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Elaeagnus umbellata leaves powder as a natural adsorbent for the removal of methylene blue

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ABSTRACT

Elaeagnus umbellata leaves powder was utilized as a natural adsorbent for the removal of methylene blue (MB) from the aqueous solution. The adsorption efficiency of *E. umbellata* leaves for the adsorption of MB was studied by changing the variables such as contact time, biosorbent dosage, pH, MB preliminary concentration and temperature. Langmuir, Freundlich and Temkin isotherms were employed for the analysis of the equilibrium data. Freundlich isotherm was better fitted than Langmuir and Temkin isotherms at various temperatures (298, 308, and 318 K), according to the values of regression coefficients (R^2). The adsorption of MB on *E. umbellata* leaves powder was investigated on the basis of Elovich, pseudo-first-order and pseudo-second-order kinetic models. The different thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were determined at various temperatures using the equilibrium concentrations. The thermodynamics factors of MB/*E. umbellata* leaves system indicated non-spontaneous and exothermic processes. It was found that a decrease in temperature favors the adsorption of MB on *E. umbellata* leaves.

Keywords: Elaeagnus umbellata; Adsorption; Removal efficiency; Methylene blue

1. Introduction

Pollution is an ever concerning the problem of modern civilization. When we look the history, we come to know that pollution is a Latin word (Polluere) which means to make dirty or to defile. Pollution is basically defined as undesirable and unpleasant changes in the chemical, physical or biological features of water, air and land that make the environment unhealthy for living by creating health hazards to the living organisms. With the development and advancement in the industries, the world is facing severe environment-related problems since mid of 19th century. There are several factors that are responsible for creating an imbalance in the environment such as increased population, automobiles, prosperous society with an aspiration for a vast array of products, greater radiation pollution due to energy usages, increased food production, etc. [1–3]. In human life, the revolution is brought by science and technology and human life became transformed into more comfortable because of modernization. The villages have become growing cities due to industrialization [4,5]. The fast industrial growth leads to environmental pollution.

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Environmental pollution is one of the major concerning issues of the present civilization and it increases day by day.

Water pollution is considered one of the major environmental pollutions. The sources which are responsible for such types of pollution are urban and agricultural runoff containing fertilizers, domestic dirt, industrial wastes, chemical contaminants, littering, eutrophication and pesticides. The main source of water contamination is industrial waste (colored dyes), which is discharged into rivers, streams and channels. At present, up to ten thousand dyes have been commercialized [6]. These dyes are utilized in textiles, tree wares, synthetic organic polymers, paints, medicinal drugs, cosmetic industry, etc. The contaminated colored water from the industries is discharged into nearby water bodies. This results in the stimulation of chemical oxygen demand. The toxic sewage reduces the penetration of sunlight, which badly affects photosynthesis [7]. Numerous techniques such as ionic substitution, adsorption, membrane sanitization, inverse osmosis, traditional coalescence, organic precipitation, etc. have been applied for the removal of the toxic dyes from the wastewater. Among different techniques for the removal of the dyes from the wastewater, adsorption is the commonly used technique [8,9]. The adsorption is a suitable and moderately venerable procedure because of its simple design, accessibility and capability for the removal of the dyes [8–10]. Activated carbon is one of the commonly used materials due to its greater dye uptake capability towards the large quantity of carbon-based/mineralized metallic ions but its high cost limits its use for the purification of wastewater to a greater extent [11]. Therefore, low-cost substitutes are required to solve this problem. Biomass or agricultural waste is abundant and can effectively remove the dyes from the industrial wastewater [12]. Several forms of agrarian by-products, such as orange rind [13], sawdust [14], melon peel [15] barley husk [16], cereal chaff [17], fly ash [18–21], pine cone [10] and castor seed shell [22] are being recycled to remove methylene blue (MB) from their aqueous mixtures. Several adsorbents such as rice husk [23], bagasse [24] coconut coir [25], tea leaves and cow dung [26], wool fibre and cotton fibre [27], chitosan [28], mahogany sawdust [29], *Parthenium hysterophorus* [30], neem husk [31], silk cotton hull [32], tuberose sticks and tamarind fruit shell [33], amino-functionalized benzene [34], Mg–Fe-layered double hydroxides [35] and fumaric acid [36] are treated as very effective, low-cost, and safe adsorbent.

The availability of several functional groups in the adsorbent makes it a good adsorbing material for the removal of pollutants from wastewater [37,38]. Several economic and easily available adsorbents have been used for the treatment of synthetic dyes in recent years. These adsorbents got much interest from the scientists for the treatment of wastewater and to protect the environment. So, there is a need for the development of an appropriate and cost-effective method for the removal of MB from wastewater. In the current study, *Elaeagnus umbellata* leaves powder was used for the removal of MB from the aqueous solution. The reasons for the use of *E. umbellata* leaves as adsorbents for the removal of MB are cost affectivity and easy availability of the biomass. In addition, to the best of our knowledge, *E. umbellata* leaves-based biomass has not been used for the adsorption process so far.

2. Experimental

2.1. Solutions and reagents

All the solutions used during the experiments were prepared in distilled water. MB (from BDH chemicals) was used in the experiments without purification. 1 g of MB was dissolved in 1,000 mL of distilled water to prepare a stock solution of MB. The solutions of different concentrations (5–25 mg/L) were prepared from the stock solution of MB using the dilution method. 0.1 M HCl and 0.1 M NaOH were used for the optimization of pH levels.

2.2. Elaeagnus umbellata (biosorbent) preparation

E. umbellata leaves were accumulated from Rairban Village of Bagh District of Azad Jammu and Kashmir, Pakistan. *E. umbellata* leaves were soaked in water for 24 h. These leaves were washed using distilled water and dried in the open air. The dried *E. umbellata* leaves were ground to powder using an electric grinder and sieved through 70 mesh sieves. For acid modification, *E. umbellata* leaves powder (10 g) was mixed with 0.1 M HCl. The magnetic stirrer was used for agitating the mixture for 24 h. The distilled water was used for washing *E. umbellata* leaves to powder and filtered. The obtained residue was kept in an oven overnight at 70°C for drying purposes. The optimized conditions were applied for acid-modified and without modified *E. umbellata* leaves.

2.3. Characterization of E. umbellata leaves

The chemical and physical properties of the biosorbents are necessary to investigate their adsorption capacities. The characterization of *E. umbellata* leaves powder was done by UV-Visible and Fourier-transform infrared (FT-IR) spectroscopy. The scanning electron microscopy (SEM) analysis was done to investigate the surface morphology of *E. umbellata* leaves powder. The Universal V 4.5A TA, SDT Q600 V 20.9 was employed in thermal studies. The Quantachrome NOVAWin V. 11.04 was used in the delineation of the surface area of *E. umbellata* leaves powder. The moisture contents and bulk density were calculated and the obtained results are given in Table 1.

2.4. Desorption studies

The desorption experiments were performed in batches with different desorbing reagents such as distilled water, 0.1 M, NaCl, 0.1 M NaOH, 0.1 M HNO_3, 0.1 M HCl and 0.1 M KCl, solutions. 0.15 g of *E. umbellata* leaves and 25 mg/L

Table 1
Physical properties of *E. umbellata* leaves

Adsorbent *E. umbellata* leaves			
Brunauer–Emmett–Teller analysis		Physical properties	
Surface area	140.780 m^2/g	Moisture content	1.62%
Pore diameter	28.568 nm	Bulk density	0.284 g/cm^3
Pore volume	0.097 cc/g		

MB solution (50 mL) were stirred at room temperature for 90 min. MB loaded biosorbent was used for the removal of unadsorbed dye after washing with distilled water and shaken with various desorbing agents (25 mL). The desorbed MB concentration was calculated. The equation used for the calculation of percent MB desorption is given in Eq. (1).

$$\%\,\text{Desorption} = \frac{m_d}{m_a} \times 100 \tag{1}$$

where m_a represents the amount adsorbed and m_d represents the amount of MB desorbed.

