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Removal of Rose Bengal dye from aqueous solutions using biosorbent obtained from *Mangifera indica*

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Rose Bengal dye is a xanthene class [4, 5, 6, 7-tetrachloro-2', 4', 5', 7'-tetraiodofluorescein] compound with high molecular weight of 1016.7 g/mol. The leaves of *Mangifera indica* has been used to prepare a homogeneous powdered biosorbent for the removal of Rose Bengal dye from aqueous solution. Maximum dye uptake capacity is achieved for initial dye concentration of 20 mg/L at biosorbent dosage of 0.2 g at neutral *p*H. Scanning electron microscope (SEM) image, Energy Dispersive X-ray (EDX) and Fourier Transform Infrared (FTIR) spectra display changes in the morphological properties, elemental compositions and functional groups respectively before and after adsorption of RB dye on MI. The maximum monolayer adsorption capacity of MI for RB dye is found to be 0.824 mg per 0.2 g of adsorbent. Freundlich isotherm model best fits the experimental data compared to the results obtained from Langmuir-1 and Langmuir-2 model equations. The pseudo-second order model-1 best describe the kinetics of the adsorption of Rose Bengal dye on MI. The thermal degradation characteristics of *Mangifera indica* before and after adsorption are studied. The pyrolysis of dye adsorbed biomass at 900°C result in a total degradation of 93.15% with peak weight reduction of 0.0508 mg/min at 528°C.

Keywords: Adsorption, Differential thermogravimetry, Rose bengal dye, *Mangifera indica*

Colour in water and wastewater poses a serious aesthetic and environmental issue while doling out a specific treatment methodology. The treatment of multiple spectra of dyes let out by the textile industries pose a huge environment risk thereby endangering the synergy of ecosystem. The colour caused by the suspended solids as in the case of real textile wastewater can be removed by various physico-chemical methods like flocculation[1], chemical precipitation[2] followed by sedimentation[3] and subsequent rapid sand filtration. The discharge of highly toxic and coloured wastewater into the river streams, drains without any prior chemical or biological treatment pose a serious challenge to the aquatic niche. But the true colour solution caused by the synthetic dyes is very difficult to separate and hence require complex treatment process like electrochemical coagulation, advanced oxidation[4] and membrane filtration[5]. While employing these high cost procedures, pre-treatment is generally considered as the primitive step that can help reduce the colour and the organic load in the wastewater. Physico-chemical treatments are generally high energy consuming which require huge amount of chemical additives while presenting a less efficiency rate and generation of sludge. The utilization of plant based adsorbents for the removal and separation of specific metals and compounds from the aqueous solution is called biosorption. There have been many literatures citing the prominent use of macro-algae species for the removal of metals from aqueous solution[6]. Similarly, biomass derived from plant materials like bark, stem, and leaves were also utilized for extraction and separation of metals and dyes from wastewater. Direct dyes like Orange-3GL, Direct Blue -67 were removed through the use of agricultural rice husk waste[7] while jute stick powder were investigated for their Congo red and Rhodamine-B adsorption capacities from their aqueous solutions[8]. The use of inexpensive adsorbents derived from agricultural waste is gaining momentum among the industries since the agro-waste is utilized for waste remediation thus reducing the raw materials cost. The efficiency of the adsorbent material corresponds to its wide range of applicability like temperature tolerance, *p*H modulation and equilibrium uptake capacity. In the line of various novel adsorbents, the leaves of *Mangifera indica* have been less utilized in the adsorption of dyes from the aqueous solutions. Generally the utilization of biomass from leaf powder poses a great risk on two different fronts: they impart colour to the solution due to presence of pigment producing compounds like chlorophyll and secondly, the finely powdered biomass is suspended in the aqueous solution thus requiring a secondary treatment like flocculation or sedimentation[9].

In the present study, the leaves of *Mangifera indica* were investigated for its potent biosorbent capacities for the removal of xanthene class dyes from their aqueous solutions. Rose Bengal dye is a type of fluorescein which have characteristically high molecular weight of 1016.67 g/mol and high aromatic carbon content linked with disodium ions (Fig. 1) as the main colour producing metal complex on chelation. Employing dye degradation techniques like advanced oxidation process might result in unprecedented production of toxic waste by-products which are difficult to detect, control and detoxify into simpler and non-toxic organic compounds. Many dyes are difficult to decolorize due to their complex structure and synthetic origin. The detection of Rose bengal dye for its presence and removal from aqueous solution at low concentrations is a tedious process. Moreover, the dye's carcinogenic effect at higher concentrations also restricts the identification for a suitable yet cost efficient treatment and safe disposal methods. The adsorption experiments were carried to determine the maximum equilibrium dye uptake capacity of the *Mangifera indica* and to compute the isotherm and kinetic parameters thereby predicting the rate of reaction through pseudo adsorption models. The spectroscopic image analysis were carried out to scrutinize the morphological changes post-adsorption[10] and the FT-IR peaks were resolved and analysed for the functional groups that take part in the adsorption of Rose Bengal dye on to *Mangifera indica* leaf powder. The adsorbents are generally desorbed and regenerated either by using 0.1N NaOH/H_2SO_4 or through organic solvents like ethanol and isopropyl alcohol. In the present study, regeneration and recycle is restricted due to following reasons: (1) Utilization of acids and organic solvents degrade the biomass with every regeneration cycle. Continuous regeneration for more than two cycles, modifies the integrity of the biosorbents thus deeming it unfit for further usage in the sorption process. (2) Rose Bengal dye is being generated from the pharmaceutical and ophthalmic industries; it is categorically advisable as not to reuse owing to their safety and biohazard precautions. Incineration was suggested as the method for disposal of the powdered MI leaves post-adsorption as it addressed two major issues: the adsorbent were saturated with the high carbon content hazardous dye which effects the higher heating value and the activation energy and secondly, the disposal through incineration generates a great demand in powdered MI adsorbent which is effectively met by fallen leaves of *Mangifera indica* thereby creating a suitable disposal system. Although there have been numerous biomass developed for the adsorption process, a cost efficient biosorbent produced from agro-waste capable of decolorizing a high molecular weighted dye has been seldom reported before. From the present study it is concluded that the adsorption of Rose Bengal dye was optimized for different equilibrium parameters using fallen *Mangifera indica* leaves as adsorbent and subsequently disposing safely through incineration.

