A characteristic study of *Zea mays* L. (sweet corn) cobs for synthetic dye degradation from aqueous media

Iram Javed, Tariq Javed and Muhammad Naeem Khan

ABSTRACT

The current study reports a systematic methodology of *Zea mays* L. (sweet corn) cobs (ZMLC) for the sequestration of synthetic dye (gentian violet) from aqueous solutions. Adsorbent was scrutinized by using scanning electron microscopy, Fourier transform infra-red spectrometry with pH_{pzc} determination. The impact of various adsorption parameters including pH effect, ZMLC (sorbent) dosage, temperature, concentration and shaking time was examined. The equilibrium sorption isotherms were determined by the batch method from 283 to 303 K at pH_{pzc}. Adsorption data were adjusted to four isothermal models: Langmuir, Freundlich, Dubinin-Radushkevich and Temkin's models, which presented the best adjustment to Freundlich, Dubinin-Radushkevich and Temkin's at 283 K. The kinetic profile fitted well to the pseudo-second order kinetic equation at three distinct concentrations 600, 700, 800 mg/L. Maximum sorption capacity was gained up to 700 $mg.g^{-1}$ for gentian violet at pH 3, respectively. The adsorption process is endothermic, non-spontaneous, favorable thermodynamically due to positive values of entropy and Gibbs free energy and randomness decreases during the adsorption process. Furthermore, after biosorption onto ZMLC the dye can be desorbed effectively by using mineral base KOH solution. Consequently, the ZMLC is said to be a promising biosorbent to remediate gentian violet-contaminated water as well as wastewater.

Key words | endothermic, gentian violet, pH_{pzc}, sorption, thermodynamics, ZMLC

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HIGHLIGHTS

- The presented bio-waste ZMLC was used for efficient removal of synthetic dye in raw form.
- ZMLC surface provides inter and intra molecular bonding with abundantly available –COOH groups without any further treatment.
- Dynamic equilibrium was rapidly attained and enhanced by acidic media in just 30 min. Reusability of ZMLC was studied under the influence of KOH with 92.5% desorption values.

INTRODUCTION

The dyeing process is commonly utilized to color products and become their basic part at an industrial level. Majorly, waste waters of industries containing dyestuffs cause various environmental threats as well as damage to human health (Singh & Singh 2019). Synthetic dyes are extensively used in many technologies such as textiles, printing, paper making, leather, rubber, food processing, plastics, photography and pharmaceuticals. Round about 12% of the synthetic dyes produced annually are believed to be lost during manufacturing and processing operations and 20% of these dyes lost enter the industrial waste water. The high solubility of dyes in water results in their wide dissemination into the environment, causing drastic effects on crops, aquatic life and also to human

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health. The increase in occurrence of many synthetic and organic dyes/substances in natural (drinking) water has led to the importance of its purification through various techniques. Adsorption is one of the effective methods for water purification (Adeyemo *et al.* 2017). To overcome the contaminated water issues, different biological and physiochemical treatments are used: coagulation/flocculation, chemical precipitation, chemical oxidation, membrane processes, electrochemical and microbial degradation, reverse osmosis, photochemical oxidation and adsorption. (Ali *et al.* 2014; Cheruiyot *et al.* 2019) Among all these purification techniques, adsorption is a major industrial separation technique/method to refine effluent media. In liquid phase, it is a most efficient and less time-taking method that has been easily applied to dye removal (Rajasekhar 2014; Adeyemo *et al.* 2017). Various low cost adsorbents such as clay (Adeyemo *et al.* 2017), flyash, silica, synthetic composites (Jiang *et al.* 2015; Janani *et al.* 2019), also modified forms of wastes, have been used for dye removal but agricultural waste such as rice husk, bio-char (Wathukarage *et al.* 2017), *Bukhulderia* (Li *et al.* 2014), wheat bran (Sujata *et al.* 2019), *Atrocarpous* sawdust (Linda *et al.* 2015), banana peel, peanut hull (Tahir *et al.* 2016), corn stalk (Usman *et al.* 2019), Maracon peel (Youssef *et al.* 2017) and other bio-wastes were proved to be low cost sorbents for cationic and anionic dye removal (Hemant *et al.* 2016). Among these agriculture bio-wastes, *Zea mays* L. (sweet corn) cobs (ZMLC) have great potential and physiochemical properties for synthetic dye removal and serve as an effective adsorbent in aqueous media. ZMLC provides high surface area for elimination of cationic dyes (Aljeboree *et al.* 2019). Gentian violet (the dye discussed here) has a carcinogenic and mutagenic nature affecting both aquatic and land ecosystem. So, in degradation, decolorization is an important consideration. In the present study, ZMLC, due to its good ability, is used for gentian violet elimination from a dye-contaminated aqueous environment. Different operations were examined that behaves as variable parameters: dye concentration, shaking time and temperature factors for adsorption treatment. The adsorbent surface was characterized by scanning electron microscopy (SEM), Fourier transform infra-red spectrometry (FT-IR) and pH at point zero charge (pH_{pzc}). Thermodynamics show the process is endothermic and spontaneous. Further isothermal adsorption assessment is also reported below. It is worth declaring that no previous works have addressed the biosorption of gentian violet from aqueous solutions in the following reported study.

