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Adsorption of methylene blue using untreated biosorbent prepared from Geranium plant waste: Isothermal, kinetic and thermodynamic study

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The potential of untreated biosorbent prepared from Geranium plant waste for the adsorption of methylene blue from aqueous solution has been investigated. The effects of various experimental parameters such as biosorbent dose, contact time, concentration of dye, pH and temperature have been studied. The maximum adsorption is found at the time of 120 min and pH 7. Sorption increases with increasing temperature. Langmuir, Freundlich, Temkin and Jovanovic adsorption isotherm have been studied. R^2 value suggested better fitment of Freundlich adsorption isotherm. Adsorption of MB followed pseudo second order kinetics with R^2 value 0.9932. The calculated values of ΔH°, ΔS° and ΔG° are found to be 20.75 kJ/mol, 0.078 kJ/mol/K and -0.04682 kJ/mol, respectively. Adsorption processed with physical interaction, it is spontaneous and endothermic in nature. Application to real wastewater, regeneration of biosorbent, cost analysis and disposal of biosorbent have also been discussed. It is found that the prepared GPW biosorbent is stable and may be utilized repeatedly without losing its affinity up to five cycles. GPW is tested against commercial activated carbon (CAC) and it showed adsorption efficiency of 88% compared to 93% of CAC.

Keywords: Biosorbent, Isotherm, Kinetic, Methylene blue, Thermodynamic

Introduction

Highly coloured species are present in huge quantities in industrial effluents from the dyeing and other associated sectors. In industrial effluents, about 10,000 colours with a yearly production volume exceeding 10 x10^6 metric tons are commercially accessible. According to estimates, during production and processing processes, about 20% of the dye stuffs are lost in industrial effluents[1]. Several techniques, including physical, chemical, and biological, have been researched for the removal of dye pigments from contaminated water. Among them, physical dye removal technique is widely used because of its simplicity and inexpensiveness[2]. Methylene blue is a cationic dye used mostly as temporary hair colourant, colouring paper, dyeing cotton and wool, etc. It may cause eye burn or permanent injury to the eyes of human and animals[3].

The widely used adsorbent known as activated carbon is distinguished by its large specific surface area, porous structure, and thermostability. It has a wide range of uses, including the elimination of odour and contaminants from liquid and gaseous phases, medicinal purposes, catalysis, gas storage, electrode materials in electrochemical devices, and elimination of organic contaminants from drinking water and wastewater treatment[4]. The adherence of atoms, ions, or molecules from a gas, liquid, or dissolved solid on a surface of a substance is known as adsorption. Adsorbent refers to the region where adsorbate collects. Adsorbate are the atoms, ions, or molecules that adhere to a solid surface. A film of the adsorbate is formed on the adsorbent's surface as a result of this action[5]. To choose the best adsorbent, equilibrium correlation of biosorbent must be established in order to forecast its behaviour under various experimental circumstances. Equilibrium isotherms are used to develop equilibrium correlation. These isotherms describe how biosorbent interacts with the adsorbent's surface, indicating whether sorption is monolayer or multilayer[6]. Thermodynamic studies are used to predict whether the adsorption is spontaneous or not. Also, it provides information about suitable temperature range for sorption and nature of sorbent and sorbate at equilibrium and kinetic studies are performed to check reaction nature of the adsorption phenomenon[7]. The aim of our work is to explore Geranium plant waste for adsorption of methylene blue dye under different operating conditions such as adsorbent dose, pH, contact time, initial concentration, and temperature. In this study, we used the most widely applied isotherm models to evaluate adsorption performance, such as Langmuir, Freundlich, Temkin and Jovanovic. The kinetic and thermodynamic studies have also been performed to check the order and spontaneity of reaction.

Experimental Section

Preparation of dye solution

Methylene blue was used for sorption study. The stock solution of MB dye was prepared by dissolving accurately weighed dye in distilled water to a concentration of 1000 mg/L. The experimental solution was obtained by diluting the MB dye stock solution in accurate proportions to different initial concentrations like 10, 15, 20, 25 and 30 mg/L. All chemicals used were of analytical grade.