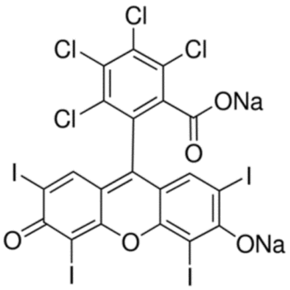

Figure 1 — Structure of Rose Bengal dye.

Experimentals Section

Preparation of adsorbent

The leaves of *Mangifera indica* were collected and washed with distilled water to be free of any surface impurities. The leaves were selected such that there was no deficiency in essential metals. The washed leaves were kept in oven at 120°C for 24 h to be devoid of moisture. The dried up leaves were then crushed, powdered and sieved at 150 micron[11]. The adsorbent thus prepared was stored in moist free desiccator and utilized as and when required.

Preparation of adsorbate

Disodium salt (30 mg) of Rose Bengal dye (CI 45440, Loba chemie, Min. 85% purity, loss on drying - max 10%) was dissolved in 1500 mL of double distilled water. The resultant concentration of the solution was 20 mg/L. The stock solution was diluted to get required concentrations of 4 mg/L, 8 mg/L, 12 mg/L, 16 mg/L and 20 mg/L. Different concentrations of Rose Bengal dye solutions were measured for their absorbance values to plot a calibration curve. From the calibration plot, the adsorbed effluent absorbance and the maximum equilibrium uptake capacities were obtained.

Characterization of adsorbent

The adsorbent prepared from *Mangifera indica* was characterized through Fourier transform infrared spectroscopy (FTIR - Perkin Elmer) to observe the resident functional groups. The FTIR scan range was kept between 4000-400 cm^{-1}. The dye adsorbed beads were also run through FTIR to identify the shift in peaks and decrease of transmission[21].

Adsorption experiments

The adsorption experiments were carried out in 100 mL Erlenmeyer flasks by taking 25 mL of Rose Bengal dye solution and varied adsorbent dosages through 0.1, 0.2, 0.3, 0.4 and 0.5g. The flasks were housed in an incubating shaker capable of variable temperatures where in which its effects were studied on the adsorption through 303, 313, 323, 333 and 343K[12]. The effect of *p*H was studied by varying the *p*H of the aqueous solution through 2-11 using 0.1N NaOH (Merck, India) or 0.1N HCl (Merck, India). Subsequently the effect of other parameters like adsorbent dosage, contact time, initial dye concentration and temperature were optimized under neutral *p*H. The adsorbate was transferred to 50 mL centrifuge tubes and was centrifuged at 4500 RPM for 10 min to separate the finely suspended particles from the solution. The removal efficiency was calculated by measuring the spectrophotometric values of the treated supernatant at λ_{max} - 547nm. All the experiments were conducted in triplicate and the concordant values are reported.

Result and Discussion

Characterization of adsorbent

The Fourier Transform Infrared (FTIR) studies conducted on the clean dried *Mangifera indica* leaf powder yield a clear picture as to what major functional groups present in them and how the sorption might be affected. The IR spectroscopic (Diamond UATR - Spectrum 2, Perkin-Elmer) analysis for the biosorbent reveals three characteristic peaks 3303, 1622 and 1028 cm^{-1} (Fig. 2). Although the alcohol –OH stretch is reflected in the range 3500-3150 cm^{-1} and is consistent with other biomass based adsorbents[13], the IR spectrum should also be compared with the spectrum of chlorophyll pigment containing compounds for their presence and likeliness. The C=C stretch at 1622 cm^{-1} and C-O alkoxy bend at 1028 cm^{-1} can be compared with the IR peaks obtained for the chlorophyll based compounds[14]. The IR spectral comparison of the control and the dye adsorbed powder reflects that a relationship can be postulated between the dye adsorption and % transmission. The subtle or minimalistic changes in the functional group only indicate that physical adsorption is more predominant compared to chemisorption. Although Freundlich isotherm may provide a better idea as to the nature and extent of chemical adsorption, the peaks for RB-MI were resolved at 3286, 2916, 1611, 1034 and 450 cm^{-1}. The transmissibility percentage was reduced compared to the control *Mangifera indica* leaf powder thus indicating a dominant physical adsorption. Also the green colour of the supernatant post-adsorption might also indicate that chlorophyll pigments[15] from the leaf might have been leached in to the aqueous solution.

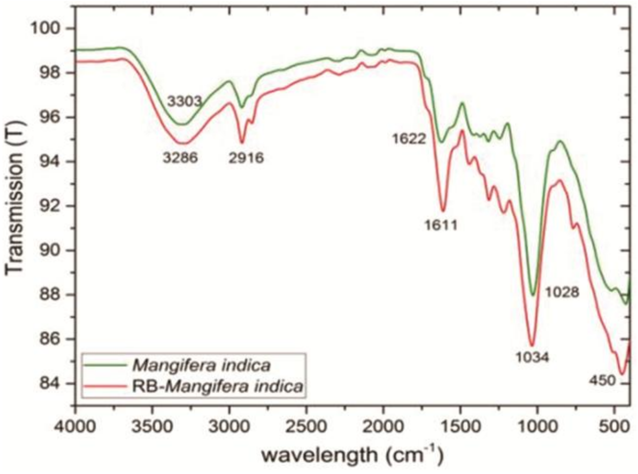

Figure 2 — FTIR comparison between *Mangifera indica* (MI) and dye adsorbed - *Mangifera indica* (RB-MI).