2.5. Batch equilibrium and kinetic studies

The batch adsorption studies were performed by adding 0.15 g of the adsorbent in 50 mL of MB solution in three conical flasks (250 mL). The mixtures in three flasks were stirred and heated at 298, 308 and 318 K, respectively. The reaction mixtures were filtered and absorbance values of the filtrates were determined using UV-Vis spectrophotometer at λ_{max} 665 nm for MB. The equilibrium concentrations of the samples were determined using Beer–Lambert law and adsorption capacity was calculated using Eq. (2).

$$q_e = \frac{\left(C_0 - C_e\right)V}{m} \tag{2}$$

where m represents *E. umbellata* leaves mass (g). C_0 is the initial concentration and C_e is the concentration of MB at equilibrium (mg/L) and V is the volume of solution (L). The percentage removal of MB was calculated using Eq. (3) [30].

$$\%R = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \tag{3}$$

The obtained data were analyzed by employing the adsorption isotherm models (Langmuir, Freundlich and Temkin) using Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \left(\frac{1}{Q_0}\right)C_e \tag{4}$$

where C_e is the concentration of the dye at equilibrium, q_e is the adsorption capacity at equilibrium, Q_0 and b are the rate of adsorption.

The dimensionless factor of the Langmuir isotherm equation is shown in Eq. (5).

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 represents the initial concentration of MB. R_L value is helpful in determining the nature of the adsorption process. The process is favorable if R_L ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$). The Freundlich model was used for determining the heterogeneity of the system using an empirical isotherm [Eq. (6)].

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_0 \tag{6}$$

where K_F (mg/g (L/mg)$^{1/n}$) is bond strength and n represents bond energy.

Temkin isotherm model can be expressed as:

$$q_e = B \ln A + B \ln C_e \tag{7}$$

The above relation shows Temkin constant of the heat of adsorption (J/mg), heat of adsorption constant ($RT/b = B$), T = absolute temperature (K) and $b = A$ = equilibrium constant for maximum binding energy (L/g) [39].

The nature of the adsorption process was determined by performing thermodynamic studies using various mathematical relations such as entropy change ($\Delta S°$ J/K mol), free energy change ($\Delta G°$ kJ/mol) and enthalpy change ($\Delta H°$ kJ/mol) [Eqs. (8) and (9)].

$$\Delta G = -RT \ln K_c \tag{8}$$

$$\ln K_c = \frac{-\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{9}$$

In the above equations, K_c is an equilibrium constant, R is a gas constant and T is absolute temperature.

3. Results and discussion

3.1. Characterization of E. umbellata leaves

The characterization of *E. umbellata* leaves powder was carried out by different characterization techniques such as FT-IR and UV-Vis spectroscopy. FT-IR spectra were recorded in the range of 400–4,000 cm^{-1}, while UV-Vis spectra were recorded in the range of 200–800 nm. SEM analysis was done to investigate surface morphology. Thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) studies were also carried out for the thermal analysis of *E. umbellata* leaves.

3.2. FT-IR analysis

FT-IR analysis was carried out prior and subsequent to the adsorption for analyzing functional groups present on *E. umbellata* leaves. The C–H stretching modes of aliphatic compounds and –OH group with prominent peaks appeared at 2,910 and 3,415 cm^{-1}, respectively. The legend peak at 1,635 cm^{-1} was found due to stretching and bending modes of the adsorbed water. After the adsorption of MB on *E. umbellata* leaves, the more intense peak at 1,031cm^{-1} was changed to less intense peak and shifted at 1,087 cm^{-1}. The prominent peak at 622 cm^{-1} was attributed to C–S linkage (Fig. 1a). These peaks were not found in the FT-IR spectrum of MB (Fig. 1b).

FT-IR spectrum of the acid-modified *E. umbellata* leaves (biosorbent) showed similar features with the FT-IR spectrum of the non-modified *E. umbellata* leaves with various changes in the band intensities. The peak at 3,415 cm^{-1} was shifted to 3,232 cm^{-1}. At 2,910 cm^{-1}, the peak appeared due to stretching vibrations of C–H and was not found in the FT-IR spectrum of the acid-modified *E. umbellata* leaves. The peak appeared at 1,647 cm^{-1} was attributed to stretching and bending modes of the adsorbed water and at peak

at 1,020 cm^{-1} was referred to C–X (X=Halogen) and peak at 622 cm^{-1} disappeared in the FT-IR spectrum of the acid-modified *E. umbellata* leaves (Fig. 1c and d).

3.3. Scanning electron microscopy

The surface morphology of the *E. umbellata* leaves powder was analyzed by SEM. The external morphology of *E. umbellata* leaves powder was analyzed before and after the adsorption experiments. Both photographs (Fig. 2a and b) indicated a clear difference in the morphology of the adsorbent before and after the adsorption. SEM image obtained after adsorption (Fig. 2b) indicated rough and porous surfaces of *E. umbellata* leaves powder and smooth surface after the adsorption of MB onto the adsorbent. The difference in the surface morphology before and after adsorption was also observed in acid-modified *E. umbellata* leaves (Fig. 2c and d). The mechanism of the adsorption of MB on *E. umbellata* leaves is shown in Fig. 3.

3.4. Thermal gravimetric analysis

The thermogram of TGA and DSC obtained is shown in Fig. 4. The initial mass loss occurred due to sublimation, vapor loss, chemical decomposition and dehydration [37]. The thermogram analysis of mass deficit was about 13.11% at 0°C–200°C (due to moisture contents), 42.94% between 200°C–380°C (due to organic matter) and 23.99% between 380°C–789°C (due to of loss of hydroxyl and decarbonation).

DSC analysis showed two phases of decomposition. The negative peak at the first phase was observed around 60°C which indicated the loss of moisture contents and evaporation of various volatile compounds [38]. The utilization of energy in evaporation, as well as drying of the volatile compounds below 250°C, showed an endothermic reaction. The second exothermic phase was observed above 250°C in which indicated the disintegration process of cellulose lignin and hemicellulose. These biomass components, that is, hemicellulose, cellulose and lignin were decomposed at different temperatures, 200°C–260°C, 240°C–350°C and 280°C–500°C, respectively [38].

3.5. Influence of pH

pH of the dye has a major effect on the dye uptake capacity. The adsorption capacity was increased (7.44 to 7.91 mg/g) by changing pH from 3 to 12 and then keeps constant up to pH 14. The effect of pH for MB adsorption over *E. umbellata* leaves is represented in Fig. 5. It was found that with the increase in pH (3–12), the removal

