



Data Article

Sorption studies of methyl red dye removal using lemon grass (*Cymbopogon citratus*)

Mohd Azmier Ahmad^a, Nur'Adilah Binti Ahmed^a, Kayode Adesina Adegoke^{b,c},
Olugbenga Solomon Bello^{b,d,*}

^a School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

^b Department of Pure and Applied Chemistry, Ladoké Akintola University of Technology P.M.B 4000, Ogbomosho, Oyo State, Nigeria

^c Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

^d Department of Physical Sciences, Industrial Chemistry Programme, Landmark University, Omu-Aran, Nigeria

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ABSTRACT

Lemongrass leaf based activated carbon (LGLAC) was prepared using physico-chemical methods for methyl red (MR) dye removal from aqueous solutions. The surface chemistry of LGLAC before adsorption revealed the presence of different functional groups: O-H, C-H, C=O, CH₃, C=C, N-O, C-O and C-N which were shifted after methyl red dye adsorption. Brunauer-Emmett-Teller surface and mesopore areas are 836.04 m²/g and 598.604 m²/g, whereas, the average pore diameter and total pore volume of LGLAC are 3.62 nm and 0.472 cm³/g respectively. Batch adsorption was studied using different parameters: initial dye concentrations (25–500 mg/L), contact time (0–24 h), solution temperature (30–60 °C) and solution pH (2–12). Adsorption of methyl red dye was observed to increase with increase in initial dye concentration, contact time and solution temperature. The methyl red dye adsorption uptake and percentage removal at equilibrium showed that the adsorption process is majorly dependent on the initial dye concentration. Optimum percentage of methyl red dye removed was observed at pH 2. The adsorption process of methyl red dye onto LGLAC was endothermic in nature. Thermodynamic parameters, including entropy change (ΔS^0), enthalpy change (ΔH^0), and Gibbs free energy change (ΔG^0) were evaluated. The adsorption process was endothermic and the mechanism followed a physisorption process.

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* Corresponding author at: Department of Pure and Applied Chemistry, Ladoké Akintola University of Technology P.M.B 4000, Ogbomosho, Oyo State, Nigeria.

E-mail address: osbello@lautech.edu.ng (O.S. Bello).

Specifications table

Subject area	Physical Chemistry, Chemical Engineering
Compounds	Methylred (MR), Lemongrass, Sodium hydroxide (NaOH)
Data category	Spectra, graphs, images, preparation and activation procedures
Data acquisition format	Elemental analyzer, FTIR, TGA analyzer, SEM, MR dye adsorption data
Data type	The data analyzed
Procedure	Data obtained from characterization of LGchar and LGLAC via TGA SEM, FTIR and other physico-chemical techniques. Adsorption studies: - Initial dye concentration from 25–500 mg/L. - pH was varied between 2 and 12. - Solution temperature ranges from 30–60 °C - Contact time ranges from 0–24 h.
Data accessibility	All data are available with this article.

1. Rationale

Industrial utilization of dyes in the past decades has increased drastically thereby increasing the challenges pose on the ecosystem thereby threatening the global peace. Many industries including paper, textile, printing, leather, plastics and food industries use dyes in their diverse applications [1–8]. However, compounds that contained dyes are toxic to animals and humans' life even at a low concentration. Their effects are teratogenic, carcinogenic, and mutagenic, which consequently results in adverse health conditions to the human and animals [4,9–11]. Since last decades, many conventional techniques have been employed to decontaminate dyes from aqueous solution. Examples are chemical, biological and physiochemical methods [12–25]. Dyes are known to be resistant to biological degradation methods and their removal by conventional physicochemical techniques are inefficient [4,26–28]. Thus, economic methods for dye removal from effluents remains a problem for textile industries [12,29,30] thus paving ways for adsorption due to its ability to meet economical demands [4,31–33]. Recently, adsorption techniques are gaining more attentions due to their simplicity in design, cost effectiveness, efficiency, ease of operation, tolerance to toxic materials, biodegradability and capability for treating dyes at high concentrations [3,34–42]. This is a greener approach to cleaning the environment [42–46].