MATERIAL AND METHODOLOGY

Adsorbent preparation (ZMLC)

Zea mays L. (sweet corn) cobs were collected from local farms of Sahiwal (Pakistan), washed properly to remove dirt and subsequently dried an oven operated at 100 °C for 20 hrs. Dried ZMLC was then pulverized and screened to a particle size of 200 μm. The raw ZMLC was stored in an airtight container for additional subsequent use.

Preparation of solutions

Stock solution of gentian violet was prepared (1,000 mg/L) by dissolving the 1.0 g dye quantity of A.R. grade in double-distilled water. The sample solutions of different concentrations ranging from 200 to 900 mg/L were prepared by diluting a stock solution to the desired concentrations. The pH of the adsorption experiments was maintained through mineral acid and mineral base (NaOH and KOH) standard solutions. The $\lambda_{max.abs}$ of the stock solution of gentian violet 575 nm was monitored by visible-spectrophotometer (721). The characteristic structure of gentian violet is shown in Figure 1, respectively.

Adsorption experiments

Batch adsorption experimental studies were carried out by varying different parameters such as dye concentration

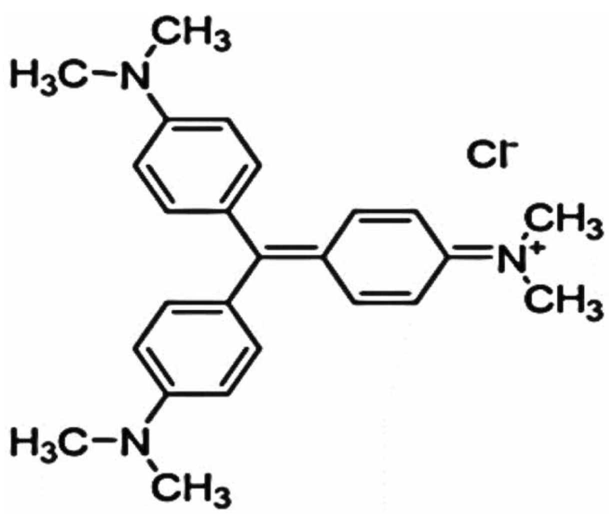

Figure 1 | Chemical structure of gentian violet molecule.

(100–1,000 mg/L), adsorbent amount (0.1–1.0 g), shaking time (5–120 min) and pH (1–12) to obtain the best adsorption conditions. The pH of the dye solution was adjusted by using 0.1 N HNO_3/KOH solutions with the help of a pH meter and obtained 3.0 pH as optimum for further batch experiments. In the establishment of adsorption equilibrium isotherm batch studies, 0.6 g of ZMLC and 10 ml of dye solution (200–1,000 mg/L) were shaken at three particular temperatures 283, 293, 303 K for 30 min (the time required for equilibrium to be reached). Removal capability and concentration of gentian violet adsorbed at equilibrium Q_e (mg/g) was computed by Equations (1) and (2) as:

$$\%\text{age dye removal} = \frac{(C_o - C_e)}{C_e} \times 100 \quad (1)$$

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

where C_o (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of gentian violet in adsorption culture medium, V is the volume of adsorption medium containing dye in liters (L), and W is the mass of ZMLC used in grams. The data was analyzed to study equilibrium adsorption isotherms: Langmuir, Freundlich, Dubinin-Radushkevich and Temkin, at 283, 293, and 303 K. The amount of gentian violet adsorbed, Q_t (mg/g) at time duration t (min) was determined with the help of the following relation:

$$Q_t = \frac{(C_o - C_t)}{W} V \quad (3)$$

where C_t is the equilibrium amount of dye adsorbed at a specific time interval.

Adsorbent characterization (ZMLC)

The adsorbent (ZMLC) was characterized by pH at point zero charge (pH_{pzc}) by pH drift method, FT-IR (FT-IR 2000, PerkinElmer): fine grained material of ZMLC mixed with KBr (Merck) by 1:100 for transparent granules, and to determine the surface porosity of ZMLC, SEM analysis (JEOL-JSM-6380 LA, Japan) (Aljeboree & Ayad 2019); to observe the adsorption behavior of gentian violet towards the adsorbent a visible spectrophotometer-721 was used.

