Original Research Article

STUDIES ON REMOVAL OF CONGORED FROM WASTE WATER USING NaOH TREATED FALLEN LEAVES OF FICUS RACEMOSA

ABSTRACT

NaOH treated biosorbent Ficus Racemosa Leaf Powder(NaFRLP) was prepared from the fallen leaves of the Ficus racemosa plant. The biosorbent was characterized by FT-IR, SEMand BET. The biosorbent was found to be mesoporous with an average pore size 18nm.Batch adsorption equilibrium experiments were conducted for the adsorption of Congo red on NaFRLP as a function of adsorbent dosage, agitation speed, dye concentration, pH, temperature and contact time. Batch adsorption studies revealed that with an increase in the time of adsorption, the percent removal of congo red increases and with an increase in the concentration of the solution, congo red removal decreases. The adsorption datawell fitted with the Langmuir isotherm. Thermodynamic analysis of the batch adsorption studies indicated that all the processes studied were spontaneous with the congo red adsorption on NaFRLP being endothermic. Intra particle diffusion model was also tested. NaFRLP was found to be an effective adsorbent for the removal of Congo red from the industrial waste water.

Comment [O1]: No numerical results stated in the abstract

Keywords: Congo red, Ficus racemosa plant leaf, FT-IR, SEM, BET Analysis.

1. INTRODUCTION

Removing pollutants from water is the crying need of the hour and developing a cost effective and environmentally safe method to achieve the same is a challenging task for chemical engineers. All the dye wastes, produced from different sorts of commercial enterprises have harmful impacts on microbial inhabitants and may be toxic and even deadly to mammals. These dyes have the potential to cause diseases such as allergic eczema, skin irritation problem, mutations and cancer. The excessive utilization of dyes causes problems in the environment. This prevents sun rays infiltration into the water and declines photosynthetic activity which additionally brings about problems in the atmosphere. The dye affects the life-cycle of amphibian creatures and plants. They cause depletion of dissolved oxygen due to conjointly increase in the biological oxygen demand (BOD) to sustain marine life. As few dyes are horrendously carcinogenic, they cause damage directly or inhibit their chemical action abilities. At low concentrations, dyes cause adverse effect on the marine life and therefore, the food cycle. Dyes have molecules in equilibrium, created to fight against the degradation by sunlight, biological, chemical and many other areas.

Approximately a million metric tons of dyes are produced annually in the era of azo dyes (R_1-N=N-R_2), which imply about 72% of the total dyes. About 60,000 metric tons of dyes are being made in India, which is roughly 1/20th of total world production. According to the recent survey, about two third of its market are being utilized in textile industries. It has been demonstrated that 14% of the artificial textile dyes utilized consistently are released to water streams. Waste water treatment plants are the real wellsprings of these to the environment. Because of the obstinate and complex nature in structure of dyes, it is extremely hard to decolorize dyes, which makes it mandatory to dispose them from waste stream before being tossed out into the main stream.

Adsorption has emerged as promising technique for dye removal. The advantages are, Dyes at low concentration can be removed, Effluent discharge concentration meets the government regulation, system operates over the broad pH ranges (2-9). System is effective over a temperature range of 4-90^0 C , system offers low capital investment and low operation cost, simple design and easy operation.

Activated carbon has been found to be a versatile adsorbent which can remove diverse types of pollutants such as metal ions, dyes, phenols and a number of other organic and inorganic compounds and bio-organisms. Due to the higher cost of activated carbon, attempts are being made chemically and thermally to regenerate the spent activated carbon. However, these methods are not very cheap and also produce additional effluents and result in considerable loss of the adsorbent.

Biosorption process is known as an attractive biotechnological process which employs naturally abundant or waste biomass for removing most types of heavy metals and dyes from aqueous solutions. The closest analogy for biosorption is represented by ion exchange resins and biosorbents can be referred to as natural ion exchangers [1]. The overall incentives of biosorption development for industrial processes are: (a) low cost of biosorbents, (b) great selectivity and efficiency for dye removal at low concentration, (c) potential for biosorbent regeneration (d) high velocity of sorption and desorption, (e) limited generation of secondary residues and (f) more environmental friendly life cycle of the material [2].

The major parts of plant leaves are composed of cellulose, hemicellulose, pectins and lignin etc., [3], which contain various types of functional groups such as carboxyl, hydroxyl, carbonyl, amino, nitro [4] and hence can interact with functional groups of dyes. This interaction in turn leads to binding of dyes with leaves biomass[5-7].Ficus racemosa plant parts have already been used as biosrbents for the removal of dyes, metal and nonmetal ions [7-9].Earlier studies for the removal of congored from textile waste water using various biosorbents like leaf, fruit shell, fly ash, teawaste etc., have been reported [10-13].

Comment [O2]: Error in spelling of biosorbents

In the present study it was therefore desired that Biosorbents as alternative raw materials be chosen that are region specific, easily available, inexpensive and without much commercial applications. In the present study,congored identified for adsorption on to NaOH treated*Ficus racemosa* fallen leaf powder(NaFRLP). Batch studies were carried out in order to examine the potential of these adsorbent for adsorption of dyes from solution.

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2.MATERIALS AND METHODS

2.1 Chemicals Used: Congored waspurchased from Merck, HCl and NaOH of Analar grade were used to maintain pH.

2.2Congored

Congo red is the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid)(formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol). It is a secondary diazo dye. Congo red is water soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol. It has a strong, though apparently non-covalent, affinity to cellulosefibers. However, the use of Congo red in the cellulose industries (cotton textile, wood pulp and paper) has long been abandoned, primarily because of its toxicity and tendency to run and change color when touched by sweaty fingers. It is investigated as a mutagen and reproductive effectors. It is a skin, eye and gastrointestinal irritant. It may affect blood factors such as clotting and induce somnolence and respiratory problems [14].