The morphological properties of *Mangifera indica* were studied through Scanning Electron Microscope (SEM). From the microscopic image (Fig. 3a), the irregular and patchy porous superficial that are responsible for adsorption of Rose Bengal dye were detected. The coarse uneven surface pores were completely permeated with the dye as can be evidently ascertained in Fig. 3b. The Energy Dispersive x-ray (EDS) Spectral analysis (Fig. 4c, 4d) of the control biomass and the dye adsorbed *Mangifera indica* were carried out (OXFORD - XMX N EDS detector) and the elemental compositions from a particular surface topography are tabulated (Table 1). From the EDS composition analysis it can be noted that while there is a marginal increase in the carbon and oxygen content, the adsorbent has also accumulated other trace elements present in the aqueous dye solution.

Optimization of adsorption parameters

The *p*H of the aqueous dye solution determines the adsorption rate and capacity of the adsorbent. Xanthene class dyes like Fluorescein, Eosin and Rhodamine have reasonably high molecular weight and the concentration of H+ and OH- ions plays a huge role in determining the synergy between adsorption and porous surface of the adsorbent. Every adsorbent have its own characteristic charge based on its elemental composition and their nature of valence

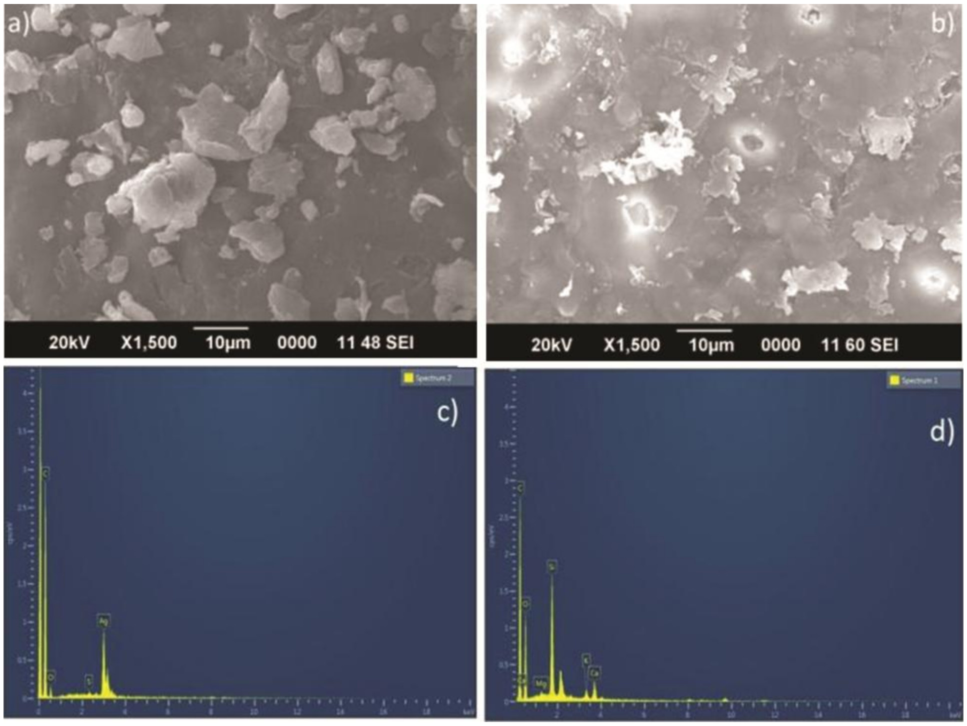

Figure 3 — a) SEM image of adsorbent *Mangifera indica* b) SEM image of dye adsorbed - *Mangifera indica* c) EDS Spectrum of adsorbent *Mangifera indica* d) EDS Spectrum of dye adsorbed - *Mangifera indica.*