Statistical analysis

The acceptability and the prime fit of a model are mostly based on the square of correlation coefficients (R^2), which may be appropriate for linearized models. Therefore, in this study, another error function was used to validate the fit kinetic models, which is the sum square error function (SSE). The expression for correlation coefficient and SSE are given as follows:

$$R^2 = \frac{\sum (C_{ads.cal} - C'_{ads.exp})^2}{\sum (C_{ads.cal} - C_{ads.exp})^2 - \sum (C'_{ads.cal} - C_{ads.exp})^2} \quad (4)$$

$$SSE = \sum_{i=1}^{N} (Q_{exp} - Q_{cal})^2 \quad (5)$$

The higher the value of regression coefficient and lower SSE error values, the more reliable the model. The values of SSE error are displayed in Tables 2 and 3 with R^2 values. According to SSE and R^2 values, Temkin's isotherm and pseudo-second order kinetics are the best models to represent the adsorption experimental data.

RESULTS AND DISCUSSION

The results of the mineral constitution of ZMLC appear in Table 1. ZMLC contained the minerals Si, K, Fe, Al and P in high proportion. These minerals contribute to defining the hydrophilic identity of ZMLC. The physiological properties of ZMLC determined that the moisture content is less than 5%, which is more favorable for the acceleration of adsorption experiments (Nwadiogbu *et al.* 2015).

pH at point zero charge (pH_{pzc})

To explore pH at point zero charge (pH_{pzc}) on surface of ZMLC was found to be 3.15 (Figure 2). pH_{pzc} was

Table 1 | Mineral content of ZMLC

Constituents	Composition (% wt)
SiO_2	58.205
K_2O	17.801
P_2O_5	4.677
Al_2O_3	4.378
Cl	3.787
Fe_2O_3	3.317

Table 2 | Parameters of adsorption isotherms for gentian violet on ZMLC

Isotherms	Parameters	283 K	293 K	303 K
Langmuir isotherm	Q_m (mg/g)	52.35	−100.0	−294.11
	K_L ($dm^3\ mol^{-1}$)	0.5291	−0.0664	−0.0246
	R^2	0.4611	0.688	0.697
	SSE	0.0236	0.008	0.001
Freundlich isotherm	K_f (mg/g)	4.093	5.480	0.366
	N	1.004	1.023	1.206
	R^2	0.995	0.991	0.985
	SSE	0.025	0.033	0.045
Dubinin-Radushkevich isotherm	β ($KJ^2\ mol^{-2}$)	-8.2×10^{-3}	-6×10^{-3}	-1.8×10^{-2}
	ε_s ($KJ\ mol^{-1}$)	7.810	7.715	5.521
	R^2	0.970	0.912	0.942
	SSE	0.034	2.942	0.056
Temkin's isotherm	B (J/mol)	2.087	2.883	1.692
	K_T (L/mol)	5.3×10^7	3.96×10^{10}	4.42×10^{17}
	R^2	0.980	0.960	0.958
	SSE	1.29×10^{-11}	2.82×10^{-11}	1.17×10^{-9}

Table 3 | Kinetic parameters for adsorption of gentian violet on ZMLC

Kinetic model	Parameters	Variable concentration (mg/L) 600	700	800
Pseudo-first order	R^2	0.907	0.946	0.820
	SSE	0.033	0.036	1.000
	K_1	−0.022	−0.023	−0.036
	Q_e (mg/g)	0.061	0.070	0.0751
Pseudo-second order	R^2	1.000	1.000	1.000
	SSE	1.7×10^{-4}	6.5×10^{-4}	9.8×10^{-4}
	K_2 (mg/g)	−7.7	0.515	0.578
	Q_e (mg/g)	9.990	11.68	13.35
Reichenberg plot model	R^2	0.916	0.883	0.764
	SSE	0.152	0.571	0.682
	C	0.425	0.808	0.263
	K(1/min)	0.956	0.592	0.322

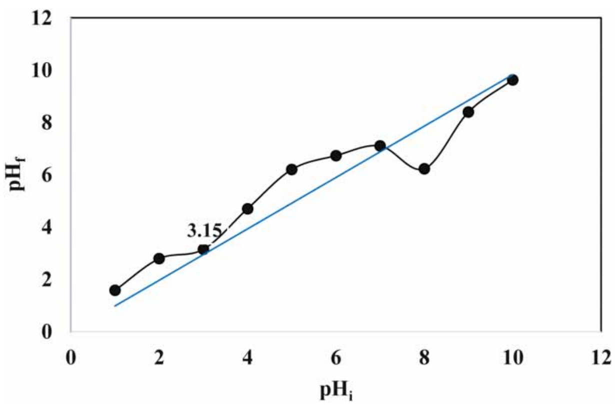

Figure 2 | Plot for pH_{pzc} determination of ZMLC.

determined by using the pH-drift method (Nasiruddin & Sarwar 2007). At 3.15 pH, the net surface charge of ZMLC becomes zero and ZMLC provides more electro-chemical potential for gentian violet adsorption in bulk fluid form. The ZMLC surface exhibits a relationship between pH_{pzc} and adsorption capacity of adsorbent and highest percentage dye adsorption takes place at 3.15 pH. The results show that sorption of gentian violet is more beneficent at pH less than point of zero charge (1–3 pH), while it is less favorable higher than pH_{pzc} (4–12 pH). This behavior investigates that, due to greater electrostatic force of attraction between ZMLC and oxygen containing surface functional groups, gentian violet molecules rapidly adjusted over the adsorbent surface. Whereas, at pH > pH_{pzc} adsorption was lewer due to less attraction between protonated oxygen of the ZMLC surface and the dye (Jawad *et al.* 2018).