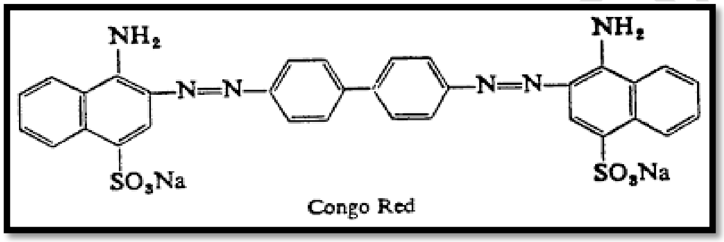

Fig.1.Structure of Congo red

2.3PREPARATION OF BIOSORBENT FROM *FICUS RACEMOSA LEAF* POWDER *(FRLP)*

Fig.2. Ficus racemosa Leaves

Ficus racemosa leaves used in this study was collected from Theni. It was washed with double-distilled water to remove any unwanted particles and dried in an air oven at 70 °C for 24 h. The raw biosorbent was then crushed and ground using ball mill and sieved to get uniform size (150-mesh) particles. Ficus racemosa leaf powder(FRLP) was treated with 2% NaOH in the ratio 1:5 under stirring speed 400rpm for about half an hour at 40°C.The then NaOH treated biosorbent (NaFRLP) was washed thoroughly with distilled water several times and dried naturally. NaOH treatment helps in the removal of lignin from the biomass, thus creating porous material.The particles were then stored in sealed glass containers and used in all the adsorption experiments.

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2.4CHARACTERIZATION OF BIOSORBENT

The biosorbent was characterized by Fourier Transform Infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) analysis.The adsorption/desorption isotherms and pore volumes of the adsorbents were determined by nitrogen adsorption–desorption isotherms, measured at 77 K using Quanta chrome Autosorb 1C system. The samples were degassed at 200°C under vacuum before starting N_2 adsorption. Surface area and pore volumes (or pore size distribution) were determined using the Brunauer–Emmet–Teller (BET) equation and Barret–Joyner–Halenda (BJH) methods respectively.

2.5BATCH ADSORPTION STUDIES

Batch adsorption equilibrium experiments were conducted for the adsorption of Congored on NaFRLP as a function of adsorbent dosage, agitation speed, dye concentration, pH, temperature and contact time. This was done by adding 1 g/L of adsorbent to 300 ml of adsorbate solution of concentration (100 mg/L) having a known pH in a conical flask and mixed on a magnetic stirrer with hot plate at 313 K for 90 mins. Based on the effect of adsorbent dosage, different adsorbent dose of 0.1, 0.3, 0.7, 1, 1.5 and 2 g/L was added in each conical flask containing 300 ml of adsorbate solution of concentration (100mg/L), and was stirred for 90 mins. Based on the effect of dye concentration, 1 g/L of adsorbent was added to each conical flask containing 300 ml of adsorbate solutions of different concentrations of 100, 200, 300, 400, 500, 600, 700 and 800 mg/L which was stirred for 90 mins. Based on the effect of contact time, 1 g/L of adsorbent was added to 300 ml of adsorbate solution of concentration (100 mg/L) and was stirred at different time intervals of 15, 30, 45, 60, 75 and 90 mins. Furthermore, the solution was withdrawn from the reaction mixture at a fixed time interval, and was filtered using Whatman no.1 filter paper. The amount of unadsorbed dye in the supernatant solutions was measured with the aid of a JASCO UV - visible spectrophotometer at wavelengths of 498nm for congored , the amount of adsorption at equilibrium (q_e) (mg/g) and the percentage adsorption were computed as follows:

$$q_e = [(C_0 - C_e) V/M]$$

Comment [O5]: Give number to equations: example (1); (2)

$$\%\ \text{of dye adsorbed} = [(C_0 - C_e)/C_0] \times 100$$

Where; Co and Ce are the initial and final dye concentration respectively (mg/L) at any time (t). V is the volume of the solution (L) and M is the mass of the adsorbent used (g).

2.6KINETICS OF BIOSORPTION

Biosorption kinetics has been divided into two steps: a very rapid initial adsorption step followed by a slow adsorption step [15]. The kinetics of biosorption is essential to determine the efficiency of the sorbent. The pseudo-first order rate equation can be described as follows:

$$\frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1\, t}$$

Where q_1 is the maximum biosorption capacity (mg/g); and qt is the amount of dye biosorbed at equilibrium (mg/g); K_1 is the pseudo first-order-rate constant (min^{-1}). The pseudo-second-order rate equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_2}^2} + \frac{1}{q_2}\, t$$

Where q_2 is the maximum biosorption capacity (mg/g); qt is the amount of dye biosorption at a certain equilibrium (mg/g); k_2 is the equilibrium rate constant (g/mg min).

Comment [O6]: Give number to all equations always

2.7INTRAPARTICLE DIFFUSION

In order to investigate, if film or pore diffusion was the controlling step in the adsorption, intra-particle diffusion model was further tested as follows [16]:

$$q_t = k_i t^{1/2}$$

Where k_i (mmol g^{-1} $min^{-1/2}$) is the intra-particle diffusion rate constant and q_t (mmol g^{-1}) represents the amount of dye adsorbed on the adsorbents at time t (min).

2.8ADSORPTION ISOTHERM

2.8.1 LANGMUIR ADSORPTION ISOTHERM

Langmuir adsorption isotherm was studied by surface kinetic approach [17,18].The linearized Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{1}{K_a Q} + \frac{1}{Q} C$$

A plot of $\frac{C_e}{q_e}$ against C_e will be linear showing the applicability of Langmuir adsorption isotherm. K_a and Q_m are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively which are calculated from slope and intercept of the plot $\frac{C_e}{q_e}$ against C_e. The essential characteristics of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter 'R_L' which is defined by

$$R_L = \frac{1}{1+bC_i}$$

Where, C_i = initial concentration of the dye and b = Langmuir constant. R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$) and linear ($R_L = 1$)

2.8.2 FREUNDLICH ADSORPTION ISOTHERM

The Freundlich isotherm model [19,20]is the earliest known equation describing the adsorption process.

$$\log q = \log K_F + \frac{1}{n} \log C$$

A plot of $\log C_e$ verses $\log q_e$was linear, where K_F is measure of adsorption capacity (mg/g) and n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible ($1/n = 0$), favourable ($0 < 1/n < 1$) and unfavourable ($1/n > 1$) [21]. The values of 1/n and K_F can be calculated from the slope and intercept respectively.