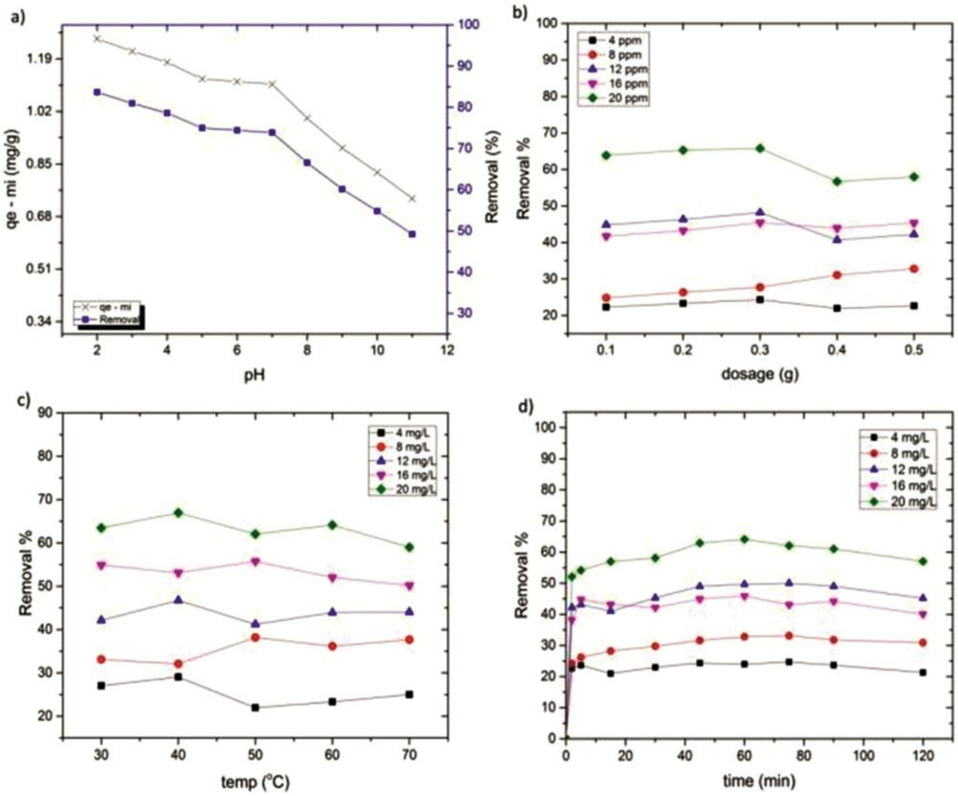

Figure 4 — a) Effect of pH on adsorption b) Effect of dosage c) Effect of temperature d) Effect of initial dye concentration and contact time on the adsorption of Rose Bengal onto *Mangifera indica*.

Table 1 — SEM EDX elemental comparison for Mangifera indica and Rose Bengal dye loaded biosorbent

Element	Wt (%)	
	MI	RB-MI
C	70.35	72.71
O	11.72	18.73
Mg	-	0.23
Si	-	6.01
K	-	0.67
Ca	-	1.65
S	0.39	-
Ag	17.54	-
Total	100	100

electrons. If the adsorbent is devoid of any charge then agglomeration or sorption of dye particles from the aqueous solution on to the adsorbent surface is not possible. Similarly, if the aqueous dye solution has distinctively high proton concentration, then a positively charged adsorbent may not be efficient and vice versa. Consequently, the zero point charge of the adsorbent plays a prominent first step in deducing the sorption mechanics[16]. In the present study, the zero point charge (pH_{zpc}) of the *Mangifera indica* leaf powder is 7.4 [figure not shown]. Therefore, it can be conceived that the adsorbent may perform well in the neutral *p*H range and the sorption of Rose Bengal is effective at *p*H 7.4. Rose Bengal dye's idiosyncratic feature is that while decreasing the *p*H to acidic range, the native pink colour of the solution is disguised or masked giving the ambiguity of colour removal. Here in the present study [Fig. 4a]. Barring the high pseudo removal percentages from *p*H 2 to 6, the adsorbent prepared from *Mangifera indica* shows a consistent 70-75% removal in the *p*H range 6.5 to 7.5. It is imperative that the experimental sorption set up is to be maintained at neutral *p*H because the natural dye *p*H is 6.7 and the adsorbent's *p*H at zero point charge is 7.4. Moreover to maintain the ionic equilibrium between the H+ and OH- ions, the *p*H of the adsorption is kept at neutral throughout.

In order to optimize the equilibrium uptake capacity the dosage of the adsorbent is fixed by varying it through different dosages and estimating their corresponding removal efficiencies[17]. The characteristic trait of physical adsorption is that as the dosage increases, the site available for adsorption increases there by increasing the dye uptake capacity. It can also be conceived that the surface area of the adsorbent is increased by the fineness of the powdered sample thereby implicating that the physical adsorption is predominant while the dosage is on surge simultaneously. Furthermore, as the dye concentration increases the dye molecules present in the aqueous solution increases thereby an increase in uptake capacity of the adsorbent. This paradox is only applicable if there are any vacant adsorption sites available[18]. In the present sorption study, two fundamentals can be postulated: as the dye concentration increases from 4ppm to 20ppm, the dye removal increases with a maximum of 67% for 20 ppm concentration (Fig. 4b). Secondly, out of 5 different dye concentrations, 3 of them viz. 4 ppm, 12 ppm and 20 ppm exhibit characteristic removal saturation at 0.2-0.3 g. It is critical that the dosage is not increased beyond the saturation limit because as the dosage increases the fine suspended adsorbent particles create complication in their removal post-adsorption. Hence 0.2 g of *Mangifera indica* leaf powder was selected as the optimum adsorbent dosage for the removal of Rose Bengal from aqueous solution. The effect of temperature on the removal efficiency was studied by varying the temperature of the incubating shaker from 30 to 70°C[28]. The different dye concentrations irrespective of the number of dye molecules present in the aqueous solution showed increased removal efficiency at 35 to 40°C with a maximum of 66.96% for 20 ppm (Fig. 4c) dye concentration, thus implying that the reaction is favourable at room temperatures.

Before determining the rate kinetics of the adsorption process, the dye retention capacity was optimized through varying the initial contact time of the adsorbent in the Erlenmeyer flask. The contact time was varied as per 2, 5, 15, 30, 45, 60, 75, 90 and 120 min and the dye concentration was varied from 4 ppm to 20 ppm. The adsorption process exhibited a similar trend of increased removal efficiency as the concentration augmented to 20 ppm. The maximum removal efficiency was reflected at 64.2% for 20 ppm (Fig. 4d) concentration in 60 min of adsorbent contact time. During the entire adsorption process, the *p*H of the solution was kept at neutral in order to optimize the equilibrium parameters[19]. All other dye concentrations showed a concordant trend by reflecting a saturated peak at 50 – 65 min at the adsorbent dosage of 0.2 g of *Mangifera indica* leaf powder. Hence the optimum equilibrium conditions were chosen as 20 ppm of initial dye concentration at 60 min contact time with 0.2 g of adsorbent dosage for the adsorption of xanthene class Rose Bengal dye on to *Mangifera indica* leaf powder. Similar literature reports can be found for the utilization of MI biomass as potential adsorbent for the removal of Pb(II) from real and simulated wastewater[20]. Adsorbents were prepared from three different MI biomass wastes, viz: native kernel, native seed and native peel. A step further, the MI waste biomass was immobilized in sodium alginate beads to test for any enhanced adsorption of Pb (II) ions. The adsorption parameters were optimized at biosorbent dose of 0.1 g, contact time-240 min for the initial Pb (II) concentration of 100 mg/mL. Although, the native MI waste biomasses showed appreciable removal efficiency up to 69% Pb(II) ions from the wastewater, immobilized biomass did not show promising uptake capacity. The native biomass was characterized through FTIR and the peaks were recorded at 3423, 2924, 2131, 1511-1631 cm^{-1}, 1324-1435 and 613-646 cm^{-1}. FTIR analysis revealed the involvement of alcoholic, amino and carbonyl functional groups in the adsorption of Pb(II). Similar peaks were resolved in the present study reiterating the adsorption capacity of MI biomass. The different biomasses used in the adsorption of Pb(II) were characterized through SEM – EDS for their composition analysis.