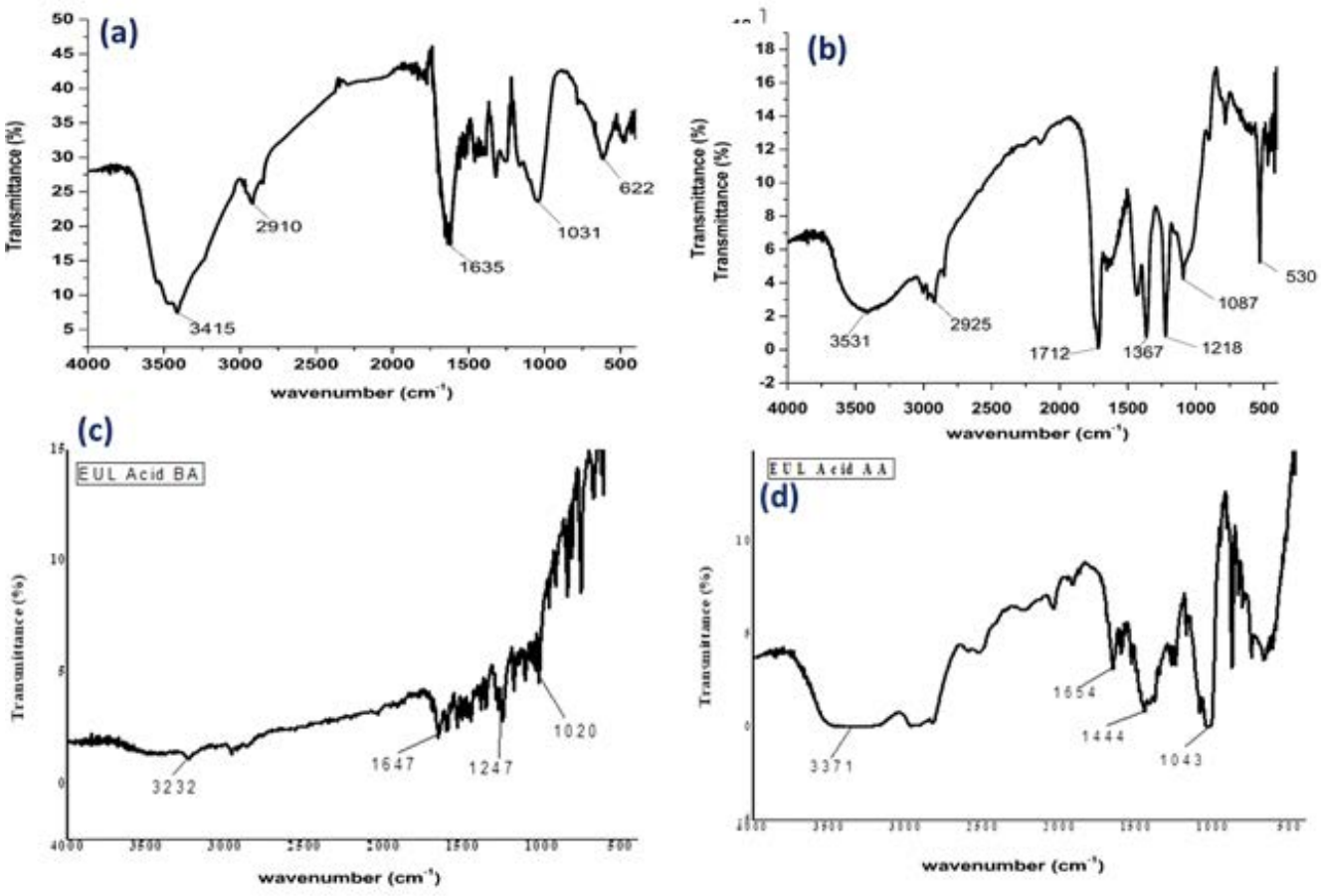

Fig. 1. FT-IR spectra of: *E. umbellata* leaves (a) before and (b) after adsorption; *E. umbellata* leaves acid-modified (c) before and (d) after adsorption.

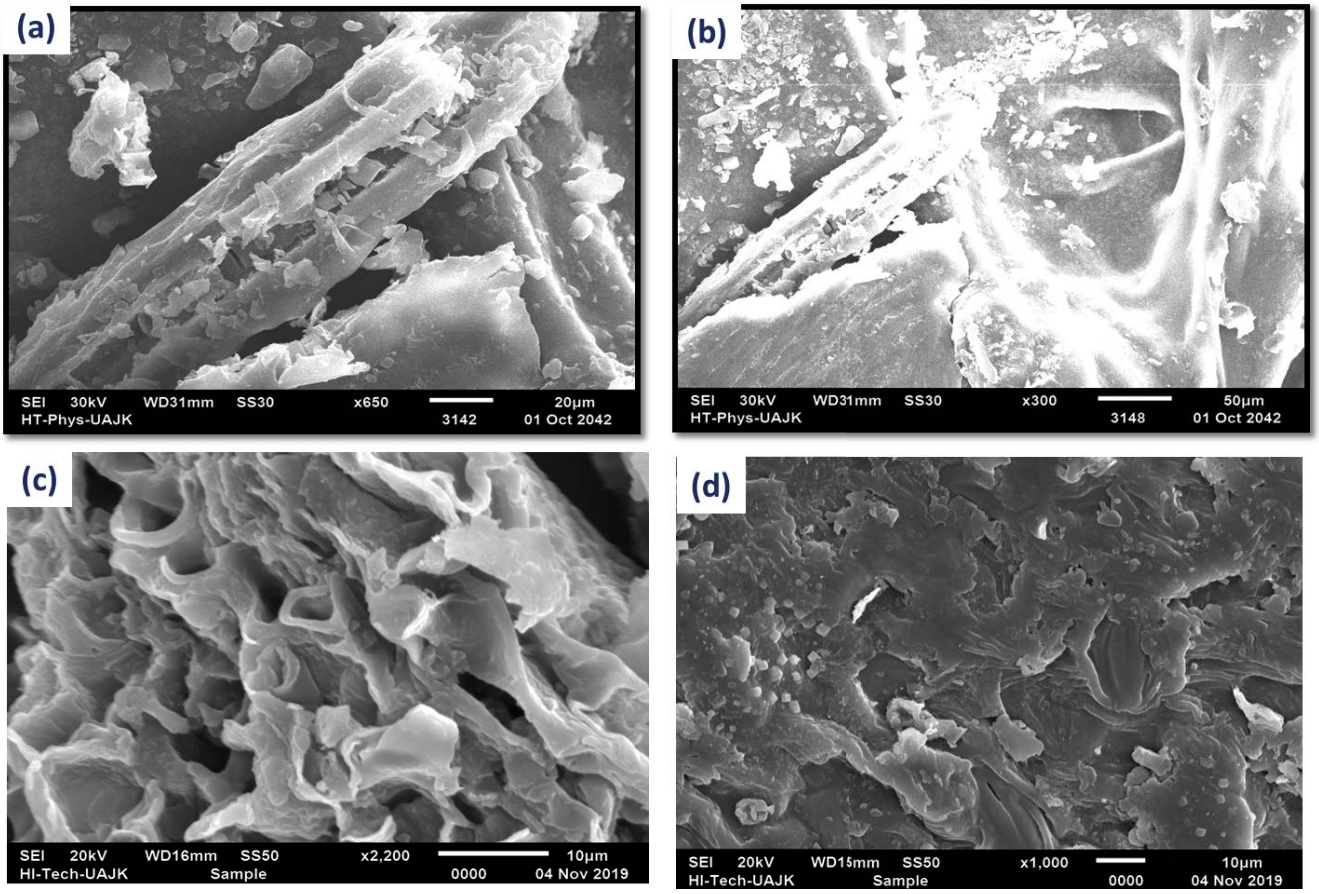

Fig. 2. SEM images of: *E. umbellata* leaves powder (a) before and (b) after adsorption; acid-modified *E. umbellata* leaves powder (c) before and (c) after adsorption.