2.9THERMODYNAMIC PARAMETERS

The equilibrium constant (K_d, L/g) for the adsorption of congored on NaFRLP biosorbent was calculated at the temperatures of 298, 303, 308 and 313 K using $\boldsymbol{K_d = \frac{Q_e}{C_e}}$

Thermodynamic parameters, Gibbs free energy change (ΔG^0), the enthalpy change (ΔH^0) and the entropy change (ΔS^0) were calculated using following equations:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where R is the universal gas constant (8.314 J/(mol K)) and T is the absolute temperature (K). The values of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the plot $\ln K_d$ versus 1/T.

3. RESULTS AND DISCUSSION

3.1CHARACTERIZATION OFNaFRLP BIOSORBENT:

The surface functional groups in biosorbent (NaFRLP) were examined using FT-IR. The spectrum was measured between 4000 to 400cm^{-1} and presented in Fig.3. The presence of peaks at 3443,2920,2377,1607 and 1329 cm^{-1} correspond to the vibrational frequencies of functional groups -OH or -NH2, - CH2, C=C or C=N , C=O and C-O[8] respectively.

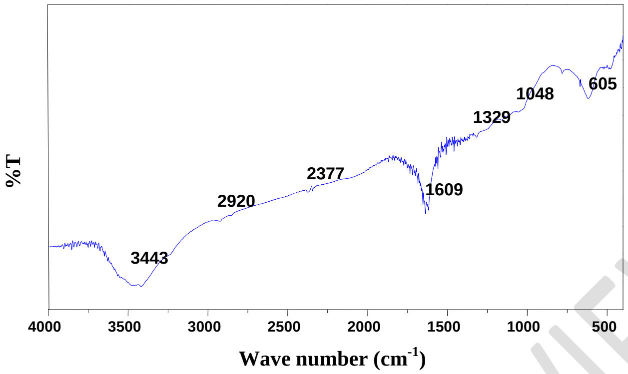

Fig.3. FT-IR spectrum of NaFRLP biosorbent

The SEM image of biosorbent in Fig.4shows the distribution of large pores and thus endowed with greater surface area.

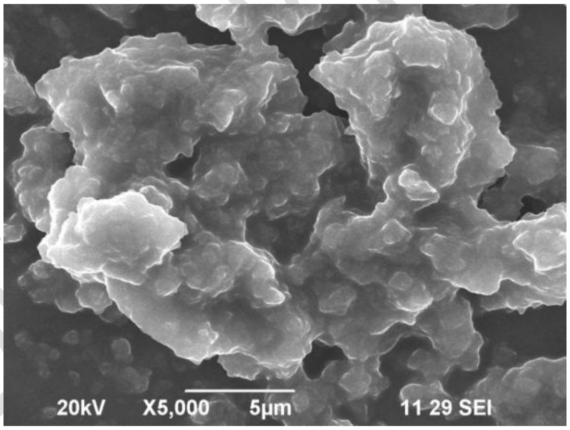

Fig.4. SEM image of NaOH treated Ficus Racemosa Leaf Powder (NaFRLP)

3.2 BET SURFACE AREA

The biosorbent sample surface area was found to be 192m^2g^{-1}, which is an indicative of the material with high pore volume (Fig.5). Adsorption byNaFRLP adsorbent follows type IV isotherm, characteristic of mesoporous materials and type H1 hysteresis loop. The pore size distribution calculated from desorption branch of the N_2 isotherms by the BJH method, showed an average pore size of 18nm, thus confirming the presence of mesopores in NaFRLP adsorbent.

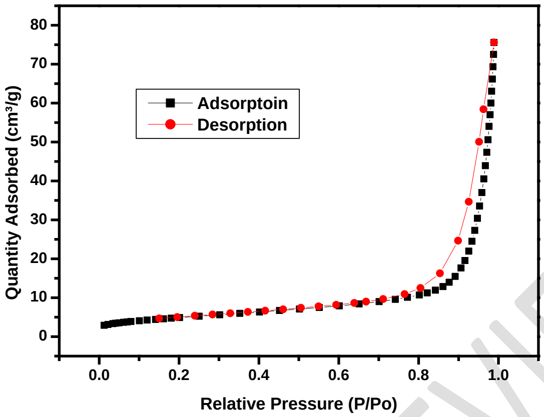

Fig.5. BET surface area

Comment [O7]: FTIR; SEM and BET analysis may be obtain before and after biosorption for detail accountability.

3.3EFFECT OF OPERATIONAL PARAMETERS

3.3.1EFFECT OF VARIATION OF INITIAL DYE CONCENTRATION

The effect of initial concentration was studied by varying the initial concentration of dye keeping other factors constant. At an optimum initial concentration of dye (100 mg/L on NaFRLP), the percentage removal was noted to be maximum. The experimental values of the extent of removal of dyes indicate that the rate of removal of dye decreases with the increase in the initial concentration of dye and vice versa. This is due to the fact that after the formation of mono layer at the lower initial concentration of dye over the surface of adsorbent any further formation of layer of dye species is highly hindered. The variation can be represented as in Fig.6. This suggest that the adsorption of dye may either block the access of dyes, to the initial pores or cause particles to aggregate and thereby reducing the availability of required number of active sites for adsorption [22].