Isotherm analysis – equilibrium modelling

The interface between the adsorbent and the adsorbate can be closely monitored and systemized through pre-existing equilibrium models. Despite the fact that the existence of numerous adsorption sites can facilitate a better removal of adsorbate, the isotherm models help in identifying the reaction parameters that can enhance the adsorption[21]. To identify and categorize the nature of adsorption based on the optimized operational parameters, numerous isotherm models have been developed. Out of these, two isotherms namely Langmuir and Freundlich have been selected to correlate the adsorption of Rose Bengal dye on to *Mangifera indica* leaf powder[22].

To delineate the adsorption occurring in the present study, the Langmuir and Freundlich isotherms' assumptions were studied and compared. The presence of compatible sites does not ensure the adsorption of Rose Bengal dye beyond the equilibrium uptake capacity as the Langmuir model hypothesizes only monolayer adsorption. From the zero point charge (pH_{zpc}) of the *Mangifera indica* leaf powder, it is palpable that there is scarce circumstance that the adsorbent facilitates interaction of adsorbate molecules between themselves. Previous literature and research studies[23] also reflect that beyond the saturation equilibrium concentration, there was no accretion in adsorption. The following equations were used to surmise the non-linear and linearized form of Langmuir isotherm for the adsorption of Rose Bengal dye on to *Mangifera indica.*

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \qquad \text{... (1)}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \qquad \text{... (2)}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \qquad \text{... (3)}$$

It can be perceived from equation 1 that q_e, the quantity of Rose Bengal dye adsorbed per unit mass of *Mangifera indica* adsorbent is proportional to q_m, the maximum equilibrium uptake capacity. The unadsorbed effluent concentration, C_e can be determined by comparing the absorbance values with the calibration graph plotted for Rose Bengal dye. The Langmuir constant, K_a can be determined from the slope and intercept of the linear plots of equation 1. Langmuir-1 model is linearized in such a way that the plot between C_e/q_e and C_e (Fig. 5a) aids in determining the maximum dye uptake capacity and the Langmuir affinity constant[24]. Although there exists many linearized equations of Langmuir isotherm model, Langmuir – 2 plot between $1/q_e$ and $1/C_e$ (Fig. 5b) as expressed in equation 2 provides a good comparison of parameters with those obtained from Langmuir – 1 model[25]. The regression coefficients obtained from the two plots are tabulated (Table 2) along with the isotherm parameters and compared. Different dye concentrations exhibit varied r^2 values but a commonality is reflected for 4 ppm and 12 ppm in both the models. The theoretical uptake capacities were compared with the actual experimental values and Langmuir –1 model exhibit a close alignment with the adsorption taking place in the present experimental study.

The synergy between the adsorbate and the adsorbent towards adsorption can be expressed in terms of dimensionless separation factor (R_L) using the equilibrium data from Langmuir isotherm plots[26].

$$R_L = \frac{1}{1 + k_1 C_i} \qquad \text{... (6)}$$

From the equation 6, the favorability of the adsorbent towards adsorption can be defined with respect to R_L which is affected by the expression k_1C_i. The generic domain of R_L which lies between 0 and 1 is deemed as favorable and can be confirmed from the