Preparation of biosorbent

Geranium plant waste (GPW) after the extraction of oil was collected from nearby Oil Plant of Narayangaon. The waste was washed with plenty of hot water and then with distilled water. The waste was dried in sun light for 2 days. The dried material was then crushed and kept in oven at 100°C for 1 h and next in muffle furnace to prepare biochars at 300°C for 3 h and sieved through 106 micron particle size mesh to obtain powdered biomass which was used for MB dye adsorption by batch study.

Results and Discussion

Effect of parameters

Initial dye concentration

Initial concentration affects the uptake capacity of the biosorbent to a large extent. The adsorption study was carried out with five different initial concentrations of 10, 15, 20, 25, and 30 mg/L. Volume of 50 mL of each concentration is taken separately and 0.05 g of biosorbent was added. These solutions were stirred for 2h at a fixed rpm of 300. Each solution was then filtered and the absorbance was measured at 665 nm using Systronics UV-visible double beam spectrophotometer. It was seen from Fig. 1 that as initial concentration of MB dye increases the removal percentage was decreased from 98.12% to 78.56%. This is because with increase in dye concentration, the driving force for mass transfer also increases. At low concentrations there will be unoccupied active sites on the adsorbent surface. At the maximum MB concentration, the active sites required for the adsorption of dye will lack and hence adsorption decreases[8].

Adsorbent dose

For this study 50 mL of 10 mg/L of MB dye solution was taken. The sorbent dose was varied from 0.01 g to 0.05 g. These solutions were stirred for 1h at fixed rpm of 300. It was found that as amount of adsorbent increases the removal percentage was also increases from 89.33% to 98.12% as shown in Fig. 2. This increase in adsorption can be attributed to the increase in the number of available adsorption sites. The increase of dye molecules are effectively removed and adsorbed, which increases the effectiveness of adsorption[9].