Table1. Effect of initial dye concentration on % removal Congored

Adsorbent dose (w) = 1 g/L, Agitation time t = 90 min, Agitation speed = 200 rpm, Temperature = 313 K

Initial dye concentration (mg/L)	% Removal
100	95
200	86
300	75
400	66
500	56
600	45
700	35
800	20

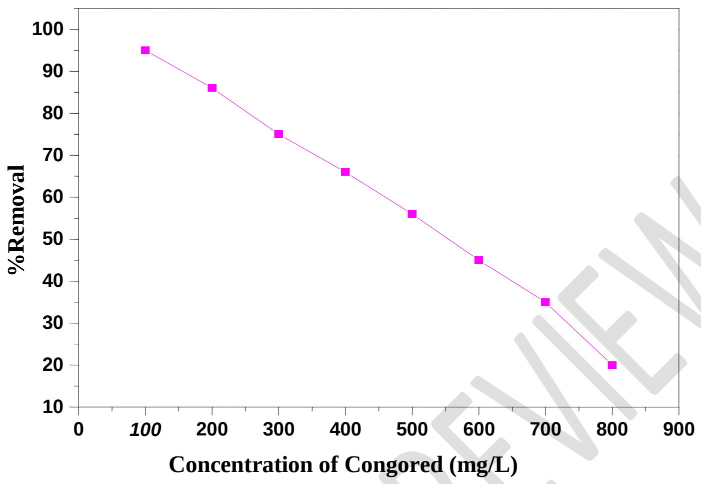

Fig.6. Effect of Dye concentration

3.3.2EFFECT OF AGITATION SPEED

The adsorption capacity of NaFRLP calculated at different agitator speed is given in Table 2. Fig.7 showed the adsorption capacity and percent removal of dye using NaFRLP increase with increasing agitator speed up to 200 rpm. Beyond that, the adsorption capacity and percent removal of dye decrease. The increase in degree of agitation speed reduces the film boundary layer surrounding the particles and hence adsorption capacity. With further increase in agitation speed, some amount of dye adsorbed in the surface of leaf powder, desorbed due to the centrifugal force, and as a result bound dye gets desorbed [23].The maximum adsorption capacity is achieved at agitator speed of 200 rpmand maximum percent removal of dye at this condition is 95.58%.

Table 2. Effect of adsorbent dosage on % removal Congored

Initial dye concentration = 100 mg/L, Agitation time t = 90 min, Agitation speed = 200 rpm,

Temperature = 313 K

Asorbent speed (rpm)	**% Removal**
50	35
100	44
150	60
200	95
250	95
300	95
350	80

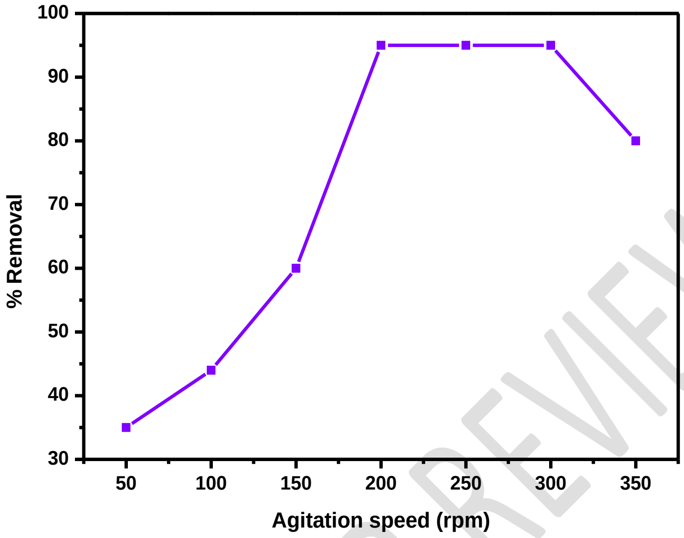

Fig.7 Effect of Agitation speed

3.3.3EFFECTS OF ADSORBENT DOSAGE

The NaFRLP dosage was varied from 0.1 to 2 g L^{-1} with a constant initial congored concentration of 100 mg L^{-1} and agitation time of 90 minat 298 K. Fig.8 shows the effect of adsorbent dosage on the % removal of dye at equilibrium conditions. It was observed that the amount of dye adsorbed varied with varying adsorbent dosage. An increase in the adsorbent dosage from 0.1 to 1 g L^{-1} resulted in a rapid increase in the uptake congored. Further increase in the NaFRLP dosage, however, did not result in a sufficient increase in the adsorption capacity of NaFRLP. The increase in the % adsorption of dye is related to the adsorption sites in NaFRLP. At lower adsorbent dosage, the dye molecules compete for adsorption at limiting adsorption sites. However, as the quantity of NaFRLP is increased, the greater availability of adsorption sites promotes adsorption resulting in agreater percentage of removal of dye [24].

Table3. Effect of adsorbent dosage on % removal Congored

Initial dye concentration = 100 mg/L, Agitation time t = 90 min, Agitation speed = 200 rpm, Temperature = 313 K