Activated carbon (AC) remains a popular adsorbent having numerous potentials for dye removal from wastewater but the cost of purchasing commercial activated carbon (CAC) limited its uses in the past years [47–50]. As a result of this high cost, scientists all over the globe are searching for suitable alternatives to CAC, such as agricultural materials due to their high efficiency [4]. Therefore ACs from agricultural origins has been utilized as potential adsorbent for remediating various kinds of dyes. Many authors in past decades have studied the adsorption of various dyes onto numerous agricultural materials which include rice husk [51,52], neem [53,54], rambutan seed [55], durian seed [56,57], watermelon rinds [58], lime peel [59], Okra [60], banana stalk [61] mango [62], walnut shells [63,64], cocoa husk [44], orange peel [65–67], *Prunus dulcis* [68,69], berry leaves [70], de-oiled soya [71] bagasse fly ash [72] and *Moringa oleifera* leaf and pod [73,74].

Methyl red (MR) is a monoazo dye, one of the toxic, mutagenic or carcinogenic pollutants in water. Its discharges into the receiving bodies and affects both aquatic and human lives [57,75,76]. It causes eyes and skins sensitization, pharyngeal, irritations to digestive tract when swallowed [57,75–77] and/or inhaled [77–80]. Recently, researches into developing low cost alternatively means to reduce or completely remove MR dye have been given more attentions due to their carcinogenic nature when discharged into the water body [79–81]. Herein, we report on the utilization of lemon grass (a readily available, no/low cost material) for the efficient removal of MR dye from aqueous systems.

2. Procedure

2.1. Preparation of adsorbents

Lemongrass leaves (*Cymbopogon citratus*) were chosen as precursors for the preparation of ACs. These materials were obtained in the area of Parit Buntar, Perak, Malaysia (5.1474° N, 100.4212° E). Lemongrass leaves were dried at 105 °C for 24 h for removal of the moisture contents. The pre-treated material was then carbonized at 700 °C under nitrogen atmosphere for 1 h (first pyrolysis). The certain amount of the char produced was then soaked in sodium hydroxide solution (NaOH) at impregnation ratio of 1:1 (NaOH pellets:char) (g/g). The mixture was stirred and dehydrated in the oven at 100 °C overnight. Thereafter, the impregnated samples were loaded into a stainless steel vertical tubular reactor placed in a tube furnace for the second pyrolysis. Pyrolysis was carried out to a final temperature of 800 °C under nitrogen (99.99%) flow at 150 cm³/min and activated for 2 h. Once the desired activation temperature was reached, N₂ gas flow was switched to CO₂ at flow rate of 150 cm³/min to complete of the activation process in 2 h. The activated products were allowed to cool to room temperature, under N₂ flow and then washed with hot de-ionized water followed by hydrochloric acid (HCl) until the solution pH reached 6.5 – 7.0. Finally, the samples were dried at 100 °C and kept in an airtight container for adsorption study.

Table 1
Properties of MR .

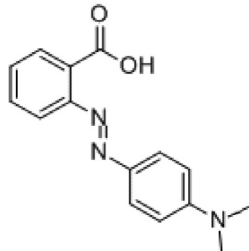
Dye name	Methyl red
Molecular formula	C ₁₅ H ₁₅ N ₃ O ₂
Molecular weight, g/mol	269.3
CAS no.	493-52-7
λ max.(nm)	520
Chemical structure	

Table 2
Adsorption isotherm and kinetics.

Adsorption model	Type	Expression	Refs.
Isotherm	Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m C_e} + \frac{1}{K_L q_m}$ (4)	[93]
		$R_L = \left[\frac{1}{(1 + K_L C_0)} \right]$ (5)	
	Freundlich	$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f$ (6)	[94]
	Temkin	$q_e = B \ln K_T + B \ln C_e$ (7)	[95]
	Dubinin-	$\ln q_e = \ln q_m + \beta \varepsilon^2$ (8)	[96]
	Radushkevich	$\varepsilon = RT \left[1 + \frac{1}{C_e} \right]$ (9)	
		$E = \frac{1}{\sqrt{2\beta}}$ (10)	[97,98]
	Koble-Corrigan	$q_e = \frac{a C_e^n}{1 + b C_e^n}$ (11)	[99]
	Vieth-Sladek	$q_e = k_{VS} C_e + \frac{Q_m \beta_{VS} C_e}{1 + \beta_{VS} C_e}$ (12)	[100]
	Radke-Prausnitz	$q_e = \frac{q_{max} K_{RP} C_e}{1 + K_{RP} C_e}$ (13)	[101]
Kinetics	Brouers-Sotolongo	$q_e = Q_m (1 - e^{-k_{BS} C_e^n})$ (14)	[102]
	Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - K_1 t$ (15)	[103]
	Pseudo-second order	$\frac{t}{q_e} = \frac{1}{K_2 q_e} + \frac{1}{q_e} t$ (16)	[104]
	Elovich	$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$ (17)	[105,106]
	Avrami	$q_t = q_e (1 - e^{-(k_{AV} t)^n})$ (18)	[107]
		$\ln(\ln(\frac{q_e}{q_e - q_t})) = n \ln k_{AV} + n \ln t$ (19)	
	Boyd	$Bt = -0.4977 - \ln(1 - \frac{q_t}{q_e})$ (20)	[108]
	Intra-particle diffusion	$q_t + K_{diff} t^{1/2} + C$ (21)	[22]

