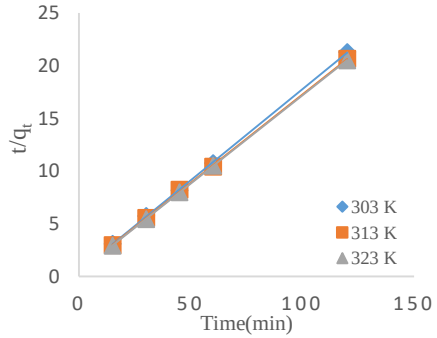


Fig. 11: Pseudo second order plots of BG dye

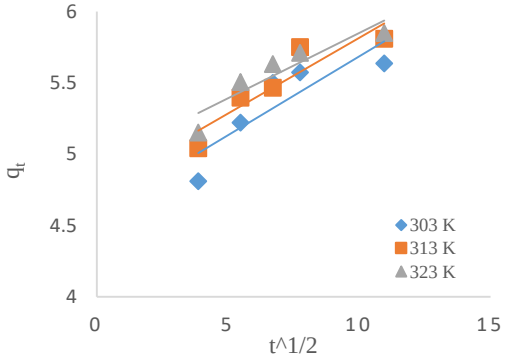


Fig. 12: Intraparticle diffusion plots of BG dye

Conclusion

The adsorption of brilliant green dye by activated sludge derived from CETP shows potential application for the removal of dyes from wastewater. The pH played an important role in adsorption of Brilliant green dye. The contact time was found to be 120 mins. Freundlich model was found to have the highest regression coefficient (0.999) and lowest χ^2 values 0.5338 and hence fitted well. Kinetic studies showed that the adsorption of brilliant green dye followed pseudo second order kinetics as supported by R^2 value (0.999) and lowest χ^2 values 0.0015.

Thermodynamic parameters showed that adsorption of brilliant green dye was spontaneous and endothermic in nature under experimental conditions. Hence, industries which are producing dye-contaminated effluents, may be benefitted from the applicability of activated sludge as dye removal strategy.

Table 7
Errors function data for adsorption isotherms and kinetic models of Brilliant Green dye onto sludge at 30°C.

Isotherms model	Errors	
Langmuir	χ^2	0.9151
	G^2	0.8047
	RMSE	0.2368
	EABS	-0.4805
	ARE	9.6328
	MPSD	32.9196
	HYBRID	10.8370
Freundlich	χ^2	0.5338
	G^2	0.2382
	RMSE	0.02648
	EABS	-0.0038
	ARE	6.3239
	MPSD	26.6729
	HYBRID	14.2289
Temkin	χ^2	0.5839
	G^2	0.2544
	RMSE	0.1939
	EABS	-0.0001
	ARE	6.6378
	MPSD	27.3268
	HYBRID	7.4675
R-P	χ^2	0.5279
	G^2	0.2212
	RMSE	0.1629
	EABS	0.0119
	ARE	6.1915
	MPSD	26.3921
	HYBRID	6.9654

Kinetic models	Errors	
Pseudo first order	χ^2	0.0479
	G^2	0.8977
	RMSE	0.1017
	EABS	-1.008
	ARE	0.9583
	MPSD	10.9452
	HYBRID	1.1979
Pseudo second order	χ^2	0.0015
	G^2	0.0006
	RMSE	2.3957
	EABS	0.0001
	ARE	0.0319
	MPSD	1.9975
	HYBRID	0.0399
Intraparticle diffusion	χ^2	0.0217
	G^2	0.0094
	RMSE	0.0679
	EABS	-3.30906E-05
	ARE	0.4373
	MPSD	7.3937
	HYBRID	0.5466

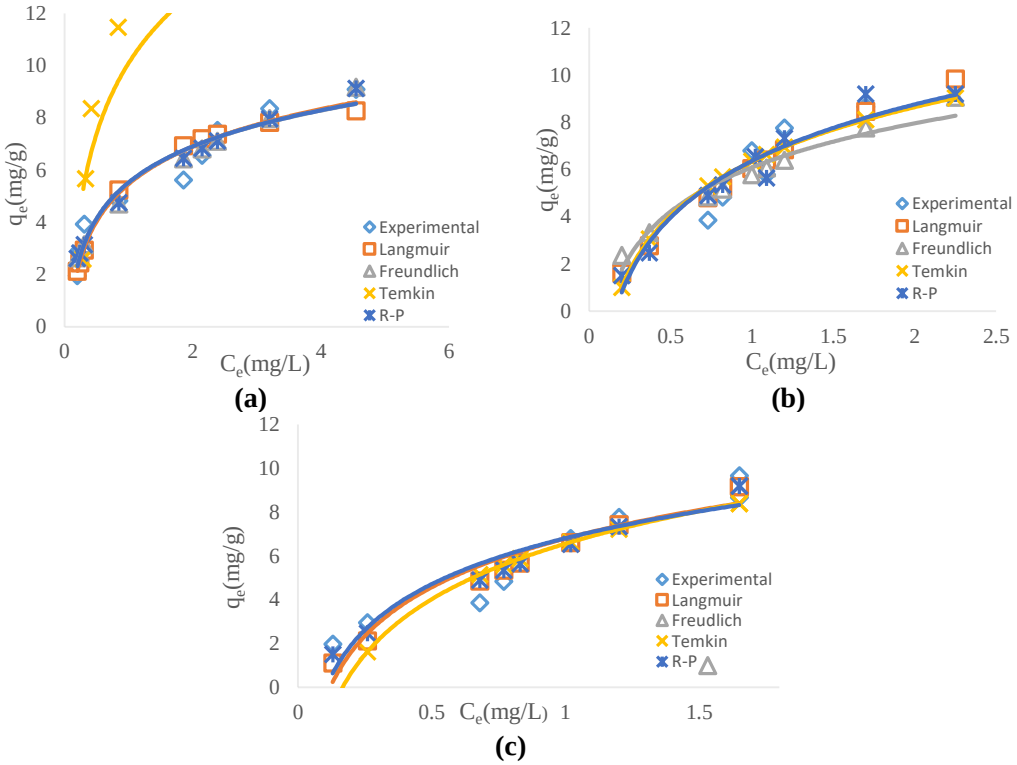


Fig. 13: Predicted curves fits for adsorption isotherms of Brilliant green (a) 30°C (b) 40°C and (c) 50°C

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