Asorbent dose (g/L)	% Removal
0.1	22
0.3	44
0.5	58
0.7	75

1	95
1.5	87
2	80

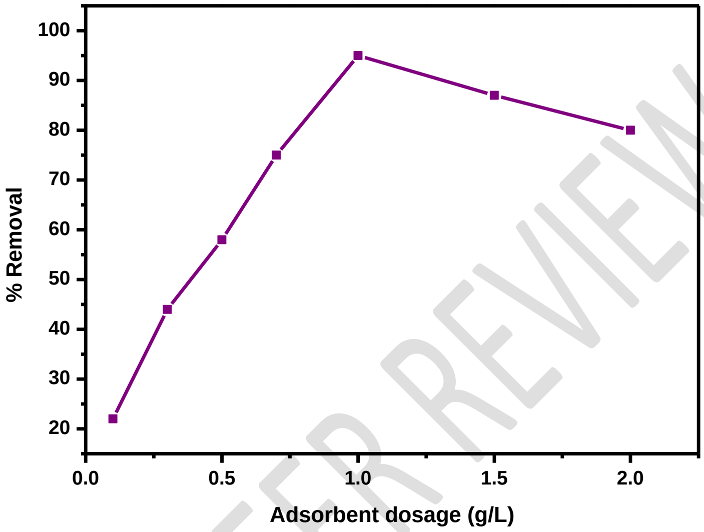

Fig.8 Effect of adsorbent dosage

3.3.4 EFFECT OF CONTACT TIME

Contact time plays an important role in affecting efficiency of adsorption. Contact time is the time needed for adsorption process to achieve equilibrium when no more changes in adsorptive concentration were observed after a certain period of time. This contact timedepends on the differences in the characteristics properties of the adsorbents. In order to optimize the contact time for the maximum uptake of congored, contact time was varied between 10 minute – 90 minute on the removal of congored from aqueous solutions in the concentration of congored100 mg/L, adsorbent dose 1 g/L, and 313 k temperature (Fig.9). The results obtained from the adsorption capacity ofcongoredonto NaFRLPshowedthat the biosorption increases with increase in contact time until it reached equilibrium [25].

Table 4. Effect of contact time on % removal Congored

Initial dye concentration = 100 mg/L, Adsorbent dosage = 1 g/L, Agitation speed = 200 rpm, Temperature = 313 K

Contact time (min)	% Removal
15	40
30	57
45	60
60	70
75	80
90	95

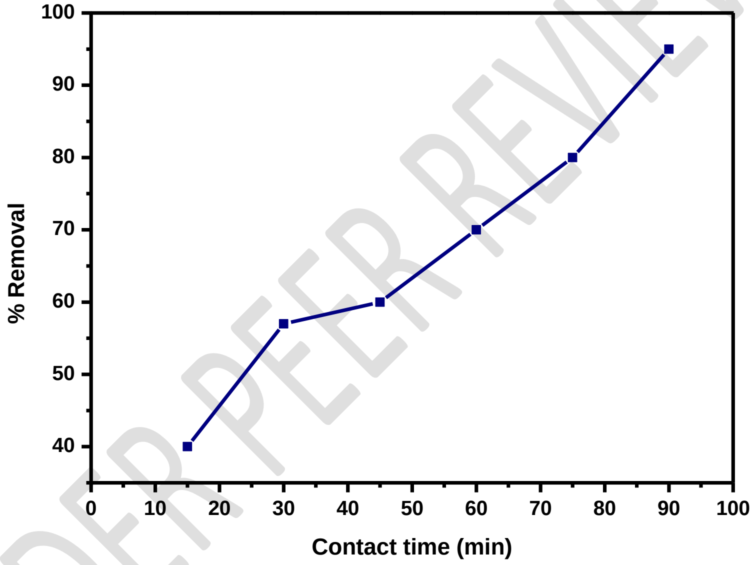

Fig.9 Effect of contact time

3.3.5EFFECT OF TEMPERATURE

The effect of temperature on the adsorption of congored by NaFRLP was studied at 298, 303, 308 and 313 K at a constant dye concentration of 100 mg/L and 90 min of contact time (Fig.10). It was observed that the adsorption capacities of congored increased with increasing the solution temperature from 298 to 313 K, indicating that the adsorption process is endothermic in nature. The enhancement in adsorption capacity with increase in temperature might be due to the increased diffusion rate of thedyemolecules across the external boundary layer and into the internal pores of the adsorbent [26].

Table 5. Effect of temperature on % removal Congored

Initial dye concentration = 100 mg/L, Adsorbent dosage = 1 g/L, Agitation speed = 200 rpm, Contact time = 90 min, pH =

Temperature (K)	% Removal
298	38
303	57
308	78
313	95

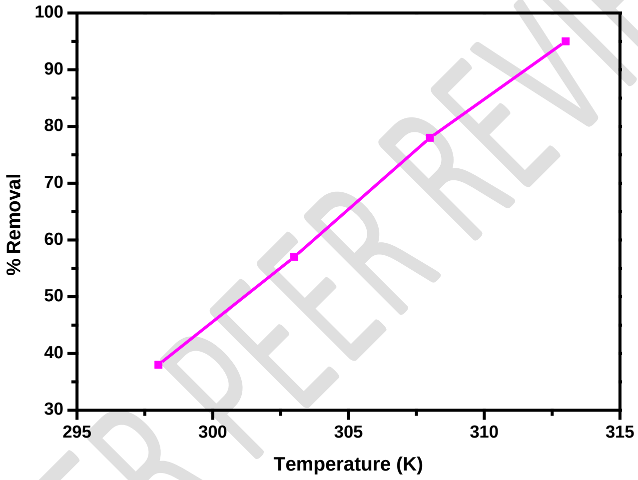

Fig.10 Effect of Temperature

Comment [O8]: Where graphs are presented Table may not be required

3.4ADSORPTION ISOTHERM

Langmuir isotherm describes the adsorption of an adsorbate on a homogeneous, flat surface of an adsorbent and monolayer adsorption onto a surface with a finite number of identical sites. Unlike the Langmuir model, the Freundlich model was used to describe the adsorption of an adsorbate onto the heterogeneous surface of an adsorbent. The isotherm parameters for adsorption of congored are summarized in Table.6. Results showed that the adsorption of congored on NaFRLP fitted well to the Langmuir model, asindicated by the higher correlation coefficient (R^2) values (Fig.11 and 12).These findings demonstrate homogenous nature of the adsorption process. The values of $R_L$were in between 0 to 1 showing favorable adsorption process [27].