2.2. Adsorbate preparation

Methyl red dye used in this study were supplied by Sigma-Aldrich (M) SDN BHD, Malaysia). To prepare a stock solution of MR dye at a concentration of 500 mg/L, 0.5 g of MR dye powder was dissolved in 1000 mL of deionized water. Solution of different initial concentrations (25, 50, 100, 200, 400 and 500 mg/L) were prepared by serial dilution process of initial stock solution into 100 mL of deionized water. The properties of MR are presented in the Table 1.

2.3. Adsorbent characterization

The surface morphology of the Lemongrass leaves char (LGLchar) and Lemongrass leaves activated (LGLAC) was examined using a scanning electron microscope (Quanta 450 FEG, Netherland). The proximate analysis was studied using simultaneous thermal analyzer (TGA) (Perkin Elmer STA 6000, USA). Elemental analysis was carried out using elemental analyzer (EA), (Model Perkin Elmer Series II 2400, USA). The surface characteristics of the samples were characterized using Fourier transform infrared (FT-IR) spectrometer (Shimadzu Model IRPrestige-21 Spectrophotometer). The determination of the samples' surface areas, pore volumes and average pore diameters were carried out using Micromeritics ASAP2020 volumetric adsorption analyzer. The surface areas were measured using Brunauer-Emmett-Teller (BET). The total pore volumes were estimated to be the liquid volume of N₂ at a relative pressure of 0.98 [41].

2.4. Batch adsorption experiment

The experiment was carried out using batch adsorption process at three different temperatures (30, 45 and 60 °C). For each temperature six Erlenmeyer flasks were used with different dye concentrations (25, 50, 100, 200, 400 and 500 mg/L).

Table 3

Surface area and pore characteristics of the prepared activated carbons.

Sample	BET surface area(m ² /g)	Mesopore surface area (m ² /g)	Totalpore volume (cm ³ /g)	Average pore diameter (nm)
LG char	152.44	71.87	0.138	3.47
LGAC	836.04	598.60	0.472	3.62

0.10g of the LGLAC was added to a series of Erlenmeyer flasks filled with 100mL of dye solution. The Erlenmeyer flasks were sealed and kept in an isothermal water bath shaker at a speed of 120rpm at a constant temperature of 30°C until equilibrium was reached. This was also applied to 45 and 60°C solution temperatures. The aqueous samples were then withdrawn at a fixed time interval. The UV/Vis spectrophotometer was employed to measure the concentrations at 520 nm wavelength. For batch and equilibrium studies, the amount of dye uptake at time *t* (i.e. q_t (mg/g)) and at equilibrium, q_e (mg/g)), are determined using Eqs. (1) and (2) while the percentage removal at equilibrium were calculated using Eq. (3)

$$q_t = \frac{(C_o - C_t)V}{W} \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

$$\text{Percentage of dye removal (\%)} = \frac{(C_e - C_t)}{C_t} \times 100 \quad (3)$$

where C_t (mg/L) is the liquid-phase concentration of MR dye at time *t*, C_o (mg/L) is the initial solute concentration and C_e (mg/L) is the liquid-phase concentrations of MR dye at equilibrium. *V* is the volume (L) of the solution and *W* is mass (g) of adsorbent [36,61].