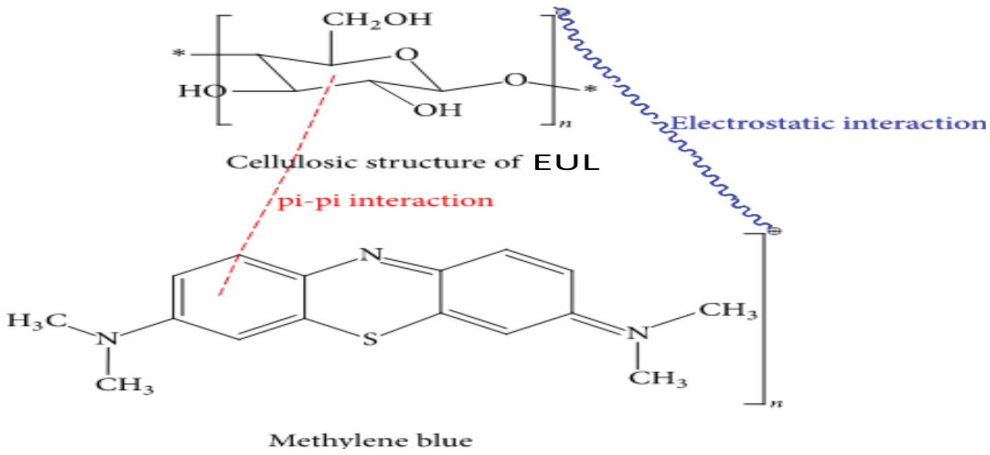

Fig. 3. Mechanism of adsorption of MB on *E. umbellata* leaves.

of MB was also increased. The maximum MB percentage removal was found to be 94.94% at pH 12. The uptake of MB (solute) was directly related to the active sites present on *E. umbellata* leaves and also to the solute chemistry in the solution. On *E. umbellata* leaves surface sites, the accumulation of positively charged ions was increased at low pH, while adsorption of MB was decreased. So, due to electrostatic forces of repulsion, the adsorption of dye cations was not favorable, which might be due to the presence of a large number of H^+ competing with the cations of dye for the sites of adsorption on *E. umbellata* leaves [39].

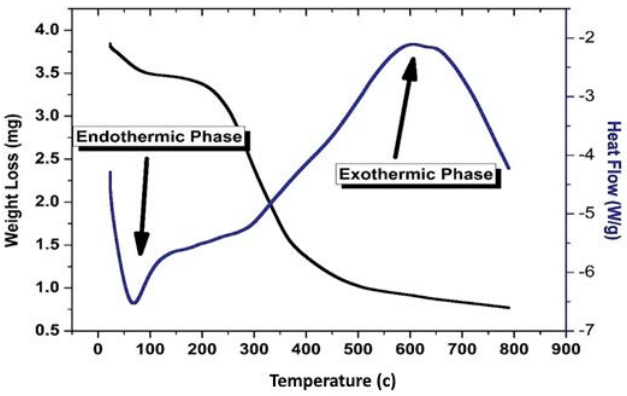

Fig. 4. Thermogram of TGA and DSC analysis.

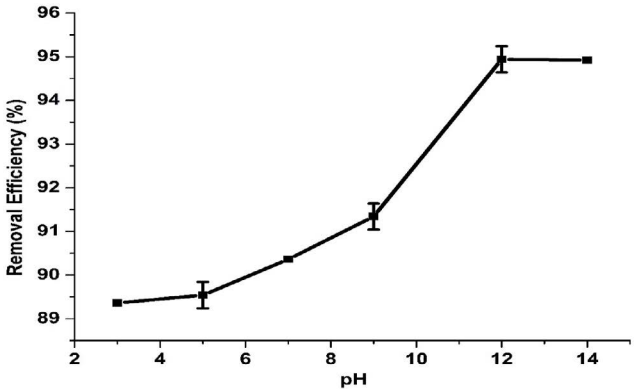

Fig. 5. Effect of pH on MB adsorption on *E. umbellata* leaves (t = 90 min; *E. umbellata* leaves dose = 0.15 g; T = 298 K; preliminary concentration = 25 mg/L).

The maximum percentage removal of MB was found to be 94.94% at pH 12. The zero point charge (pHzpc) was used to explain the effect of pH on the percentage removal of *E. umbellata* leaves. When the pH of the solution was above pHzpc, the surface of the adsorbent becomes more negatively charged. These negatively charged ions interacted with cationic sites of MB through electrostatic forces of attraction.

3.6. E. umbellata leaves dosage effect

The effect of *E. umbellata* leaves dosage on the adsorption of MB was studied at contact time 90 min, pH 12 and at 298 K (Fig. 6). It was found that by increasing *E. umbellata* leaves dosage (0.15–0.45 g), the percentage removal of MB was increased from 88.26% to 91.3%. The increase in adsorbent dosage (0.15–0.45 g) decreased the dye uptake capacity (7.60–2.20 mg/g). The removal efficiency of MB was increased with the increase in *E. umbellata* leaves (adsorbent) dosage because of increased availability of surface area for adsorption, so the adsorption sites also increased [40]. The adsorption capacity decreased, like the dosage of biomass (adsorbent) was increased because the significant part of the adsorption sites due to random enmeshment remained unavailable at a greater amount of adsorbent. At lower adsorbent

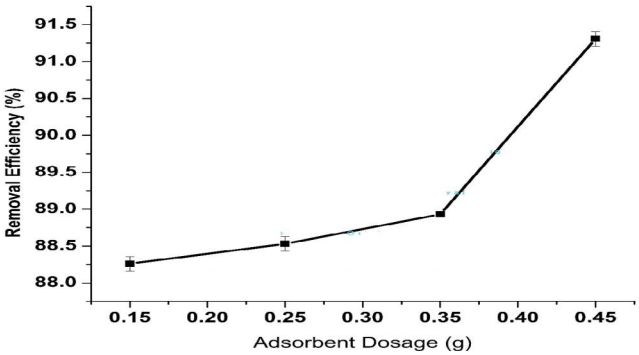

Fig. 6. *E. umbellata* leaves dosage effect on MB percentage removal (preliminary pH = 12; T = 298 K; preliminary concentration = 25 mg/L).

dosage, the adsorption capacity was increased because the number of active sites became saturated with the dye [41].

3.7. Influence of MB initial concentration

The influence of MB initial concentration on adsorption of MB on *E. umbellata* leaves was studied by taking MB concentrations (5–25 mg/L) with 0.15 g biosorbent dosage in a conical flask (250 mL), the mixture was shaken for 90 min at 298 K and at pH 12. The absorbance measurement was done using a UV-Vis spectrophotometer after filtration. The percent removal of MB was obtained to be (17.54% to 91.59%) and adsorption capacity (0.98–7.62 mg/g) by varying the initial concentration of MB 5–25 mg/L (Fig. 7). The change in the initial concentration of the dye gave suitable energetic forces that hindered the mass movement of MB between two phases (aqueous and solid) [42]. Therefore, the dye concentration affected the percentage removal efficiency of *E. umbellata* leaves.

3.8. Effect of contact time

The effect of contact time on the percentage removal efficiency of *E. umbellata* leaves was observed by taking MB concentration (5–25 mg/L) in a 250 mL conical flask with *E. umbellata* leaves dose (0.15 g) by varying the agitation time from 10–120 min. UV-Vis. spectrophotometer was used for determining the absorbance of the filtrate solution. The dye uptake capacity and percentage removal were calculated at equilibrium using Eqs. (2) and (3), respectively. The percentage removal and MB uptake capacity were increased with the increase in contact time (10–120 min) and then remained constant with time. The percentage removal efficiency was increased from 17.54% to 91.59% for the samples having an initial dye concentration (25 mg/L). The percentage removal and dye uptake capacity of the acid-modified *E. umbellata* leaves were obtained to be 93.65% and 9.98 mg/g, respectively at optimized experimental conditions. The rise in contact time has also improved the dye uptake capacity from 0.98 to 7.62 mg/g (Fig. 7). The comparison of the dye uptake capacity with previous studies is given in Table 2. The early adsorption phase is represented by maximum removal efficiency and

adsorption capacities together with the accessibility of considerable surface area of the adsorbent [43].