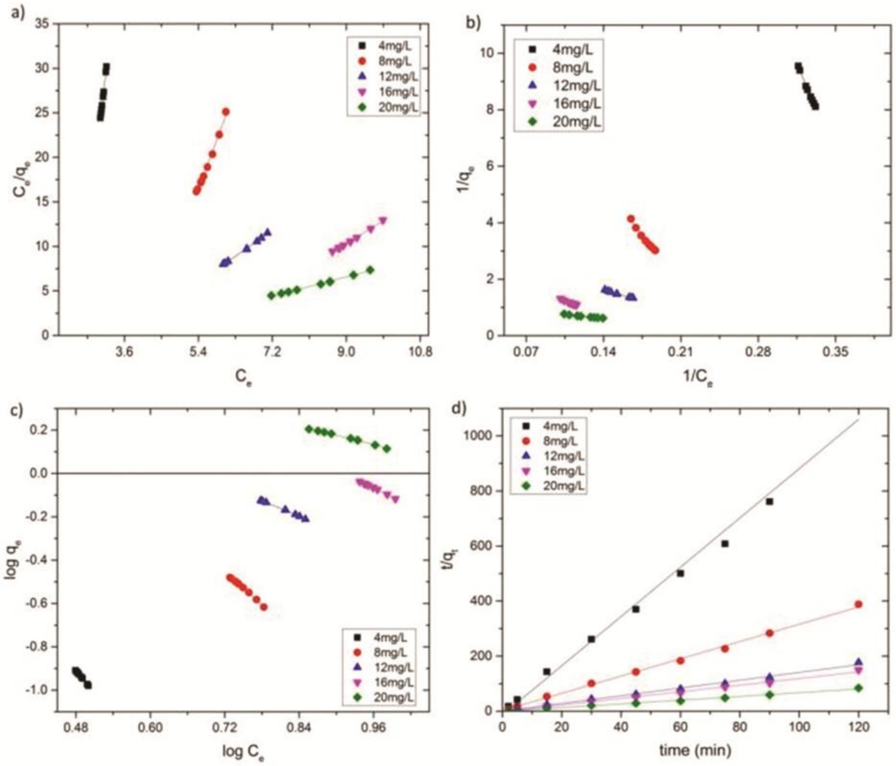

Figure 5 — a) Langmuir – 1 isotherm model b) Langmuir – 2 isotherm model c) Freundlich isotherm model d) Pseudo second order – 1 model for the adsorption of Rose Bengal onto *Mangifera indica*.

Table 2 — Langmuir and Freundlich isotherm parameters calculated from isotherm plots

Isotherm plot	parameter	Rose Bengal dye concentrations (mg/L)				
		4	8	12	16	20
	q_m	0.025	0.079	0.306	0.344	0.824
langmuir 1	k_a	0.416	0.243	0.280	0.183	0.280
	r^2	0.998	0.991	0.997	0.997	0.996
	R_L	0.603	0.514	0.297	0.341	0.178
	q_m	0.025	0.079	0.308	0.345	0.832
langmuir 2	k_a	0.417	0.244	0.281	0.184	0.284
	r^2	0.996	0.983	0.991	0.990	0.977
	R_L	0.599	0.513	0.296	0.340	0.176
	1/n	3.440	2.544	1.204	1.405	0.731
Freundlich	k_F	2.096	3.966	2.256	3.604	2.304
	r^2	0.999	0.996	0.998	0.998	0.994

Langmuir plots. The adsorption is presumed linear, when k_1 is 0 and RL is equal to 1. This linear adsorption can be conceived to be an asymptote which is similar to a typical adsorption reaction after equilibrium. The linear adsorption can also be arbitrated as a system which is dependent on maximum equilibrium uptake capacity q_m and effluent concentration C_e, has no free adsorbent molecule for adsorption. For the reaction to be unfavorable, the k_1 value has to be negative suggesting $-1 < C_i*k_1 < 0$ which is possible if the entire system begins in desorption. This hypothesis can be applied if the adsorbent is reused after regeneration where there is presence of trace amount adsorbate molecules resident from previous adsorption. In the present study, the biosorbent is not regenerated or recycled and hence the $R_L > 1$ hypothesis is not pertinent to the sorption of Rose Bengal dye onto MI biosorbent. Similarly at $R_L = 0$, the sorption is said to be irreversible suggesting that the k_1 value of the system is predominantly high and cannot be controlled. From the Langmuir plots (Fig. 5a and 5b), the R_L value for all the dye concentrations in the present study was found to be less than 1 (Table 2). The linear fit of the Langmuir 1 plot is fairly good under whole range of concentrations (4-20mg/L) studied and were found to be similar with previous findings[27].

On the contrary, Freundlich isotherm considers the maximum adsorptive capacity is proportional to concentration of the adsorbent[28]. This adequately surmises that, as the concentration increases and the sorption site availability increases, the adsorption increases. Following equations represent the isotherm model based on the assumption that process follows a single-solute sorption.

$$q_e = K_F C_e^{\frac{1}{nF}} \quad \text{... (4)}$$

$$\log(q_e) = \log(K_F) + \frac{1}{nF}\log(C_e) \quad \text{... (5)}$$

From the above equations, a linear plot log q_e vs log C_e (Fig.5c) aids in identifying the adsorption intensity 1/n, and the Freundlich isotherm constant K_F, for the adsorption of Rose Bengal on to *Mangifera indica* powdered biosorbent. From the tabulated correlation r^2 values, it can be noted that apart from 4ppm and 12ppm, other dye concentrations also fitted perfectly with the model thus implicating our assumption that multi-adsorption may be prevailing over Langmuir.

Adsorption kinetics

The adsorbent's architectural framework of the pores and their surface morphology arbitrates the efficiency of the adsorption system. Envisioning the rate of sorption for the present study depends on the adsorbate contact time and the reactor's physical dimensions. For a batch process, the adsorbent's dosage per equivalent of adsorbate concentration can satisfy the parameters required for determining the system kinetics. The complexion involving the adsorbate-adsorbent synergy and the rate of reactions were depicted using many mathematical expressions in the past. However Lagergren's modified pseudo-first order[29] and Ho-Mckay's pseudo second order[30] models are the two most decisive equations that are preferred over others in determining the adsorption mechanisms. Following equations represent the Lagergren's linearized pseudo first order model for the adsorption of Rose Bengal on to *Mangifera indica* leaf powder.