3. Data, value and validation

3.1. Surface area and pore characteristics

The BET surface and mesopore areas were observed to be 836.04 m²/g and 598.6 04 m²/g, whereas, the average pore diameter and total pore volume of LGLAC are 3.62 nm and 0.472 cm³/g respectively. The activation process in association with NaOH and CO₂ gasification promoted the mesoporous formations that directly resulted in LGLAC high surface area in comparison with LGchar which has low BET and mesoporous surface areas of 152.44 and 71.87 m²/g (Table 3).

3.2. Surface morphologies

Fig. 1 (a and b) shows the SEM images of LGchar and LGLAC. From Fig. 1(a), the surface and pores of LGchar were rough and not properly developed. However, in Fig. 1(b), several pores are clearly observed, many pores are formed on the LGLAC surface. This is an indication that the activation process using NaOH have contributed to the widening and formations of pores on the LGLAC surface which could enhance MR dye removal. This is requisite for dye adsorption as reported in the literatures [35,41,42,63,73,82,83]

3.3. Surface chemistry

The FTIR spectra of LGLAC before and after adsorption of MR dye are shown in Fig. 2. The stretching bands are O-H, (3500–3200 cm⁻¹), C-H of alkane (2980–2960 cm⁻¹), C=O (1700 cm⁻¹), CH₃ (1385–1380 cm⁻¹), Aliphatic C=C (1675–1600 cm⁻¹), N-O asymmetry (1600–1500 cm⁻¹), C-O (1050 cm⁻¹) and C-N (1340–1250 cm⁻¹), bending bands are C-H (1470–1430 cm⁻¹) and O-H from carboxylic acid (1350–1260 cm⁻¹). However, majority of the functional groups were affected after adsorption of MR dye (Fig. 2b) resulting into bands disappearance, reductions or shifting to lower wavelengths (Fig. 2b). This indicates involvement of these functional groups for binding MR dye to LGLAC [42,44,84]. The spectrum of the MR dye loaded lemon grass showed similar characteristics as the lemon grass in raw form except for slight changes as indicated by the disappearance, shift and reduction in some bands after adsorption. The FTIR spectrum of the dye loaded adsorbent indicates that the peaks are slightly shifted from their position and the intensity gets altered. These results indicated the involvement of some functional group in the adsorption of dye ions on the surface of the lemon grass through weak electrostatic interaction or Van der Waals forces. This can be considered as further evidence for the interaction between lemon grass and the MR dye ions. Similar observation were reported by other researchers [85–88].

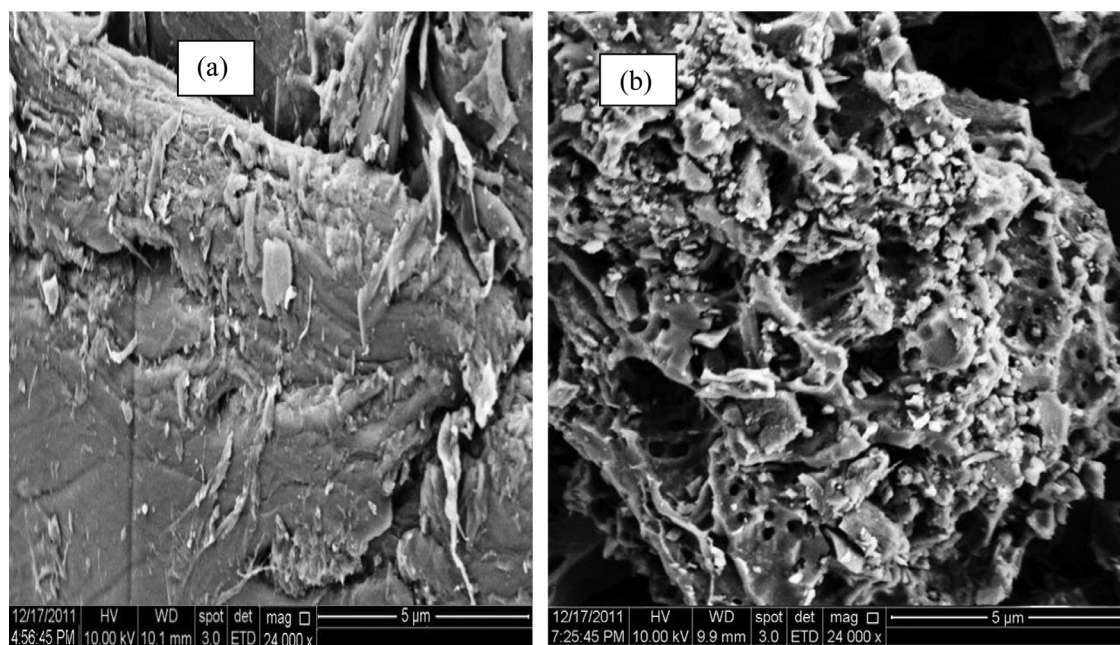


Fig. 1. SEM micrographs of (a) LGLchar and (b) LGLAC (Magnification = X 24000).