FT-IR studies

The pattern for adsorption of gentian violet onto ZMLC due to the availability of active binding sites and bonds on the adsorbent surface was examined by FT-IR spectral analysis. The adsorbent was chemically composed of lignin, cellulose, hemicelluloses and plentiful collections of hydroxyls like tannins (Oluyori *et al.* 2018; Qaisar *et al.* 2019). The lignocellulose portion of the adsorbent follows the ion-exchange mechanism with respect to the corresponding dye (gentian violet). The hydrocarbon sites actively react with the cationic portion of the dye (Sobhy & Mahmoud 2015). FT-IR spectra of native ZMLC source (a) and loaded with gentian violet dye (b) illustrated by Figure 3 to various functional groups with respect to wavenumber (cm^{-1}). The peaks at 3,750 and 3,772 cm^{-1} symbolized the –OH phenolic group growing from cellulose and the lignin portion of ZMLC. At 2,800 cm^{-1} the peak that expressed the stretching vibrations of N-H and O-H functional groups indicates the presence of nitrogen in the methylene and hydrocarbons in ZMLC surface. The 1,810 and 1,780 cm^{-1} peaks show the existence of $–CH_2$ of the aliphatic portion randomly distributed on the ZMLC surface with $C=O$ bond stretching. The bands between 1,600–920 cm^{-1} give stretching of $C=C$ bonds of alkenes, alkynes and olifenes. The given peaks in Figure 3 are the result of functional groups, stretching behavior, collection of dye and also proposed the density location of gentian violet molecules on the ZMLC surface. The adsorption of the ZMLC surface area exhibits continuous spectrum peaks in FT-IR analysis demonstrating that adsorption is due to the electrostatic force of attraction that is the result of physiosorption, which may be weak or strong, no chemical correlation proceeded. (Aljeboree *et al.* 2019) Trough regions appeared as the system absorbs energy from the surroundings but the FT-IR spectra of the ZMLC surface revealed that it requires less energy for adsorption, thus there is less difference between native and loaded ZMLC peaks. Moreover, after gentian violet adsorption the presence of new IR-bands is due to many functional groups undergoing red or blue shifting (Figure 3(b)) in the finger print region and proposes the presence of dye molecules adsorbed on the ZMLC surface.

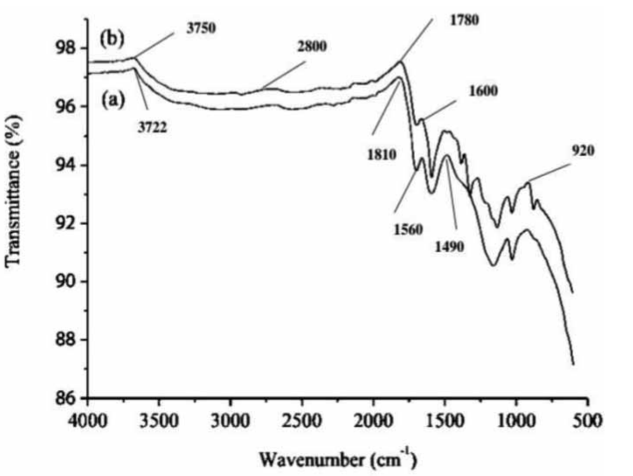

Figure 3 | FT-IR spectra of native (a) and loaded (b) ZMLC by gentian violet (adsorbent dosage 0.6 g, pH = 3.0 and contact time 30 min).

SEM analysis

Scanning electron microscopy provides information about the surface morphology of ZMLC and also gives the fundamental physical features. An SEM diagram of the adsorbent (ZMLC) was examined (Figure 4). The good pore size ability before adsorption (Figure 4(a)) and loaded with dye (Figure 4(b)) after equilibrium show the pore filling by the adsorbent. Figure 4(a) determines that the ZMLC surface is crowded with hoops and lumps that are clearly visible, then after equilibrium (Figure 4(b)) dye molecules have created a film-like mass on the surface of the adsorbent that hides the porosity. The resulting pore structures of the ZMLC provide suitable surface area for gentian violet removal from aqueous media (Aljeboree & Ayad 2019).

Effect of pH

pH is an abundant property that controls the whole adsorption process and adsorption capacity of the adsorbent. It is not only affecting the surface charge of the adsorbent but also the degree of ionization of dye molecules present in solution and dissociation of active bonding site functional groups on ZMLC. It is observed that cationic dyes are absorbed quickly at lower pH due to the positively charged adsorbent surface. In the present adsorption system, pH is measured from 1 to 12; the adsorption capacity for gentian violet is highest at 3.0 pH as shown in Figure 5. The adsorption is more favorable at pH_{pzc} of ZMLC due to the massive electrostatic attractive force between the dye and the negatively protonated charged surface of the cobs.