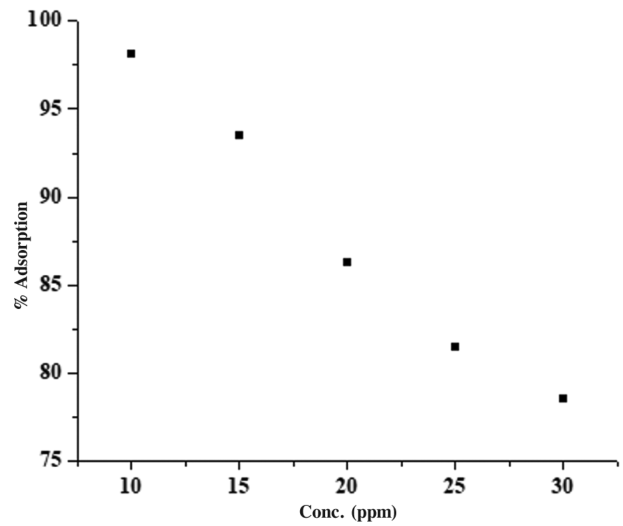

Fig. 1 — Change in % adsorption with initial dye concentration

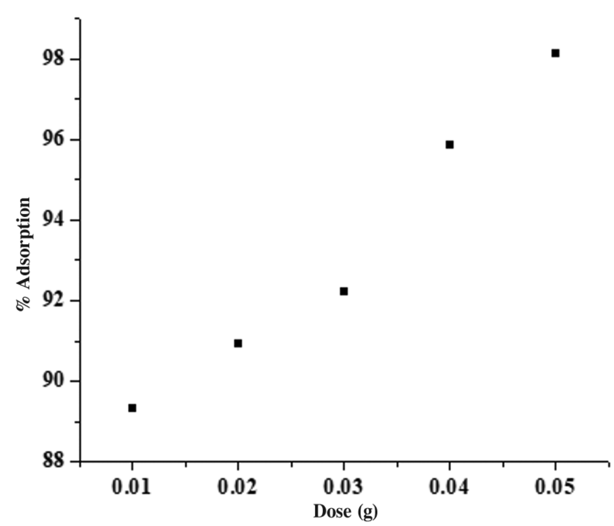

Fig. 2 — Change in % adsorption with dose of adsorbent

Effect of contact time

The percentage of sorption increases with time. No change was observed after 2 h. For this study 50 mL of 10 mg/L of MB dye solution was taken and 0.05 g of biosorbent was added. As observed from Fig. 3, for a contact time of 10 min the adsorption was 64.75%, while it increases with increase in contact time of 60 min to about 88.06%. This may be the cause of the changes in the rate of adsorption. All the adsorbent sites are initially empty and the solute concentration gradient is quite high. Later, a reduction in the number of open adsorbent sites is what causes the reduced adsorption rate. Particularly toward the end of the studies, a drop in adsorption rate suggests that MB may have formed a monolayer on the adsorbent surface[10].

Effect of pH

The pH of an aqueous solution is one of the most crucial parameters in the adsorption of dyes as it affects both the surface binding sites of the adsorbent and the ionization of the dye molecule[11]. The effect of pH on the sorption process of MB dye was studied by adjusting the pH (Instrument by Systronics µ pH System 361) of dye solution in the range of 3 to 9 by adding 0.1 M HCl or 0.1 M NaOH. It was observed that adsorption increases when solution pH increases from pH 3 (35.55 %) to pH 7 (83.14 %) and decreases when solution pH increases from pH 7 (83.14 %) to pH 9 (74.40 %). The maximum adsorption was observed at pH = 7 as indicated in Fig. 4. This might be due to preferential adsorption of H^+ ion or OH^- ion in acidic or alkaline medium on the surface of adsorbent. Increasing solution pH decreases the H^+ ion concentration and increases the OH^- ion concentration, thus, increases the number of negatively charge sites and increases the attraction between dye and adsorbent surface. Generally, the net positive charge decreases with increasing pH value leads to the decrease in the repulsion between the adsorbent surface and the dye, thus improving the adsorption capacity[12].

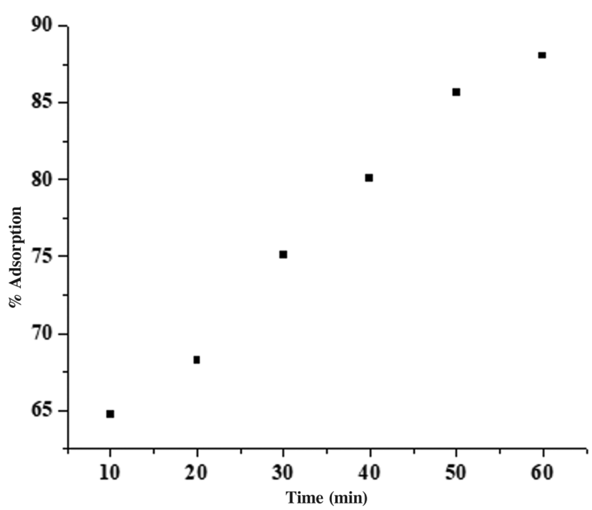

Fig. 3 — Change in % adsorption with contact time

Effect of temperature

The effect of temperature of the solution must be considered while analyzing the factors influencing the adsorption process. Three different temperatures (23, 33 and 43 ± 0.2°C) were tested. It was seen from Fig. 5 that with the increasing temperature adsorption percentage increases from 73.71% to 82.73%. This