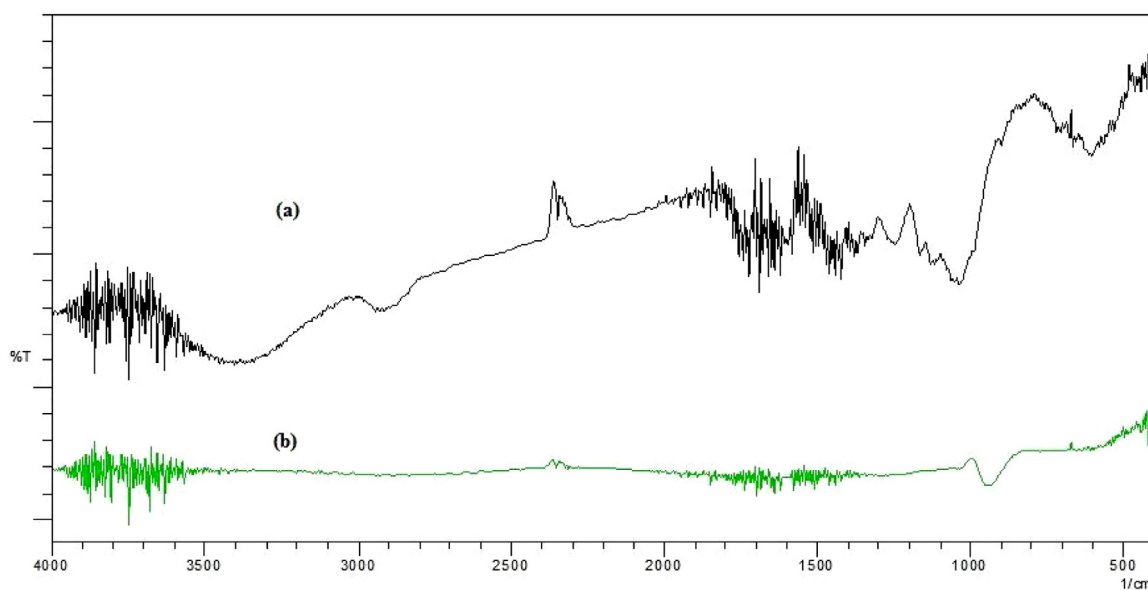


Fig. 2. FT-IR of LGLAC; (a) before adsorption (b) after adsorption.

3.4. Proximate analysis

The volatile matter and moisture contents of the raw lemon grass (LGrass) leaf are 67.94% and 8.80% respectively. During activation, there was a reduction in moisture content 2.93% and volatile matter 15.80% of LGLAC sample. The fixed carbon contents follow the sequence LGAC (77.41%) > LGchar (57.51) > LGrass (18.59%) (Table 4). During carbonization and activation processes at high temperature, the volatile matter is released as gases and liquid products which completely evaporated, leaving only materials with higher carbon contents. A lower ash content of 3.86% was obtained for LGLAC. In accordance with observations from literature, the lower ash content signifies the applicability of the material as good adsorbent for dye adsorption while higher ash content reduce the performance and efficiency of the adsorbent for dye removal [89–94].

Table 4

Proximate content of precursor, char and activated carbon.