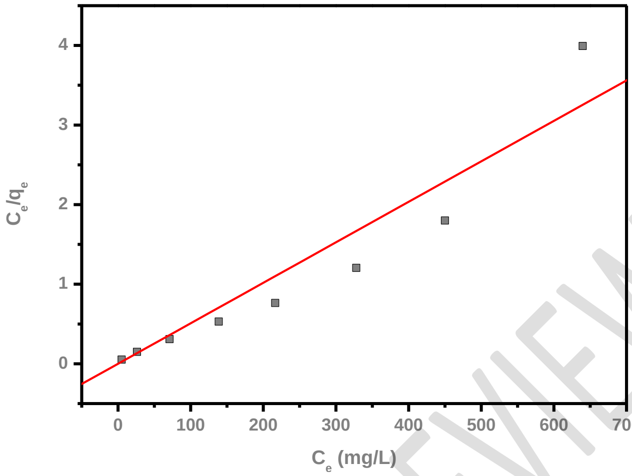

Fig.11 Linear plot of Langmuir isotherm for adsorption of Congored on to NaFRLP

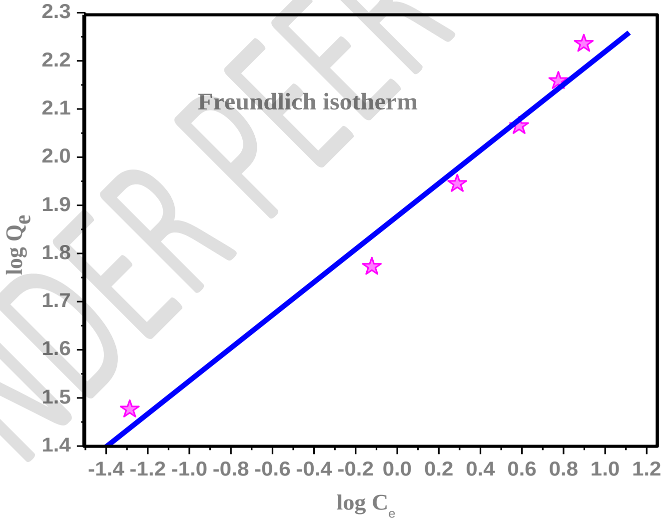

Fig.12 Linear plot of Freudlich isotherm for adsorption of Congored on to NaFRLP

Table 6. Parameters of various isotherms for Congored adsorption by NaFRLP

Isotherm	Parameters	Congored
Langmuir	R^2	0.962
	Q_m	9.612
	R_L	0.0276
	K_a	3.512
Freundlich	R^2	0.906
	n	4.2016
	K_f	1.5204

3.5ADSORPTION KINETICS

Adsorption kinetics is of great significance in evaluating the performance of a certain adsorbent and in gaining insight into the underlying mechanisms [28]. Hameed [29] reported that kinetic modeling is generally used to investigate the mechanism of adsorption and the potential rate-controlling processes, such as mass transfer and chemical reaction. In the present study, the modeling of the kinetics of the adsorption of congored on NaFRLP was investigated using two common models, namely, pseudo-first order and pseudo-second-order models.

The kinetic plots of congored on NaFRLP are depicted in Fig. 13 and 14 forpseudo-first order model and pseudo-second order model respectively, while the calculated kinetic parameters are presented in Table.7. The results clearly show that pseudo-second order model correlated with the experimental data much better than pseudo-first order model, since the simulated curves better fit to the experimental data; the calculated $q_{e,calc}$ values were closer to experimental ones ($q_{e,exp}$); and also higher correlation coefficients than those of pseudo-first order model. All these results indicate that the chemical adsorption was the rate controlling step for NaFRLP [30].

Fig.15 shows the intra-particle diffusion plot for congored adsorption on NaFRLP. It is observed that more than one linear portion appear in all of the plot, which indicates that the adsorption is affected by two or more steps [31]. This can be illustrated as follows: the first portion with steep slope represents the instant diffusion stage, in whichlarge number of dye molecules from bulk phase were adsorbed rapidly by the surface functional groups of NaFRLP. After almost all the exterior active sites were occupied, the dye molecules got ready to enter into the pores of the adsorbents and then were adsorbed by the interior surface of pores, which arose in the second stage. In the third portion, the intra-particle diffusion rate constants were close to zero, indicating equilibrium state reached at last. As a summary of the kinetic studies, it isimplied that both the intra-particle diffusion and the chemical chelatingreaction betweendye molecules and active sites of the adsorbents had effects on the adsorption processes [30].