Effect of shaking time

Influence of shaking time on adsorption of gentian violet with ZMLC was measured at three different dye concentration: 600, 700, 800 mg/L, 3.0 pH, 0.6 g ZMLC amount and shaking time varying from 5 to 120 min (Figure 6). The time duration at which the adsorption culture medium attains equilibrium was measured, after which no further more effective percentage of dye uptake occurs. 30 min equilibrium time was determined from the plot of dye uptake versus contact time (min) with equilibrium sorption capacity. From the results, 700 mg/L gentian violet at 30 min contact time serve as better conditions for dye removal in less time in bulk fluid form. This contact time is very important for the highest dye uptake from aqueous media, even from wastewater at the industrial level. Figure 6 explains the relationship between adsorption capacity and contact time at different

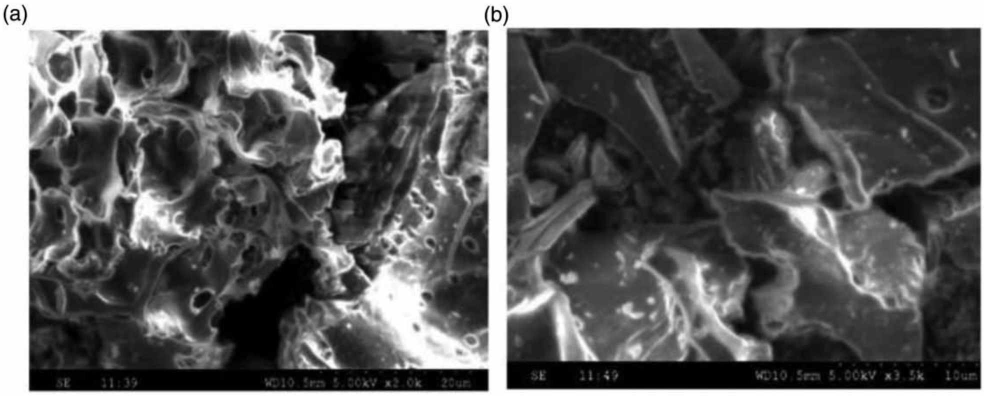

Figure 4 | SEM images of ZMLC before (a) and after (b) gentian violet adsorption.

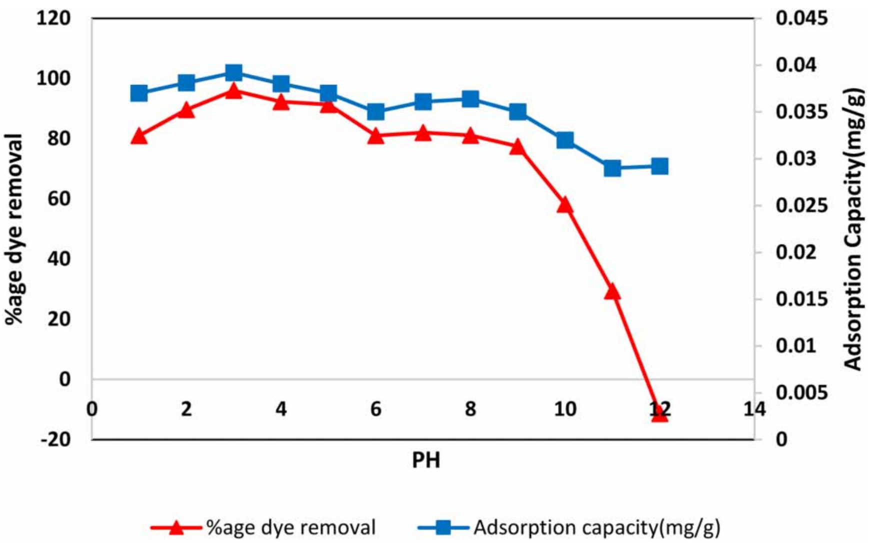

Figure 5 | Relationship between pH and ZMLC surface for gentian violet removal from aqueous media.

concentration in bulk form. However, adsorption capacity remains constant throughout variable contact time durations due to similar availability of active sites of ZMLC in the adsorption culture medium but percentage adsorption varies from 78 to 96% for 600 mg/L, 76–95.5% for 700 mg/L and 76.2–93.8% in the case of 800 mg/L concentration. This explains that even at very high concentration of gentian violet in adsorptive medium, ZMLC provides an actively large surface area for dye extraction from aqueous medium.

Adsorption isotherms

The adsorption equilibrium data related to dye concentration (200–1,000 mg/L) at three variable temperatures 283, 293, 303 K was further applied to the four adsorption isothermal models: Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, respectively. Freundlich and Temkin's isotherm proved to be the best adsorption isotherms related to experimental data on the basis of the R^2 and SSE error values given in Tables 2 and 3.