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \text{... (7)}$$

The relationship between the first order rate constant k_1 and the dye adsorbed at equilibrium concentration q_e, helps in distinguishing the reaction kinetics of the present study. The kinetic parameters were determined from slope and intercept of the graphical plot between log (q_e-q_t) vs t (figure not shown). From the tabulated results (Table 3) the model showed poor compatibility thus concluding that the adsorption's dynamism cannot be represented through pseudo first order model.

$$\frac{dq}{dt} = k_2(q_e - q_t) \quad \text{...(8)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{...(9)}$$

Equations 8 and 9 represent the pseudo second order and its linear form respectively that aids in determining the rate of reaction. The fundamental principle underlying the pseudo second order model is that the chemical forces are predominant and the adsorption is adapted and transmogrified due to the sharing of valence electrons between *Mangifera indica* leaf powdered adsorbent and Rose Bengal dye molecules. The second order kinetic constant k_2 was

Table 3 — Pseudo adsorption dynamic parameters

Isotherm plot	parameter	Rose Bengal dye concentrations (mg/L)				
		4	8	12	16	20
pseudo 1st order	k_1	0.091	0.046	0.067	0.047	0.058
	q_e	0.105	0.336	0.384	0.245	0.570
	r^2	0.311	0.966	0.681	0.214	0.867
pseudo 2nd order 1	q_e - exp	0.120	0.320	0.745	0.917	1.603
	k_2	13.959	1.816	0.942	5.615	0.908
	q_e - cal	0.108	0.313	0.689	0.806	1.440
	r^2	0.990	0.997	0.993	0.993	0.995
pseudo 2nd order 2	k_2	51.329	4.231	3.463	3.396	1.474
	q_e - cal	0.113	0.308	0.688	0.858	1.486
	r^2	0.316	0.836	0.347	0.393	0.651

determined through the plot between t/q_t and time - t (Fig. 5d), where q_t is the dye uptake quantity at given time. The correlation r^2 co-efficient values from the tabulated results predict that pseudo second order might be favourable in determining the kinetics for the adsorption of Rose Bengal dye. The dye uptake capacities for different concentrations were predicted using the second order model and compared with the experimental values. The experimental error appears to be minimal as they align intricately with the r^2 values ranging 0.990, 0.997, 0.993, 0.993 and 0.995 for 4 mg/L, 8 mg/L, 12 mg/L, 16 mg/L, and 20 mg/L dye concentrations respectively.

Thermal degradation studies

The kinetics involved in the thermal degradation of biomass is crucial in the yield of biofuel through thermochemical pyrolysis[31]. The fuel's volatility is determined through the rate of change of mass due to thermal degradation at a constant heating rate. Albeit the heat flow into the biomass vs. heat capacity projects the rate and amount of thermal release per mass of the sample, the decomposition of biomass is a complex 3-step process (4 stages, in certain biomass samples). The thermal degradation of biomass was carried out in range 35 to 900°C. Extensive literature survey reveals that between 100–300°C, non-combustible gases comprising water vapor generated from the hydroxyl groups and weak acids that may be existent in the biomass. In this temperature range, the biomass would be converted to char simultaneously while releasing non-combustible gases and tars. The effective pyrolysis is known to occur between 300–600°C wherein which the combustion products are released from char-like biomass. While TGA analysis of activated carbon prepared from biomass materials reveal abundant fixed carbon, the pyrolysis of biomass samples may exhibit a complex two stage degradation in between 300-600°C due to the presence of both fixed and volatile carbon content[32]. In certain biomass samples, owing to the high carbon content in its native state, the rate of degradation would be slow thereby affecting the kinetics and the activation energy of the biomass.

In the present study, 1.565 mg of finely powdered *Mangifera indica* biomass was subjected to thermal degradation in nitrogen atmosphere with gas flow 20 ML/min at a constant heating rate of 20°C /min. The homogenous lignocellulosic biomass exhibited an initial weight loss of 9.35% owing to the hydroxyl components present [Fig. 6a]. A rapid weight loss peak was noted at 44.97°C with a maximum weight loss rate of 0.0689 mg/min. a second stage major weight loss of 55.16% was identified between 220–400°C wherein the char production and preliminary degradation of hemicellulose content in the biomass. Between 400–530°C, majority of volatile gases are released which can be studied from the thermogram. In this 200–530°C temperature range, 85.8% of biomass' weight loss occurs with total of 1.043 mg thus revealing that the active degradation of biomass has taken place. This can be corroborated through the second significant derivative weight peak at 526°C with a weight loss rate of 0.0567 mg/min. Beyond 550°C, there is no appreciable weight loss and at 900°C the residue is computed to be 4.85% of the total biomass.

The rationale behind the thermogram of dye adsorbed *Mangifera indica* biomass is that the potential of fuel capabilities are studied due to the high carbon content in their adsorption sites. The Rose Bengal dye was adsorbed on *Mangifera indica* biomass and the adsorption was optimized at maximum equilibrium uptake efficiency of 67%. This emblematically delineates that roughly 67% of increased carbon content is present on the surface of the biomass which may or may not be homogeneous. In order to tap the carbon content and utilize them as a potential fuel source, the activation energy and thermal weight degradation rate at constant heating rate is studied. 1.42 mg of dye adsorbed *Mangifera indica* biomass was subjected to thermal degradation and the TGA-DTA profile exhibit an initial weight loss of 9.5% [Fig. 6b] due to surface and interstitial moisture. The lignocellulosic and hemicellulosic degradations were computed at 46.06% and 37.59% respectively. The total weight loss of the dye loaded biomass was enumerated at 1.323 mg and 6.85% of the biomass was residue after 900°C. This peculiarity could be substantiated with two logical conclusions. The physical adsorption of Rose Bengal dye on to *Mangifera indica* hatched and housed high molecular weighted and interlinked carbon which in-turn affected the rate of degradation. This can be clearly noted at the two derivative peaks marked at 46.04°C and 528.5°C with corresponding rate of weight loss of 0.0406 mg/ min and 0.0506 mg/min respectively. Furthermore, the sample continued to degrade till 650°C thus prolonging the saturation residue point.