Sample	Proximate analysis (%)			
	Moisture	Volatile	Fixed carbon	Ash
LG raw	8.80	67.94	18.59	4.67
LG char	5.13	32.86	57.51	4.50
LGAC	2.93	15.80	77.41	3.86

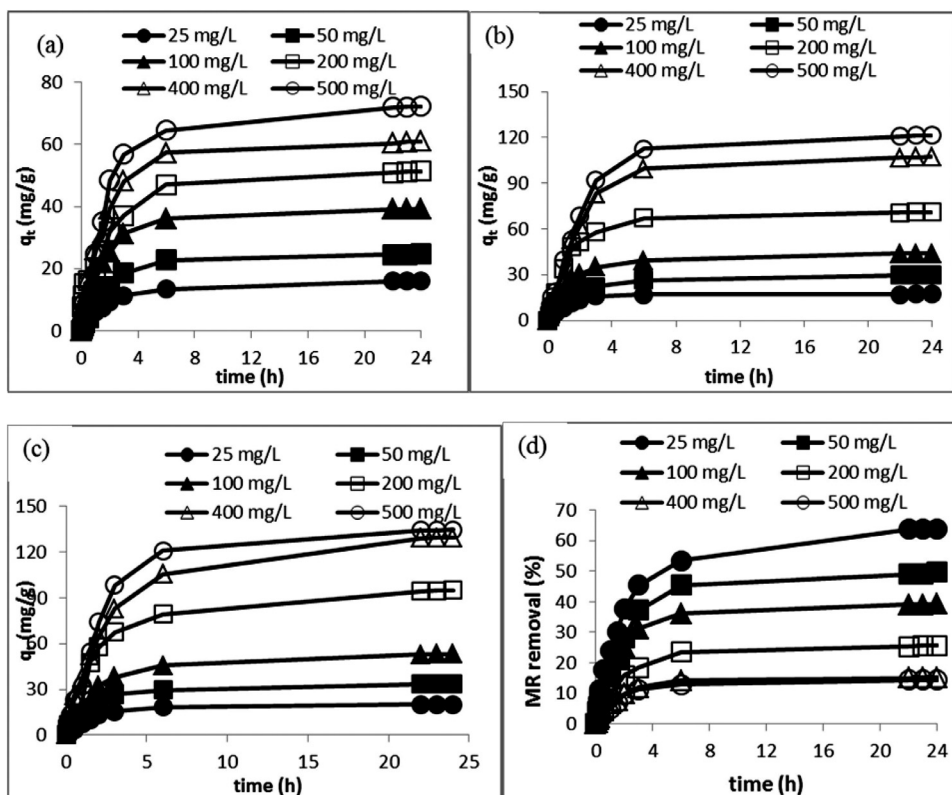


Fig. 3. MR Dye adsorption uptake onto LGLAC at different initial concentrations and contact time at (a) 30 °C, (b) 45 °C, (c) 60 °C, and (d) Percentage removal of MR dye by LGLAC at various initial dye concentration and contact time at 30 °C.

3.5. Effect of initial MR dye concentration and contact time

Fig. 3a–c showed the effect of contact time and initial dye concentrations for MR dye uptake onto LGLAC at different temperatures of 30–60 °C. The adsorption of MR dye increased with time. The MR dye uptake were rapid in the early stages of the contact time between 0–5 h, after 5 h, it became very slow until it reached equilibrium in 24 h. This is attributable to larger numbers of vacant sites accessible for MR dye adsorption during the initial stages [95] which decreases with time. Fig. 3d shows the percentage removal of MR dye onto the LGLAC at various contact times and different initial dye concentration at 30 °C. A gradual increase of percentage MR dye removal was observed as the initial dye concentration increases (Table 5).

Table 5

Adsorption of dyes uptakes and Percentage of dyes removal at equilibrium.

Concentration (mg/L)	MR dyes uptake (mg/g)	MR dye removal (%)
25	15.97	63.87
50	24.83	49.66
100	39.30	39.30
200	51.32	25.66
400	60.99	15.25
500	72.32	14.46

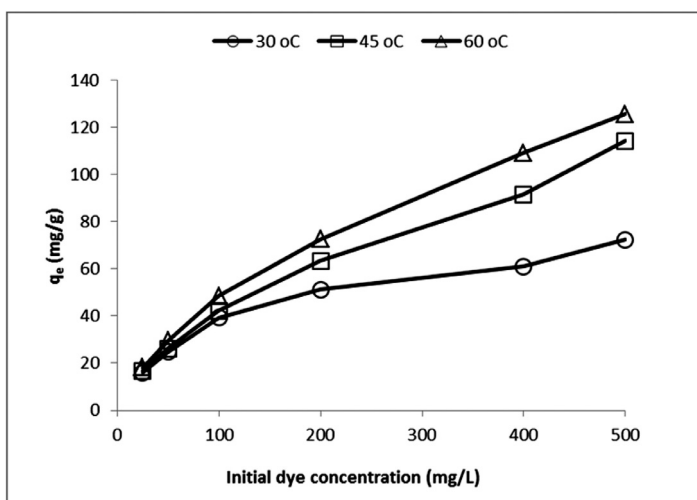


Fig. 4. Effect of solution temperature on the MR dye uptake.