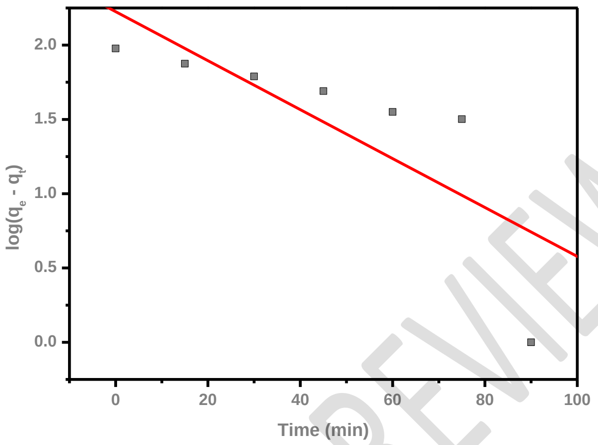

Fig.13Pseudo first order kinetics for adsorption of Congored on to NaFRLP

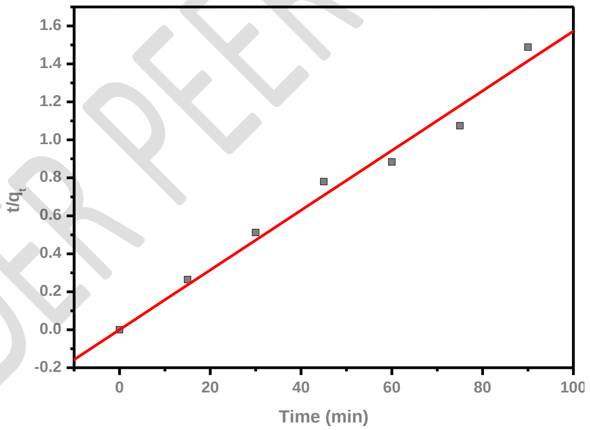

Fig.14Pseudo second order kinetics for adsorption of Congored on to NaFRLP

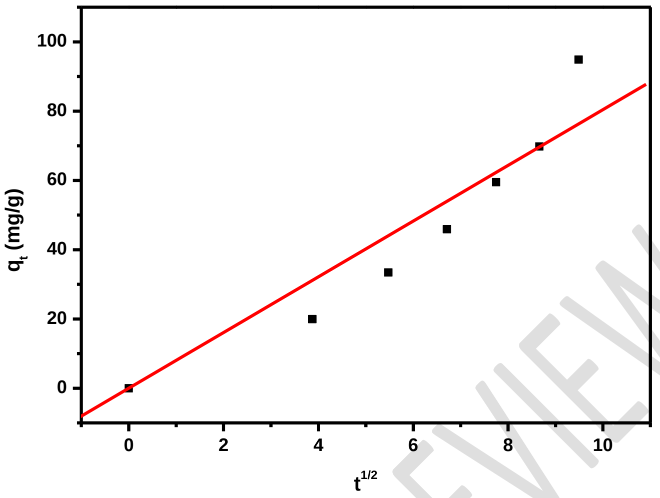

Fig.15 Linear plot of intra particle diffusion

Table 7. Parameters of adsorption kinetic models of Congored on to NaFRLP

Adsorption kinetic model	**Parameter**	**Congored**
Pseudo-First order	R^2	0.334
	k_1 (min^{-1})	0.0184
	q_e(mg/g)	1.0876
Pseudo-Second order	R^2	0.960
	k_2 (min^{-1})	0.0408
	q_e(mg/g)	95.5367
	h	0.1863
Intraparticle diffusion model	R^2	0.983
	K_{diff}	0.210
	C	0.099

3.6THERMODYNAMIC PARAMETERS

The Gibbs free energy change (ΔG◦) was calculated to be -1.218, -2.66, -3.312 and -7.712 kJ/mol for congored adsorption at 298, 303, 308, and 313 K, respectively (Table.8). Negative ΔG◦ values indicated the feasibility of the process and spontaneous nature of the adsorption, were obtained for congored, at each of the temperatures studied. Moreover, the ΔG◦ values decreased with an increase in temperature, indicating an increased trend in the degree of spontaneity and feasibility of congored adsorption. The ΔH◦ parameter was found to be 79. KJ/mol for congored adsorption. The positive values of ΔH◦ further confirmed the endothermic nature of adsorption process. The heat of adsorption value between 40 and 400 kJ/mol indicates the chemisorption process [32]. Hence, the adsorption of congored on NaFRLP was chemical in nature. The ΔS◦ parameter was found to be 79.86 (J/(mol K)) for congored adsorption. The positive values of ΔS◦ suggested that the degrees of freedom increased at the solid–liquid interface during the adsorption. During the adsorption process, the coordinated water molecules were displaced by dyes, resulting in increased randomness in the adsorbent–adsorbate system [33].Van't Hoff plot for the adsorption of congo red on to NaFRLP is given in Fig.16.

Table 8. Thermodynamic parameters for adsorption of Congored on to NaFRLP

Temperature (°C)		**ΔG°(kJ/mol^{-1})**	**ΔH° (kJ mol^{-1})**	**ΔS° (JK^{-1} mol^{-1})**	**K$_d$**
Congored	298	-1.218	241.42	79.86	0.4083
	303	-2.66			0.9140
	308	-3.312			3.6451
	313	-7.712			19.439

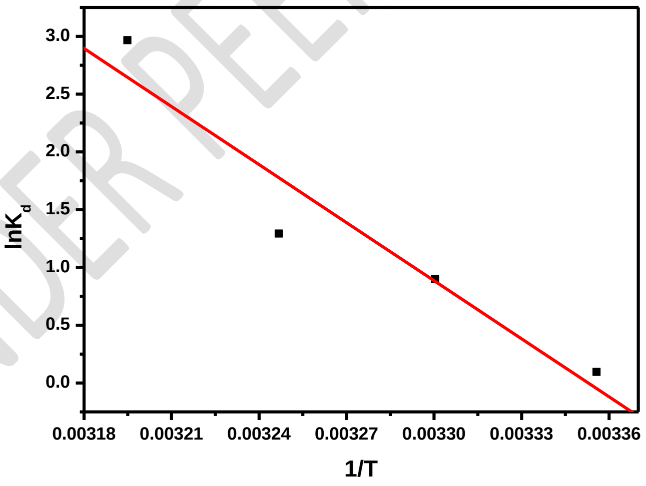

Fig.16Van't Hoff plot for the adsorption of Congoredon to NaFRLP

4. CONCLUSION

Ficus racemosa fallen leaf powder treated with NaOH(NaFRLP) was studied as biosorbent for congored dye removal from industrial waste water. FT-IR and SEM analysis were carried out to characterize the biosorbent.BET Surface area analysis showed the presence ofmesoporous particles in biosorbent. Batchadsorption studies revealed that with an increase in the time of adsorption, the percent removal of congoredincreases and with an increase in the concentration of the solution,congored removal decreases.NaFRLP was found to be an effective adsorbent for the removal of congored in a concentration range up to 100 mg/L.The adsorption data best fittedwith the Langmuir isotherm .Thermodynamic analysis of the batch adsorption studies indicated that all the processes studied were spontaneous with the congored adsorption on NaFRLP being endothermic .Thus the NaFRLP can be used as the best biosorbent for the effective removal of congored.

REFERENCES

1.Robson C. Oliveira, Mauricio C. Palmieri and Oswaldo Garcia Jr., Progress in Biomass and Bioenergy Production, InTech, (2011) 151-176.
2.Ozdemir, S., Kilinc, E., Poli, A., Nicolaus, B., & Guven, K. *Chemical Engineering Journal*, *152*(1) (2009) 195-206.