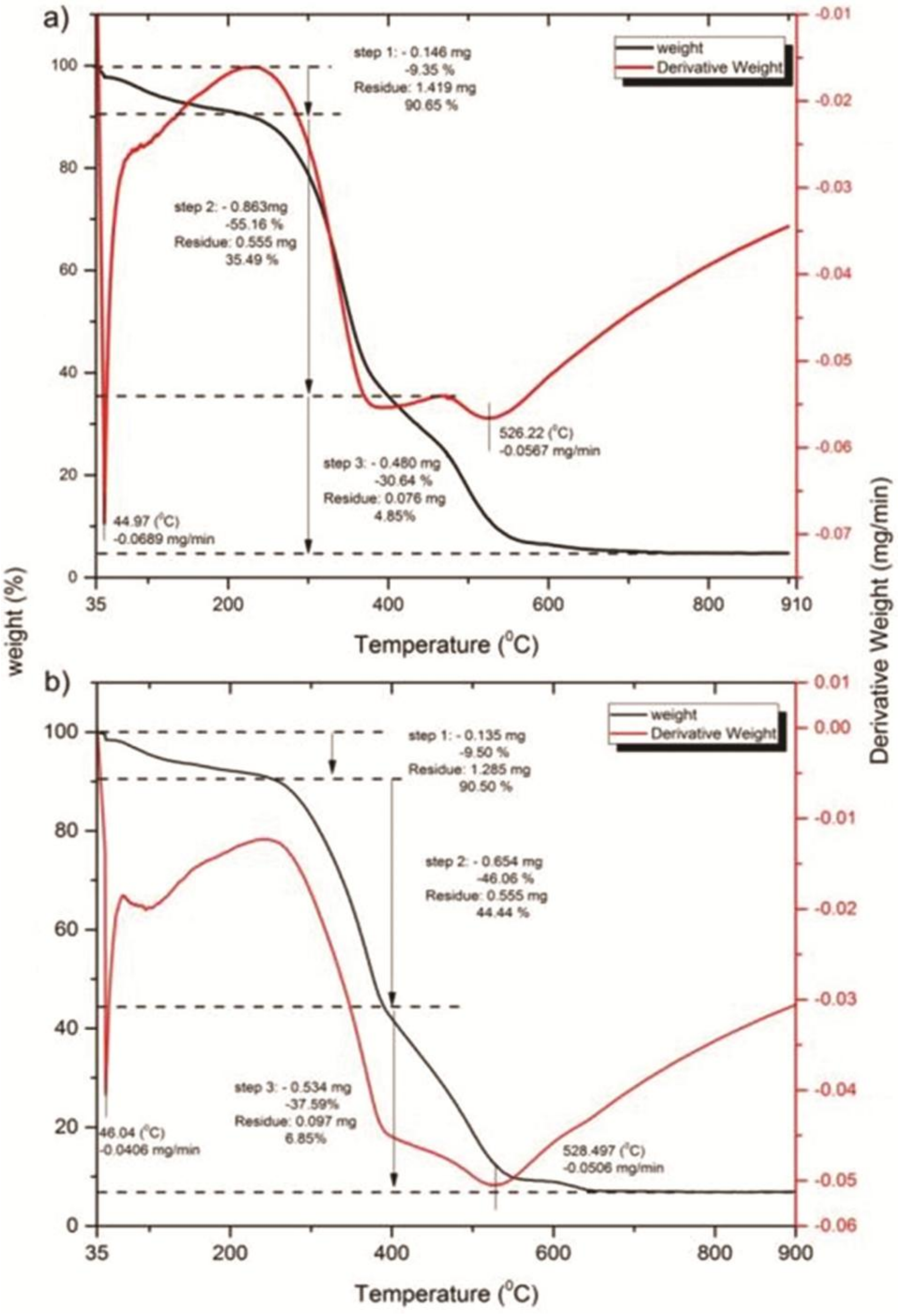

Figure 6 — a) TGA plot for *Mangifera indica* b) TGA plot for Rose Bengal dye adsorbed *Mangifera indica* biomass

Conclusion

In the present study, *Mangifera indica* (MI) leaf was powdered and used as biosorbent for the removal of Rose Bengal dye from aqueous solutions. The following conclusions were drawn from the present study.

1 The adsorbent's dosage was optimized at 0.2 g while keeping the *p*H of the solution at neutral in order to facilitate the H^+ and OH^- ionic equilibria. The equilibrium conditions were optimized at 20 ppm of dye concentration with adsorbent's contact time of 60 min. The adsorption's temperature was kept at room temperature (30 ± 3°C) which had a maximum of 67% removal efficiency.

2 The IR spectroscopic analysis for the MI biosorbent reveals three characteristic peaks 3303, 1622 and 1028 cm^{-1}, while the peaks for dye adsorbed

biomass were resolved at 3286, 2916, 1611, 1034 and 450 cm^{-1}. The surface morphology was studied under scanning electron microscope and energy dispersive x-ray spectroscopy to ascertain the difference before and after adsorption.

3 The MI adsorbent exhibited the highest q_e value of 0.824-0.832 mg/g for 20 mg/L dye concentration while it offered a least uptake capacity of 0.025 mg/g for 4 mg/L. The pseudo second order model – 1 was found to be a perfect fit for the determination of kinetics and the rate of adsorption which can be corroborated with the r^2 values ranging 0.998 and 0.997 for 4 ppm and 8 ppm while 0.999 for all other dye concentrations.

4 The adsorbents were subjected to thermogravimetric analysis the lignocellulosic and hemicellulosic degradations were computed at 46.06 and 37.59% respectively. The total weight loss of the dye loaded biomass was enumerated at 1.323 mg and 6.85% of the biomass was residue after 900°C.

Future Scope and recommendations based the present study

In the present study, the Rose Bengal dye has been studied at the concentration range of 4-20mg/L. As a future scope, the adsorption can be studied for higher dye concentrations using different adsorbents. Moreover, degradation studies can be taken in future and the dye degradation pathway through various advanced oxidation process can be studied.

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