Langmuir model

That equilibrium model, based on suspicion of monolayer adsorption mechanism on studied adsorbent surface with respect to the corresponding adsorbate and its linearized form is as:

$$\frac{C_e}{C_{ads}} = \frac{1}{q_m} \cdot \frac{1}{K_L} + \frac{C_e}{q_m} \tag{6}$$

where C_{ads} is the quantity of dye adsorbed on ZMLC surface at equilibrium (mg/g), C_e is the concentration of dye in total

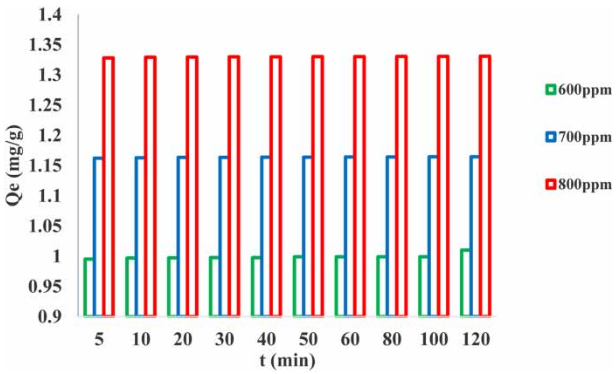

Figure 6 | Sorption capacity of ZMLC for dye removal at variable shaking time.

volume of solution at equilibrium (mg/L), q_m is said to be mono-layer adsorption capacity of ZMLC (mg/g) and K_L serve as Langmuir model constant measured in L/mg, respectively. Adsorption capacity of ZMLC compared with other adsorbents given in Table 4. A plot was obtained C_e/C_{ads} verses C_e (283–303 K) as shown in Figure 7 which determines that adsorption mechanism is not monolayer it is said to be multilayer-physiosorption process. The values of isothermal parameters given in Table 2. Monolayer adsorption capacity at 283 K is more than at 303 K, thus adsorption of gentian violet on ZMLC surface is more dominating at 283 K.

Freundlich isotherm

This isotherm representation based on the heterogeneity of adsorbent surface towards adsorbate adsorption. The linear representation of this model given as:

$$\log C_{ads} = \frac{1}{n}\log C_e + \log K_f \quad (7)$$

where, C_{ads} is the conc. of gentian violet (mg/g) adsorbed on ZMLC at equilibrium, C_e is the conc. of dye at equilibrium in bulk form, K_f (mg/g.L) the Freundlich mechanism constant and 1/n is the adsorption intensity or surface heterogeneity of adsorbent. Their numeric values are calculated from slope and intercept by plotting graph between $\log C_{ads}$ vs $\log C_e$ as shown in Figure 8 at variable temperatures (283, 293, 303 K). The linear plot of Freundlich proposed that adsorption mechanism is heterogeneous in nature determined on the basis of R^2 values which are 0.9957, 0.9915, 0.9858, respectively.

Dubinin-Radushkevich model

From the D-R isotherm the sorption capacity was measured which may be meso or macro porous and the value of mean free energy was monitered at 283–303 K temperatures. For D-R isotherm a graph is plotted between ln C_{ads} and ε^2 (Figure 9 in the Appendix) with the help of Equation (8) which is linearized representation of that model:

$$\ln C_{ads} = \ln C_m - \beta\varepsilon^2 \quad (8)$$

From the linear plot of D-R value of β was determined (KJ^2/mol). By substituting the values of β the mean adsorption energy can be easily calculated (ε_s):

$$\varepsilon_s = \frac{1}{\sqrt{-2\,\beta}} \quad (9)$$

The values of mean free energy are given in Table 2. From these values it is concluded that the heterogeneous, macro porous ZMLC surface on gentian violet sorption

Table 4 | Comparison of adsorption capacity and optimum parameters for gentian violet adsorption on to different adsorbents

Sr no.	Adsorbent	pH	Concentration (mg/L)	Adsorbent capacity (mg/g)	Reference
1.	Coal	6	50	6.25	Schoonen & Schoonen (2014)
2.	Coffee husk	3	15	12.03	Cheruiyot *et al.* (2019)
3.	Activated carbon	6	100	32.8	Kazeem *et al.* (2018)
4.	Atrocarpous	6.4	50	11.8	Linda *et al.* (2015)
5.	Raw cassava peel	10	100	26.6	Nnaemeka *et al.* (2019)
6.	Wheat bran	8	100	25.6	Sujata *et al.* (2019)
7.	Acid modified clay	10	500	50	Adeyemo *et al.* (2017)
8.	Water hyacinth	7.8	300	32.2	Kulkarni *et al.* (2017)
9.	ZMLC	3	700	58.8	This work

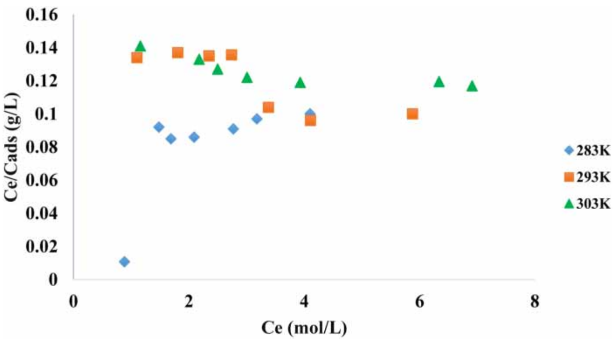

Figure 7 | Langmuir non-linear plot of ZMLC for gentian violet removal.