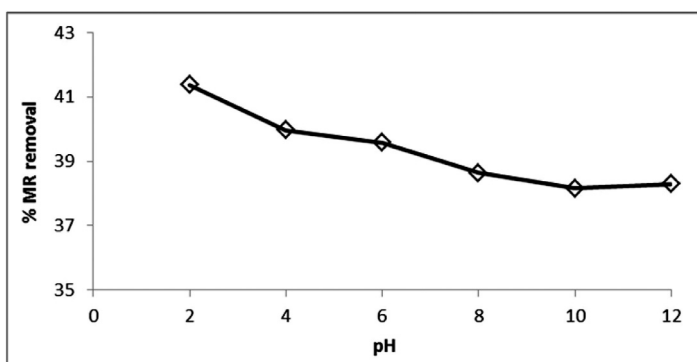


Fig. 5. Effect of initial pH on the MR dye uptake. .

3.6. Effect of solution temperature

Fig. 4 presents the influence of solution temperature on the MR dye uptake onto LGLAC. The amount of MR dye uptake, q_e (mg/g) increased with the increase in solution temperature from 30–60 °C at all initial dye concentration. This suggests that the adsorption of MR dye onto LGLAC is endothermic in nature. When solution temperature was increased, the chemical interactions between MR dye and the adsorbent's surface functionalities also increased. In other words, there is increase in mobility of MR dye to penetrate deeper into the pores of the LGLAC. In addition, the physical bonding between MR dyes and LGLAC active sites become enhanced [57]. Besides, increasing the solution temperature, the viscosity of MR dye solutions also decreased. Therefore, the diffusion rate of the MR dye molecule across the external boundary layers and in the internal pores of the LGLAC is greatly improved [41,55,96].

3.7. Effect of solution pH

Fig. 5 presents the effects of solution pH on the MR dye removal with the optimum percentage removal of 41.38% for MR dye at pH 2. This inferred that the LGLAC surfaces would be attracted to the positively charged functional groups on MR dye thereby improving the adsorption capacity. At lower pH value, more protons will be available to protonate the dye molecule resulting in electrostatic attraction between the positively charged MR dye and negatively charged LGLAC. Increasing the initial pH of the system, the negatively charged LGLAC sites predominates, thus establishing electrostatic repulsion between the negatively charged surface of the LGLAC and negatively charged MR dye molecule [97]. The trend of MR dye adsorption in pH range 2–12 is shown in Fig. 5. The amount of MR dye adsorbed decreased with increase in initial pH. The optimum pH value for MR dye was found to be 2. The difference in percentage removal in this pH range was largely due to the structural changes observed in the MR dye molecules and the surface adsorption characteristics of LGLAC indicating that the adsorption capacities of the adsorbent is pH dependent [97,98]. It is well known that reactive dyes upon dissolutions release

Table 6

Isotherm parameters for MR dye adsorption unto LGLAC at 30 °.

Langmuir	Freundlich	Temkin	Dubinin-Radushkevich	Koble-Corrigan	Radke-Prausnitz	Vieth-Sladek	Brouers-Sotolongo
$q_m = 76.923$ $k_L = 1.84 \times 10^{-2}$	$k_F = 7.396$ $1/n_F = 0.38$	$B = 14.076$ $A = 0.281$	$q_s = 49.30$ $E = 158.11$ $b_{DR} = 2 \times 10^{-5}$	$A_{KC} = 5.39$ $B_{KC} = 4.2 \times 10^{-2}$ $n = 0.55$ $q_m = 342.9$ $R^2 = 0.997$	$q_m = 16.254$ $k_{RP} = 0.240$ $m_{RP} = 0.754$ $R^2 = 0.987$	$k_{VS} = 5.9 \times 10^{-2}$ $q_m = 47.120$ $B_{VS} = 4.7 \times 10^{-2}$ $R^2 = 0.989$	$q_m = 94.254$ $k_{BS} = 6.43 \times 10^{-2}$ $\alpha = 0.499$ $R^2 = 0.985$

Table 7

Kinetic model constant parameters for MR dye adsorption unto lemon grass at 30 °C.