3. A.E. Al Prol, M.A. El Azzem, A. Amer, M.E. El-Metwally, H.T.A. El-Hamid, K.M. ElMoselhy, Adsorption of cadmium (II) ions from aqueous solution onto mango leaves, Asian Journal of Physical and Chemical Sciences 2 (2017) 1–11.

4. H.N. Tran, S.-J. You, A. Hosseini-Bandegharaei, H.-P. Chao, Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review, Water Res. 120 (2017) 88–116.

5. I. Guerrero-Coronilla, L. Morales-Barrera, T.L. Villegas-Garrido, E. Cristiani-Urbina, Biosorption of amaranth dye from aqueous solution by roots, leaves, stems and the whole plant of E. crassipes, Environ. Eng. Manag. J. 14 (2014) 1917–1926.

6. N. Gupta, A.K. Kushwaha, M.C. Chattopadhyaya, Adsorption studies of cationic dyes onto Ashoka (Saraca asoca) leaf powder, J. Taiwan Inst. Chem. Eng. 43 (2012) 604–613.

7. S.N. Jain, P.R. Gogate, Adsorptive removal of acid violet 17 dye from wastewater using biosorbent obtained from NaOH and H_2SO_4 activation of fallen leaves of Ficus racemosa, J. Mol. Liq. 243 (2017) 132–143.

8.Sujitha Ravulapalli, Ravindhranath Kunta, Journal of Fluorine Chemistry 193 (2017) 58–66.

9. S.N.Jain and P.R.Gogate, NaOH treated dead leaves of Ficus racemosa as an efficient biosorbent for Acid Blue 25 removal, International Journal of Environmental Science and Technology, Volume 14,pages 531-542 (2017).

10.Youssef Aoulad El Hadj Ali 1* , Abdoulaye Demba N'diaye 2 , Driss Fahmi 1 , Mohamed Sid'Ahmed Kankou 2 , Mostafa Stitou , Adsorption of Congo Red from Aqueous Solution using Typha australis Leaves as a Low Cost Adsorbent, Journal of Environmental Treatment Techniques 2021, Volume 9, Issue 2, Pages: 534-539.

11.Aisha Kitemangu, Maheswara Rao Vegi and Nyemaga Masanje Malim, Biosorption of Congo Red Dye from Aqueous Solution Using Adsorbent Prepared from Vangueria infausta Fruit Pericarp, Hindawi Adsorption Science & Technology Volume 2023, Article ID 4319053, 17 pages.

12.Maria Harja1*, Gabriela Buema2* & Daniel Bucur3, Recent advances in removal of Congo Red dye by adsorption using an industrial waste, Scientific reports (2022), 12:6087.

13. Mohammad Foroughi-dahr1 , Hossein Abolghasemi1,2*, Mohamad Esmaili1 , Alireza Shojamoradi1 , and Hooman Fatoorehchi, Fixed-bed adsorption of congo red onto tea waste in the presence of Fe_2O_3 nanoparticles: an experimental and modeling study, Journal of Petroleum Science and Technology (2013),3(2), 35-44.

14.Material Safety Data Sheet Congored MSDS. http://www.sciencelab.com/xMSDS-Congo_red-9927502.

15.Tunali, S., Cabuk, A., & Akar, T. Chemical Engineering Journal, 115(3) (2006) 203-211.

16.Langmuir, I. The Constitution. Journal of the American Chemical Society, 38 (*1916*) 2221-2295.

17.Aksu, Z.; Donmez, D.; Chemosphere. 2003, 50, 1075-1083.

18.Elisane Longhinotti, Fabíola Pozza, Lígia Furlan, Maria de Nazaré de M. Sanchez, Marilene Klug, Mauro C.M. Laranjeira, and Valfredo T. Fávere, J. Braz. Chem. 9(5) 1998.

19.H.M. Freundlich, Uber die adsorption in losungen, Zeitschrift fur PhysikalischeChemie 57A (1906) 385–470.

20.Hall, K.R.; Eagleton, L.C.; Acrivos, A.; Vermevlem, T.; Indian. Eng. Chem. Fundam. 5 (1966) 212-219.

21.Ho, Y.S., Scientometrics 59 (2004) 171-177.

22. Montanher, S.F., Oliveira, E.A. and M.C. Rollemberg *J. Hazard. Mater.*, B117 (2005)207-211.

23.Crini, G., Peindy, H. N., Gimbert, F., & Robert, C. Separation and Purification Technology, 53 (2007) 97–110.
24.Xu, X., Li, Q., Cui, H., Pang, J., Sun, L., An, H., Zhai, J., 2011. Adsorption of fluoride from aqueous solution on magnesia-loaded fly ash cenospheres. Desalination 272, 233–239.
25. Ramanaiah, S.V., Mohan, S.V., Rajkumar, B., Sarma, P.N., J. Environ. Sci. Eng. 48 (2006) 129–134.
26.Ismat H. Ali and H. A. Alrafai, Ali and Alrafai *Chemistry Central Journal (2016) 10:36*
27.Chen, N., Zhang, Z., Feng, C., Li, M., Zhu, D., Chen, R., Sugiura, N., 2010. J. Hazard. Mater. 183, 460–465.
28. H. Qiu, L. Lv, B. Pan, Q. Zhang, W. Zhang, J. Zhejiang Univ.-Sci. A 10 (2009) 716–724.
29.B. Hameed, J. Hazard. Mater. 161 (2009) 753–759.
30.E. Repo, J.K. Warchol, T.A. Kurniawan, M.E.T. Sillanpa, Chem. Eng. J. 161 (2010) 73–82.
31. Y. Chen, J. Hu, J. Wang, Environ. Technol. 33 (2012) 2345–2351.
32. N. Unlu, M. Ersoz, Sep. Purif. Technol. 52 (2007) 461–469.
33. A. Baraka, P.J. Hall, M.J. Heslop, React. Funct. Polym. 67 (2007) 585–600.