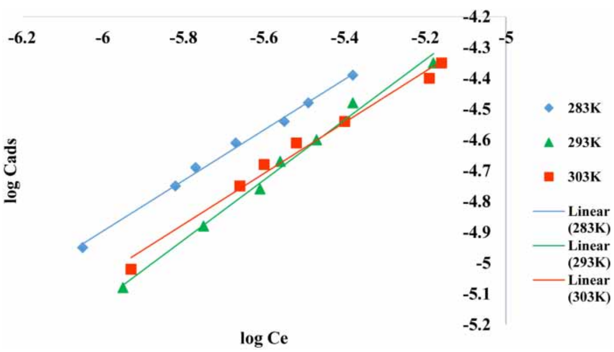

Figure 8 | Linear plot of Freundlich for gentian violet on ZMLC.

provides physiosorption adsorption mechanism properties of adsorbent.

Temkin's isotherm

The linear form of the Temkin isotherm deals with the heat of adsorption, which is the resultant of adsorbent and adsorbate interaction expressed as:

$$C_{ads} = B \ln A_T + B \ln C_e \quad (10)$$

where,

$$B = \frac{RT}{K_T} \quad (11)$$

where B is the heat of adsorption (J/mol), T is the maintained temperature (K), R is the universal gas constant ($JK^{-1}.mol^{-1}$), and $1/K_T$ indicates the adsorption potential of ZMLC (mg/L), A parameter is the equilibrium maximum binding energy constant (L/mg). A plot between C_{ads} and ln C_e gives a straight line at 283, 293, and 303 K temperatures shown in Figure 10 (Appendix). On the basis of maximum R^2 values, Temkin's isotherm is said to be the more appropriate isotherm for experimental data of gentian violet on ZMLC.

Kinetics explanation

Kinetic studies provide information about the effectiveness of adsorption and viability of the applied operations. On governing the order of adsorption, data related to contact time were applied to the first-order Lagergren (Equation (12)) (Yuh-Shan 2004) and pseudo-second-order (Equation (13)) rate equation using the linearized forms as:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{20303} t \quad (12)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

where q_t and q_e are the concentrations of dyes (mg/g) appearing in equilibrium at a particular time and K_1 and K_2 are the equilibrium rate constants of the pseudo-first model and second order kinetic adsorption models. The above linearized expressions for both models are represented in the form of plotted graphs of log (q_e − q_t) vs. t and t/q_t vs. t in Figures 11 and 12 (Appendix) and their parametric values are reported in Table 3. To compare the applicability of different models, a regression equation was applied (Equation (4)).

The plotted graphs at variable concentrations revealed that the pseudo-second order model is the more defined model for gentian violet adsorption on ZMLC on the basis of R^2 values.

Film diffusion mechanism

To determine the nature of adsorption through film diffusion, a kinetic model was observed by applying the experimental data to liquid film diffusion model (Reichenberg 1953):

$$-\ln(1 - F) = Rt \quad (14)$$

where F is the quantitative relation of dye adsorbed at specific time interval t (min) and at equilibrium establishment time (t). Value of βt can be obtained from the linearized form of this model as:

$$\beta_t = -0.4977 - \ln (1 - F) \quad (15)$$

$$F = \frac{q_t}{q_e} \quad (16)$$

The plotted graph between βt and t for gentian violet adsorption on ZMLC is presented as Figure 13 (Appendix) and parametric values expressed in Table 3. The small values of intercept obtained represent that intra-particular film kinetics is the rate controlling diffusion mechanism of gentian violet on ZMLC.

Thermodynamics

The adsorption of gentian violet dye on ZMLC at 700 mg/L dye concentration was carried out using optimized conditions at specific designed temperatures varying from 273 to 333 K and the results are shown in Figure 14 (Appendix). It was observed that dye adsorption decreases at higher temperatures such as at 323 and 333 K.