3.9. Influence of temperature

MB adsorption on *E. umbellata* leaves was carried out using 25 mg/L of MB initial amount (50 mL) pH (12) and 0.15 g adsorbent dose for investigating the effect of temperature. The samples were filtered after shaking the solutions in an electric thermostat shaker at a temperature (298–323 K). The concentration at equilibrium was determined by measuring the filtrate absorbance. It was found that with the increase in temperature, the percentage removal efficiency of *E. umbellata* leaves was decreased from 93.26% to 80.44% and adsorption capacity was also decreased from 7.77 to 6.70 mg/g. The decreased dye uptake capacity with the increased temperature (298–323 K) occurred and was observed maximum at 298 K (Fig. 8). The decrease in adsorption capacity with temperature represented the exothermic process. The lower temperature declined the surface activity suggested that the adsorption of MB on the adsorbent was an exothermic process, so low temperature favored the process of biosorption whereas higher temperature increased the surface activity signified that the adsorption process was endothermic [44].

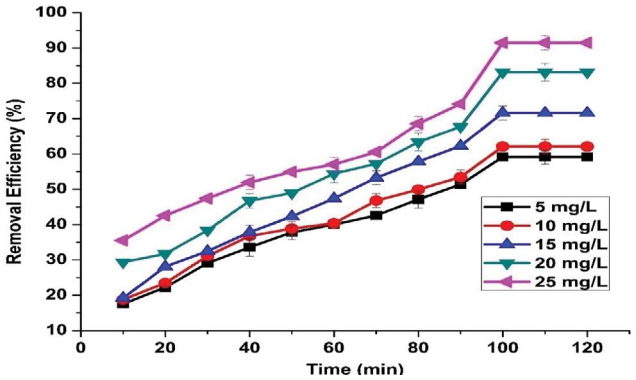

Fig. 7. Contact time and MB concentration effects on the percentage removal efficiency of *E. umbellata* leaves (pH = 12; *E. umbellata* leaves dosage = 0.15 g; preliminary concentration 25 mg/L).

3.10. Adsorption kinetics

Lagergren pseudo-first-order (PFO) model [45] was used to calculate the rate constant of adsorption [Eq. (10)]. The graph of $\log(q_e - q_t)$ vs. time was employed for calculating K_1 and q_e for different concentrations of MB (Table 3). According to isotherm data, the best constraint with the pseudo-second-order (PSO) model having $R^2 \geq 0.99$ for different concentrations was used during the analysis. PSO model is also applicable for the calculation of kinetic data using Eq. (10) [46].

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{K_1}{2.303}\right)t \tag{10}$$

The parameters such as pseudo-second-order constant (K_2) as well as equilibrium adsorption capacity (q_e) were calculated from the graph of t vs. t/q_t.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{11}$$

Table 2
Comparison of removal efficiency of the present work with previous work

Adsorbents	q_m (mg/g)	References	Adsorbent	Adsorption capacity (K_F)	References
Cashew nut shell	5.31	[49]	Alcian Blue	0.1012	[56]
Coarse grinded wheat straw	3.82	[50]	Natural red	0.00112	[56]
Neem leaf powder	3.67	[51]	Brilliant Blue	0.1474	[57]
Fine grinded wheat straw	2.23	[52]	Corn husk	14.58	[58]
Chitosan cross-linked (beads)	5.60	[53]	*Elaeagnus umbellata* leaves	28.97	This study
Coir pith carbon	5.87	[54]			
Ficcus palmata	6.89	[55]			
Elaeagnus umbellata leaves	7.91	This study			

Table 3
Adsorption kinetics results of MB removal

	Pseudo-first-order kinetic			Pseudo-second-order kinetic				Elovich model		
C_0 (mg/L)	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (×10^3) g/(mg min)	R^2	SSE	a	b	R^2
10	1.407	0.06	0.88	2.07	0.02	0.98	0.44	0.24	0.06	0.98
20	4.470	0.05	0.93	5.98	0.05	0.99	2.28	0.55	0.01	0.97
30	7.247	0.04	0.94	7.24	0.02	0.98	1.00	0.80	0.02	0.99
40	10.33	0.03	0.96	11.62	0.04	0.98	1.66	1.60	0.03	0.98
50	15.55	0.04	0.93	19.23	0.06	0.99	13.54	2.72	0.03	0.97

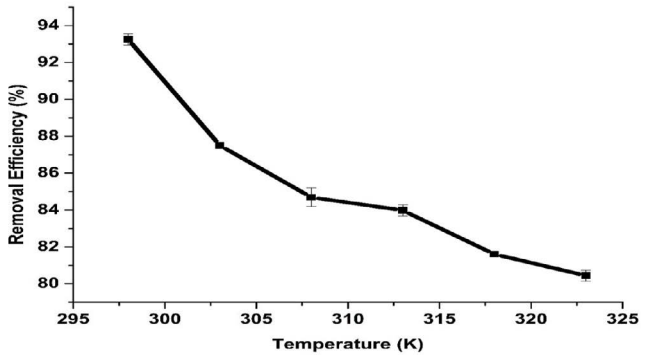

Fig. 8. Effect of temperature on the percentage removal efficiency of *E. umbellata* leaves (t = 90 min).

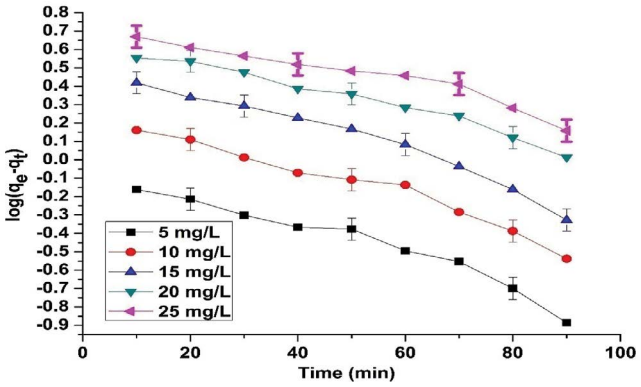

Fig. 9. Pseudo-first-order kinetics studies of MB adsorbed *E. umbellata* leaves.

The results showed ($R^2 \geq 0.99$) that the PSO model closely follows the model instead of PFO and also indicated the favorable MB adsorption on *E. umbellata* leaves (Figs. 9 and 10). The Elovich kinetic model (EM) was also employed and expressed as:

$$q_t = a + b\ln t \tag{12}$$

The straight-line graph of ln$t$ vs. q_t was used for the calculation of constants, a and b [47,48]. The following order PSO > PFO > EM of kinetic models in adsorption kinetics of MB over *E. umbellata* leaves was observed on the basis of R^2 values obtained.

3.11. Intraparticle model

The adsorption mechanism is commonly identified by the intraparticle diffusion model. In the processes of adsorption, the dye uptake mostly changes proportionately with $t^{1/2}$ rather than with the contact time [59] and can be represented as follows:

$$q_t = K_i t^{1/2} + C \tag{13}$$

where q_t is the amount of MB adsorbed, $t^{1/2}$ is the square root of the time, and K_i (mg/g min$^{0.5}$) is the rate constant of intraparticle diffusion. The two different linear parts have been observed in the plot of $t^{1/2}$ vs. q_t. The diffusion of dye outer boundary layers surrounded by the adsorbent is represented by the first part. The second part is related to the dye equilibrium formation at the adsorbent surface as well as gradual dye diffusion into internal pores [60]. The multilinear slopes for the adsorption process showed that intraparticle diffusion is not rate-limiting step but boundary layer adsorption involvement was seen.