Model	Kinetic parameters	Initial MR dye concentration (mg/L)					
		25	50	100	200	400	500
Pseudo-first-order	$Q_e, \text{exp (mg g}^{-1}\text{)}$	15.968	24.828	39.296	51.32	60.988	72.32
	$K_1 \text{ (min}^{-1}\text{)}$	0.406	0.445	0.503	0.387	0.508	0.509
	$Q_e \text{cal (mg g}^{-1}\text{)}$	15.214	25.503	37.003	44.492	60.087	72.298
	R^2	0.990	0.989	0.992	0.968	0.994	0.986
Pseudo-second-order	$\Delta q_e \text{ (%)}$	4.722	2.719	5.835	13.305	1.477	0.030
	$K_2 \text{ (min}^{-1}\text{)}$	0.0344	0.0070	0.0170	0.0194	0.0058	0.0067
	$Q_e \text{cal (mg g}^{-1}\text{)}$	17.182	38.023	43.860	51.814	79.365	84.034
	R^2	0.976	0.964	0.988	0.951	0.983	0.948
Elovich	$\Delta q_e \text{ (%)}$	7.603	53.146	11.614	0.963	30.132	16.198
	$\alpha \text{ (mg g}^{-1} \text{min}^{-1}\text{)}$	3.822	1.751	2.211	2.591	1.022	0.862
	$\beta \text{ (g mg}^{-1}\text{)}$	2.915	4.809	6.965	8.327	11.417	13.36
	R^2	0.982	0.952	0.696	0.962	0.961	0.947
Avrami	$k_{AV} \text{ (min}^{-1}\text{)}$	0.0051	0.0041	0.0062	0.0070	0.0054	0.0053
	n_{AV}	0.718	0.782	0.646	0.532	0.736	0.674
	R^2	0.879	0.894	0.857	0.834	0.866	0.872

Table 8

Intraparticle diffusion model parameters for MR dye adsorption on LGLAC at 30 °C.

Initial MR dye conc. (mg/L)	(mg/g h ^{1/2})								
	k_{p1}	k_{p2}	k_{p3}	C_1	C_2	C_3	$(R_1)^2$	$(R_2)^2$	$(R_3)^2$
25	3.019	6.025	3.218	0	-0.102	56.664	1	0.958	0.999
50	2.754	11.105	1.499	0	-2.846	53.565	1	0.975	0.996
100	8.16	15.52	1.729	0	1.391	42.846	1	0.961	0.998
200	27.816	17.874	1.306	0	4.417	32.901	1	0.983	0.997
400	8.32	26.565	0.836	0	-2.333	20.615	1	0.964	0.993
500	21.655	30.972	1.096	0	-3.67	10.69	1	0.941	0.996

Table 9

Thermodynamic parameters for adsorption of MR dyes on LGLAC.

Dye	$\Delta H^\circ \text{ (kJ/mol)}$	$\Delta S^\circ \text{ (J/mol.K)}$	$E_a \text{ (kJ/mol.K)}$	$-\Delta G^\circ \text{ (kJ/mol)}$		
				303 K	318 K	333 K
MR	18.221	20.383	11.025	12.045	11.739	11.434

colored dye anions into solutions. The adsorption of these charged dye groups onto an adsorbed surface is influenced by the surface charge on the adsorbent [97].

3.8. Isotherm, kinetic and thermodynamic studies

Table 6 shows the isotherm parameters for MR dye adsorption unto LGLAC at 30 °C while Table 7 presents the kinetic model constant parameters for MR dye adsorption unto lemon grass at 30 °C. The Intraparticle diffusion model parameters for MR dye adsorption on LGLAC at 30 °C are reported in Table 8. The adsorption process was found to be endothermic (ΔH is positive) and spontaneous (ΔG is negative) in nature as shown in Table 9.

4. Conclusion

LGL was successfully used as precursor to produce ACs for the removal MRdye by physiochemical activation method. Batch adsorption was studied using different parameters. The percentage dye removal for MR dyes decreased as the initial

dye concentration increase. Adsorption of MR dye was found to increase with increase in initial MR dye concentrations, contact time, and solution temperatures.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.cdc.2019.100249](https://doi.org/10.1016/j.cdc.2019.100249).

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