Van't Hoff plot was used to demonstrate thermodynamic parameters for gentian violet adsorption on ZMLC from its slope and intercept values, respectively. And the relation is as:

$$\ln \mathrm{K_c} = \frac{\Delta S^\circ}{\Delta R} - \frac{\Delta H^\circ}{RT} \tag{17}$$

where K_c is equilibrium constant, ΔS^o and ΔH^o are the change in entropy and enthalpy for the process, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is absolute provided temperature in kelvin. To numerate the value of K_c (equilibrium constant), the following expression was employed:

$$\mathrm{K_c} = \frac{C_{ads}}{C_e} \tag{18}$$

In the above equation C_{ads} and C_e are the equilibrium concentration of dye adsorbed on ZMLC and in solution in bulk form. The values of Gibbs free energy and enthalpy change can be calculated by the following equations:

$$\Delta G^\circ = -RT \ln \mathrm{K_c} \tag{19}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{20}$$

ΔH^o was calculated by plotting the graph between ln K_c versus 1/T as shown in Figure 15 (Appendix) and the values of thermodynamic parameters are presented in Table 5. The positive values of Gibbs free energy indicate that the thermodynamic process for gentian violet removal is non-spontaneous in nature and endothermic due to positive values of enthalpy change. Moreover, the increase in temperature and increase in numeric values of ΔG proposed that adsorption of gentian violet on ZMLC surface is favorable at both lower as well as higher temperatures. Similarly, negative values of entropy change represent decrease in the random degree of freedom of dye molecules.

ZMLC weight

0.1–1.0 g of adsorbent weight was examined by keeping other batch parameters constant. At first, percentage adsorption increases rapidly because of accessibility of ZMLC porous sites during the course of experimental determination. After 0.6 g, no further gentian violet was removed from dye solution and was said to be constant. This phenomenon demonstrated the lower availability of active bonding sites of ZMLC for the same concentration of dye in bulk form. Figure 16 (Appendix) proposes the characteristic effect of ZMLC weight to remove excess amount of gentian violet in an adsorption medium.

Table 5 | Effect of thermodynamic parameters on sorption of gentian violet on ZMLC

T (K)	1/T (K^{-1}) × 10^{-3}	Concentration adsorbed (mol/L) × 10^{-6}	K_c	lnK_c	ΔG (kJmol^{-1})	ΔH (kJmol^{-1})	ΔS (Jk^{-1} mol^{-1})
273	3.66	2.60	657.69	6.48	14.70		–3.12
283	3.53	2.94	580.61	6.36	14.96		–3.38
293	3.41	3.33	512.31	6.20	15.10		–3.52
303	3.30	4.55	374.72	5.97	15.30	11.58	–3.72
313	3.19	4.75	358.50	5.88	15.39		–3.81
323	3.09	4.77	355.30	5.75	15.44		–3.86
333	3.00	6.49	260.40	5.57	15.69		–4.11

Table 6 | Percentage recovery of pre-adsorbed ZMLC using KOH

KOH solution conc.	Recovery (%)
0.001 N	86.2
0.01 N	88.8
0.1 N	92.5

Table 7 | Percentage removal of dye from perforated tap water by ZMLC at optimized conditions

Contact time (min)	Percentage adsorption
10	84
20	88
30	96
40	96.5

Basic treatment

Reusability of the adsorbent is an important feature of waste water treatment. Experimental analysis was performed to study desorption from ZMLC pre-adsorbed surface by using basic media. Mineral base potassium hydroxide (KOH) solution with variable normality was utilized in batch medium. Results are placed in Table 6, which determine that an increase in base concentration increases the percentage of desorption from pre-treated ZMLC with gentian violet and the highest value of percentage desorption was 92.5, respectively.

Application of adsorption procedure

The application of the developed adsorption procedure on tap water was examined to remove 700 mg/L gentian violet concentration by applying optimized batch conditions. From the results (Table 7), 84–96.5% adsorption efficiency was recorded and adsorption equilibrium was attained at 30 min shaking time duration. On the basis of this study, it is concluded that abundantly available ZMLC shows maximum potential for gentian violet removal from aqueous medium even from perforated water, which can also be used for safe ejection of highly toxic synthetic dye from industrial effluents.

CONCLUSION

ZMLC has effective and suitable adsorption characteristics for the removal of hazardous, carcinogenic synthetic dye gentian violet from an aqueous environment. The adsorption experimental data were well fitted to Freundlich, Temkin's as well as the D-R isotherm on the basis of regression coefficient analysis at three distinctive temperatures 283 K (0.995, 0.991, 0.985), 293 K (0.970, 0.912, 0.942), 303 K (0.980, 0.96, 0.958) and the SSE values show inverse behavior in accordance with each isothermal R^2 value. Dye adsorption on ZMLC well obeyed the pseudo-second order kinetic model rate expression on a regression coefficient basis at three concordant concentrations 600, 700 and 800, having 1.0 value at each concentration of adsorption replication and SSE shows values in the range of 10^{-9} to 10^{-11}, which is an insignificant error. The dye uptake slightly decreases at higher temperatures (323, 333 K) and thermodynamics justified that the adsorption mechanism is endothermic due to positive values of enthalpy change. On the basis of this analysis, it is concluded that ZMLC, an abundantly available agriculture waste, proved to be an eco-friendly, more efficient and less cost adsorbent with significant potential for removal of gentian violet in aqueous media even from tap and polluted waste water effluents and can be recycled in a basic environment.

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CONFLICT OF INTEREST

There is no conflict of interest by the authors.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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