3.12. Thermodynamic parameters

Gibb's free energy (20.88, 19.23 and 19.27 kJ/mol) for the adsorption of MB on *E. umbellata* leaves at various temperatures (298, 308 and 318 K) was calculated (Table 4). MB showed a spontaneous adsorption process over *E. umbellata* leaves, as indicated by negative values of Gibbs free energy. The enthalpy and entropy change assessment were analyzed

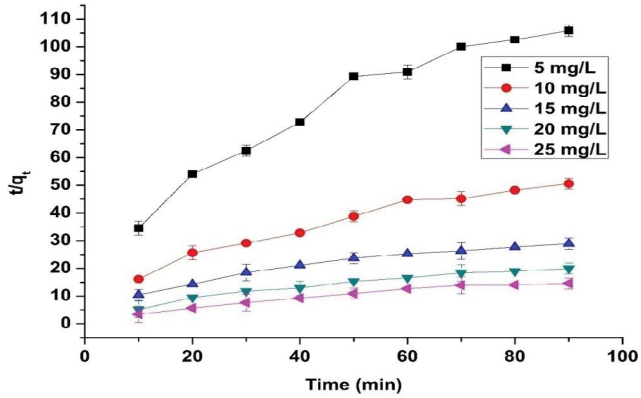

Fig. 10. Kinetic studies of pseudo-second-order of MB adsorbed on *E. umbellata* leaves.

by plotting ln$K$ vs. 1/T values (Fig. 12). The values of K (8.43, 7.51 and 7.29) were calculated from the graph plotted between 1/T and ln$K$ at different temperatures. The enthalpy change ($\Delta H°$) value was found negative (–31.46 kJ/mol). The negative value indicated the non-spontaneity and exothermic reaction nature of MB adsorption on *E. umbellata* leaves. The decreased randomness at the solution–solute interface during the adsorption process was indicated by Gibbs free energy (–35.78 J/K mol) and entropy change ($\Delta S°$) [61].

3.13. Adsorption equilibrium

The adsorbate (dye) was removed by the adsorbent and the adsorption isotherm described the remaining adsorbate concentration in the solution. The experimental data and adsorption isotherm models are comparable at equilibrium [62]. The Langmuir, Freundlich and Temkin isotherms were employed for the data analysis. The Langmuir isotherm [63], plots C_e/q_e vs. C_e, showed straight lines (Fig. 13) for the adsorption of MB on *E. umbellata* leaves. The Langmuir constants (b and Q_0) were calculated and are shown in Table 5. The dimensionless equilibrium constant R_L has been narrated by Kumar et al. [64].

In this study, 0.017, 0.020 and 0.031 are R_L values at 298, 308 and 318 K, respectively. R_L values represented

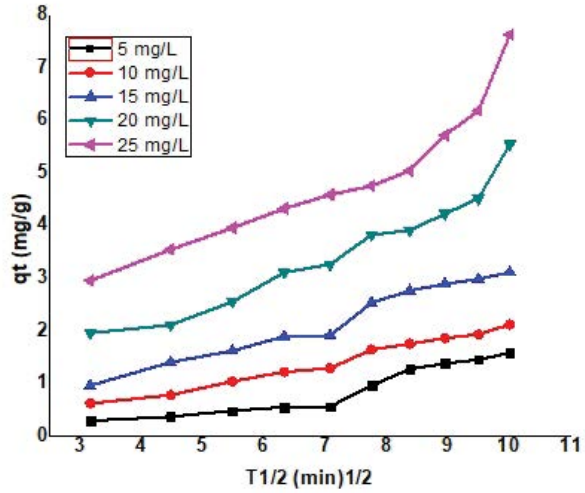

Fig. 11. Intraparticle diffusion models.

Table 4
Thermodynamics data

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
298	–20.88		
308	–19.23	–31.46	–35.78
318	–19.27		

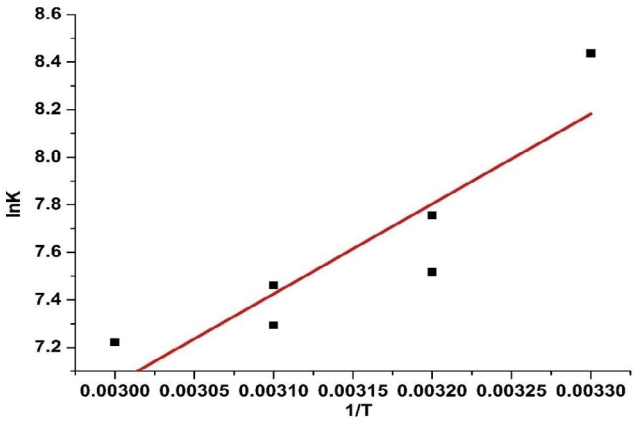

Fig. 12. Thermodynamics analysis for MB adsorbed on *E. umbellata* leaves.

that *E. umbellata* leaves are suitable for the adsorption of MB. The adsorption intensity and surface heterogeneity were calculated from the slope (1/*n*) between 0 and 1 in the Freundlich isotherm model. Whereas, because of decreased slope value, there is more heterogeneity [65]. Fig. 12 $\ln q_e$ vs. $\ln C_e$ showed smooth lines represented that the adsorption of MB over *E. umbellata* leaves is persistent to the Freundlich isotherm model (Table 5). The graph of the Temkin isotherm model was plotted between $\ln C_e$ vs. q_t (mg/g) (Fig. 14). On the basis of R^2 values, the Freundlich isotherm was found to best conformed with correlation isotherm determination parameters after a comparison of analysis of isotherms than Langmuir.

3.14. Statistical analysis

The error analysis method (sum of squared error (SSE)) was used for the calculation of appropriateness using Eq. (14) and applied to the data obtained experimentally. The lower SSE values best fitted with the obtained data (Tables 3 and 5).

$$\text{SSE} = \sum_{i=1}^{n}\left(q_{e\ \text{calc}} - q_{e\ \text{meas}}\right)^2 \tag{14}$$

3.15. Desorption

The different desorbing agents used during studies are HCl, KCl, NaOH, 0.1 M NaCl, 0.1 M HNO_3 and distilled H_2O. The study revealed that the maximum desorption (25.39%) was accomplished by 0.1 M NaOH and designated as a favorable desorbing agent for the desorption of *E. umbellata* leaves (Table 6).

4. Conclusion

E. umbellata leaves powder was used as a biosorbant for the removal of MB from the aqueous solution. The effect of several factors such as initial concentration of MB, temperature, pH, the dosage of *E. umbellata* leaves and contact time was studied on the adsorption of MB. The adsorption equilibrium time was attained for MB on *E. umbellata* leaves with an initial concentration (25 mg/g) of the dye at 90 min. It was found that with the increase in the dosage of the adsorbent, the removal efficiency of MB was increased. The removal efficiency of *E. umbellata* leaves for MB was also analyzed at different pH. The maximum removal percentage was found at pH 12,

Table 5
Results of adsorption isotherm models

Linear regression analysis												
	Langmuir constant					Freundlich constant				Temkin constant		
T (K)	Q_0 (mg/g)	*b* (L/mg)	R^2	R_L	SSE	K_F	*N*	1/*n*	R^2	*B*	K_t	R^2
298	5.37	1.26	0.96	0.017	208.2	20.94	3.41	0.29	0.99	0.973	3.903	0.93
308	8.84	0.81	0.96	0.020	141.1	18.49	2.96	0.33	0.99	0.796	3.165	0.91
313	23.25	0.28	0.98	0.031	504.4	28.97	4.14	0.24	0.99	1.615	5.437	0.97

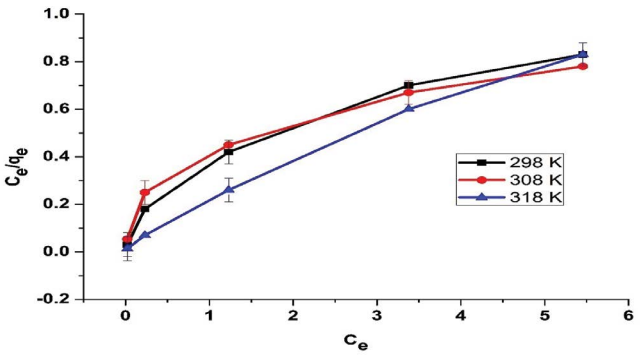

Fig. 13. Langmuir isotherm for MB adsorbed *E. umbellata* leaves.

Table 6
Percentage desorption results of MB loaded on *E. umbellata* leaves

Desorbing reagents	% desorption
0.1 M NaOH	25.39
0.1 M HCl	10.81
0.1 M KCl	8.74
0.1 M NaCl	6.84
0.1 M HNO_3	4.12
Distilled water	3.26

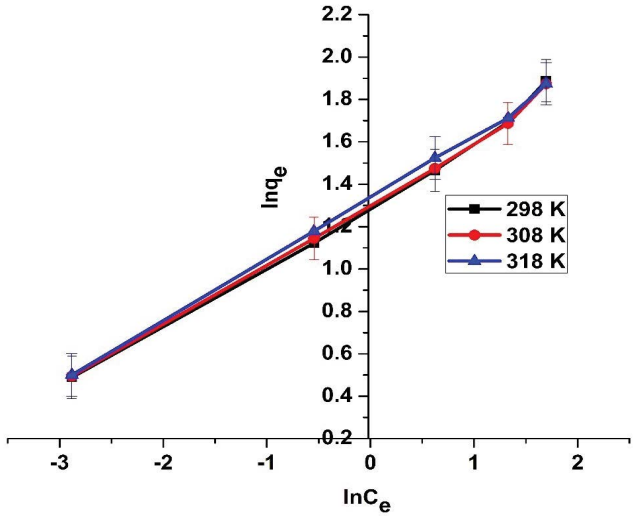

Fig. 14. Freundlich isotherm studies.

which was 91.59%. After acid-modification of *E. umbellata* leaves with HCl, the adsorption capacity and removal efficiency were increased to 9.29 mg/g and 93.65%, respectively. The kinetic studies were performed to demonstrate the adsorption process followed by PSO models, whereas equilibrium data followed the Freundlich isotherm model with R^2 = 0.99. The maximum adsorption measurements were found to be 20.94, 18.49 and 28.97 mg/g at temperatures 298, 308 and 318 K, respectively. In distilled water, the maximum percentage desorption of MB-loaded *E. umbellata* leaves was found to be 25.39%. It was concluded that low-cost bio-waste *E. umbellata* leaves have the potential to adsorb MB from an aqueous solution. Therefore, *E. umbellata* leaves can efficiently be utilized as an effective adsorbent for the removal of MB from the aqueous solution.

References

[1] R. Ayyappan, A. Carmalin Sophia, K. Swaminathan, S. Sandhya, Removal of Pb(II) from aqueous solution using carbon derived from agricultural wastes, Process Biochem., 40 (2005) 1293–1299.
[2] S. Dawood, T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design, Water Res., 46 (2012) 1933–1946.
[3] Z. Yu, T. Qi, J. Qu, L. Wang, J. Chu, Removal of Ca(II) and Mg(II) from potassium chromate solution on Amberlite IRC 748 synthetic resin by ion exchange, J. Hazard. Mater., 167 (2009) 406–413.
[4] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, J. Hazard. Mater., 122 (2005) 161–170.
[5] T.K. Sen, S. Afroze, H.M. Ang, Equilibrium, kinetics and mechanism of removal of methylene blue from aqueous solution by adsorption onto pine cone biomass of *Pinus radiata*, Water Air Soil Pollut., 218 (2011) 499–515.
[6] V.K. Gupta, Suhas, I. Ali, V.K. Saini, Removal of rhodamine B, fast green, and methylene blue from wastewater using red mud, an aluminum industry waste, Ind. Eng. Chem. Res., 43 (2004) 1740–1747.
[7] W.-T. Tsai, K.-J. Hsien, H.-C. Hsu, Adsorption of organic compounds from aqueous solution onto the synthesized zeolite, J. Hazard. Mater., 166 (2009) 635–641.
[8] N.M. Mahmoodi, B. Hayati, M. Arami, C. Lan, Adsorption of textile dyes on pine cone from colored wastewater: kinetic, equilibrium and thermodynamic studies, Desalination, 268 (2011) 117–125.
[9] L Cui, C. Liu, G. Wu, Performance and mechanism of methylene blue biosorption on orange peel, Environ. Technol., 29 (2008) 1021–1030.
[10] M. Šćiban, M. Klašnja, B. Škrbić, Adsorption of copper ions from water by modified agricultural by-products, Desalination, 229 (2008) 170–180.
[11] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions, Water Air Soil Pollut., 223 (2001) 5267–5282.
[12] T. Robinson, B. Chandran, P. Nigam, Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk, Environ. Int., 28 (2002) 29–33.
[13] V. Vadivelan, K. Vasanth Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, J. Colloid Interface Sci., 286 (2005) 90–100.
[14] V.K. Garg, R. Gupta, A.B. Yadav, R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust, Bioresour. Technol., 89 (2003) 121–124.
[15] P. Janos, H. Buchtova, M. Ryznarova, Sorption of dyes from aqueous solutions onto fly ash, Water Res., 37 (2003) 4938–4944.
[16] M. Visa, C. Bogatu, A. Duta, Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash, Appl. Surf. Sci., 256 (2010) 5486–5496.
[17] N. Oladoja, C. Aboluwoye, Y. Oladimeji, A. Ashogbon, I. Otemuyiwa, Studies on castor seed shell as a sorbent in basic dye contaminated wastewater remediation, Desalination, 227 (2008) 190–203.
[18] R. Han, W. Zou, W. Yu, S. Cheng, Y. Wang, J. Shi, Biosorption of Methylene Blue from Aqueous Solution by Fallen Phoenix Trees Leaves, J. Hazard. Mater., 141(2007). 156–162
[19] A.K. Rasheed, H. Tahir, F. Uddin, U. Hameed, Adsorption of Methylene Blue from aqueous solution on the surface of wool

fibre and cotton fibre, J. Appl. Sci. Environ. Manage., 9 (2005) 29–35.
[20] B.A. Dar, A. Tahir, M. Arif, A. Wani, M. Farooqui, Lawn grass: an excellent and low cost sorbent for the removal of Ni(II) ions from wastewater, Electron. J. Environ. Agric. Food Chem., 11 (2012) 1259–2641.
[21] U. Kouakou, A.S. Ello, J.A. Yapo, A. Trokourey, Adsorption of iron and zinc on commercial activated carbon, J. Environ. Chem. Ecotoxicol., 5 (2013) 168–171.
[22] V. Rajeshwarisivaraj, V. Subburam, Activated parthenium carbon as an adsorbent for the removal of dyes and heavy metal ions from aqueous solution, Bioresour. Technol., 85 (2002) 205–206.
[23] B.A. Dar, A. Tahir, A. Wani, M. Farooqui, Isotherms and thermodynamic studies on adsorption of copper on powder of shed pods of *Acacia nilotica*, J. Environ. Chem. Ecotoxicol., 5 (2013) 17–20.
[24] K. Alau, C.E. Gimba, J.A. Kagbu, Removal of dyes from aqueous solution using neem (*Azadirachta Indica*) husk as activated carbon, Arch. Appl. Sci. Res., 2 (2010) 456–461.
[25] P. Saha, Assessment on the removal of methylene blue dye using tamarind fruit shell as biosorbent, Water Air Soil Pollut., 213 (2010) 287–299.
[26] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metals ions from aqueous solutions, Bioresour. Technol., 87 (2003) 129–132.
[27] A. Habib, M. Zahidul Hasan, M. Shajedur Rahman, S. Alam, Tuberose sticks as an adsorbent in the removal of methylene blue from aqueous solution, Pak. J. Anal. Environ. Chem., 7 (2006) 112–115.
[28] S. Shakoor, A. Nasar, Removal of methylene blue dye from artificially contaminated water using citrus limetta peel waste as a very low cost adsorbent, J. Taiwan Inst. Chem. Eng., 66 (2016) 154–163.
[29] R. Fiaz, M. Hafeez, R. Mahmood, *Ficcus palmata* leaves as a low-cost biosorbent for methylene blue: thermodynamic and kinetic studies, Water Environ. Res., 91 (2019) 689–699.
[30] B.T. Pelosi, L.K.S. Lima, M.G.A. Vieira, Removal of the synthetic dye Remazol Brilliant Blue R from textile industry wastewaters by biosorption on the macrophyte *Salvinia natans*, Braz. J. Chem. Eng., 31 (2014) 1035–1045.
[31] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, Fuel, 86 (2007) 1781–1788.
[32] A. Marcilla, A. Gómez-Siurana, C. Gomis, E. Chápuli, M.C. Catalá, F.J. Valdés, Characterization of microalgal species through TGA/FT-IR analysis: application to *nannochloropsis* sp., Thermochim. Acta, 484 (2009) 41–47.
[33] B.H. Hameed, D.K. Mahmoud, A.L. Ahmad, Sorption of basic dye from aqueous solution by pomelo (*Citrus grandis*) peel in a batch system, J. Hazard. Mater., 158 (2008) 499–506.
[34] A. Jeyaseelan, Mu. Naushad, N. Viswanathan, Development of multivalent metal-ion-fabricated fumaric acid-based metal–organic frameworks for defluoridation of water, J. Chem. Eng. Data, 65 (2020) 2990–3001.
[35] A. Jeyaseelan, Mu. Naushad, T. Ahamad, N. Viswanathan, Fabrication of amino functionalized benzene-1,4-dicarboxylic acid facilitated cerium based metal organic frameworks for efficient removal of fluoride from water environment, Environ. Sci. Water Res. Technol., 7 (2021) 384–395.
[36] D.N. Ahmed, L.A. Naji, A.A.H. Faisal, N. Al-Ansari, Mu. Naushad, Waste foundry sand/Mg–Fe-layered double hydroxides composite material for efficient removal of Congo red dye from aqueous solution, Sci. Rep., 10 (2020) 2042, doi: 10.1038/s41598-020-58866-y.
[37] R. Ahmad, R. Kumar, Adsorption studies of hazardous malachite green onto treated ginger waste, J. Environ. Manage., 91 (2010) 1032–1038.
[38] R. Ahmad, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP), J. Hazard. Mater., 171 (2009) 767–773.
[39] V.C. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics, Colloids Surf., A, 272 (2006) 89–104.
[40] T. Santhi, S. Manonmani, Removal of methylene blue from aqueous solution by bioadsorption onto *Ricinus communis* epicarp activated carbon, Chem. Eng. Res. Bull., 13 (2009) 1–5.
[41] B.H. Hameed, Equilibrium and kinetic studies of methylene violet sorption by agriculture waste, J. Hazard. Mater., 154 (2008) 204–212.
[42] Y. Bulut, H. Aydın, A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, Desalination, 194 (2006) 259–267.
[43] D. Ozdes, C. Duran, H.B. Senturk, H. Avan, B. Bicer, Kinetics, thermodynamics, and equilibrium evaluation of adsorptive removal of methylene blue onto natural illitic clay mineral, Desalination, 52 (2014) 208–218.
[44] D. Kavitha, C. Namasivayam, Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, Bioresour. Technol., 98 (2007) 14–21.
[45] M. El-Guendi, Homogeneous surface diffusion model of basic dye stuffs onto natural clay in batch adsorbers, Adsorpt. Sci. Technol., 8 (1991) 217–225.
[46] F.A. Batzias, D.K. Sidiras, E. Schroeder, C. Weber, Simulation of dye adsorption on hydrolyzed wheat straw in batch and fixed-bed systems, Chem. Eng. J., 148 (2009) 459–472.
[47] I. Langmuir, Adsorption of gases on plain surfaces of glass mica platinum, J. Am. Chem. Soc., 40 (1918) 136–403.
[48] P. Saha, S. Dutta, Assessment on thermodynamics and kinetics parameters on reduction of methylene blue dye using flyash, Desalination, 12 (2009) 219–228.
[49] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–470.
[50] T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed-bed adsorbers, AIChE J., 20 (1974) 220–228.
[51] S. Lagergren, Zur Theorie Der Sogenannten Adsorption Geloester Stoffe, Kungliga Svenska Vetenskapsakad, Handl., 24 (1898) 1–39.
[52] F. Haghseresht, G. Lu, Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents, Energy Fuels, 12 (1998) 1100–1107.
[53] S.G. Muntean, A. Todea, M.E. Rădulescu-Grad, A. Popa, Decontamination of colored wastewater using synthetic sorbent, Pure Appl. Chem., 86 (2014) 1771–1780.
[54] R. Babuta, A. Popa, C. Pacurariu, E.S. Dragan, I. Lazau, Adsorption of some phenolic compounds on a new styrene-15% divinylbenzene copolymer functionalized with carboxylic groups, Ser. Chem. Environ. Eng., Chem. Bull. "Politehnica" University of Timisoara, ROMANIA, 60 (2015) 1–6.
[55] I.Y. Kimura, M.C.M. Laranjeira, V.T. Fávere, L. Furlan, The interaction between reactive dye containing vinylsulfone group and chitosan microspheres, Int. J. Polym. Mater., 51 (2002) 759–768.
[56] R. Mallampati, S. Valiyaveettil, Application of tomato peel as an efficient adsorbent for water purification—alternative biotechnology?, RSC Adv., 2 (2012) 9914–9920.
[57] R. Mallampati, L. Xuanjun, A. Adin, S. Valiyaveettil, Fruit peels as efficient renewable adsorbents for removal of dissolved heavy metals and dyes from water, ACS Sustainable Chem. Eng., 3 (2015) 1117–1124.
[58] C.P. Paşka, C. Păcurariu, S.G. Muntean, Kinetic and thermodynamic studies on methylene blue biosorption using corn-husk, RSC Adv., 4 (2014), 62621–62630.
[59] A. Bhatnagar, A.K. Minocha, Assessment of the biosorption characteristics of lychee (*Litchi chinensis*) peel waste for the removal of Acid Blue 25 dye from water, Environ. Technol., 31 (2010) 97–105.
[60] S.G. Muntean, A. Todeaa, S. Bakardjievab, C. Bologac, Removal of non benzidine direct red dye from aqueous solution by using natural sorbents: beech and silver fir, Desal. Water Treat., 66 (2017) 235–250.
[61] T. Calvete, E.C. Lima, N.F. Cardoso, J.C.P. Vaghetti, S.L.P. Dias, F.A. Pavan, Application of carbon adsorbents prepared from

Brazilian-pine fruit shell for the removal of reactive orange-16 from aqueous solution: kinetic, equilibrium and thermodynamic studies, J. Environ. Manage., 91 (2010) 1695–1706.
[62] A. Ayla, A. Çavuş, Y. Bulut, Z. Baysal, C. Aytekin, Removal of methylene blue from aqueous solution onto *Bacillus subtilis*: determination of kinetic and equilibrium parameters, Desalination, 51 (2013) 7596–7603.
[63] F. Boudrahem, F. Aissani-Benissad, A. Soualah, Removal of basic yellow dye from aqueous solutions by sorption onto reed as an adsorbent, Desalination, 54 (2015) 1727–1734.
[64] P.S. Kumar, R.V. Abhinaya, K.G. Lashmi, V. Arthi, R. Pavithra, V. Sathyaselvabala, S.D. Kirupha, S. Sivanesan, Adsorption of methylene blue dye from aqueous solution by agricultural waste: equilibrium, thermodynamics, kinetics, mechanism and process design, Colloid J., 73 (2011) 651–661.
[65] M. Hasan, A.L. Ahmad, B.H. Hameed, Adsorption of reactive dye onto cross-linked chitosan/oil palm ash composite beads, Chem. Eng. J., 136 (2008) 164–172.