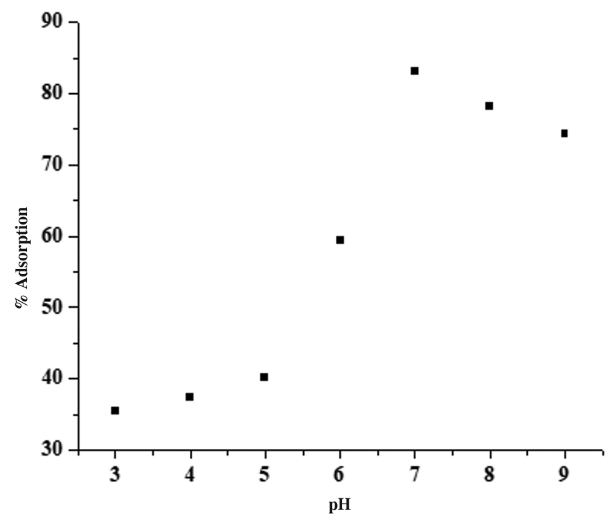

Fig. 4 — Change in % adsorption with pH of dye solution

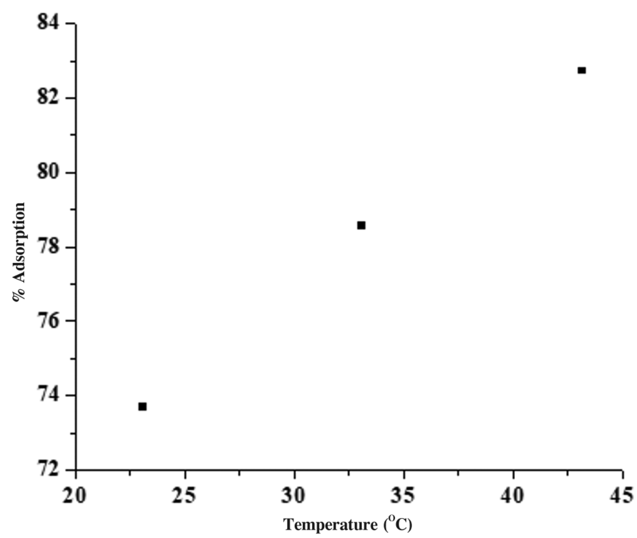

Fig. 5 — Change in % adsorption with temperature of dye solution

Table 1 — Isotherm models tested in this study

Isotherms	Equations	Meaning of terms involved
Langmuir	$\frac{1}{Q_e} = \frac{1}{Q_{max}K_L}\frac{1}{C_e} + \frac{1}{Q_{max}}$ $R_L = \frac{1}{1+K_L C_e}$	Qe is the amount of adsorbed adsorbate molecule per gram of adsorbent (mg/g), Qmax is the capacity of the adsorbent monolayer (mg/g), Ce is the adsorbate equilibrium concentration (mg/L), and KL is the Langmuir adsorption constant, separation factor RL.
Freundlich	$lnQ_e = lnK_f + \frac{1}{n}lnC_e$	Kf is Freundlich constant, Ce is the concentration of adsorbate under equilibrium conditions (mg/L), Qe is the amount of adsorbate absorbed per unit of adsorbent (mg/g), and $n$is the value indicating the degree of linearity between the adsorbate solution and the adsorption process
Temkin	$Q_e = B_T lnA_T + B_T lnC_e$	BT is the adsorption heat constant (if the BT < 8 kJ/mol, the adsorption process occurs physically), AT is the binding equilibrium constant, and T is the absolute temperature.
Jovanovic	$lnQ_e = lnQ_{max} - K_J C_e$	Qe is the amount of adsorbate in the adsorbent at equilibrium (mg/g), Qmax is the maximum uptake of adsorbate, and KJ is the Jovanovic constant.

suggests that the effect of temperature is endothermic in nature on the adsorption process. This might be as a result of the dye being more mobile with rising temperature. A growing number of molecules might also develop the necessary energy to engage in a surface-based interaction with active sites. Furthermore, a swelling effect caused by rising temperature may allow big dye molecules to enter farther in the interior structure of the biosorbent[13].

Adsorption isotherm

To optimize the design of an adsorption system for the adsorption of adsorbate, it is important to establish the most appropriate correlation for the equilibrium curves. Table 1 showed various isotherm equations such as Langmuir, Freundlich, and Temkin and Jovanovic adsorption isotherms that were applied.

Langmuir isotherm- Langmuir adsorption isotherms are based on monolayers, assumed uniform and finite adsorption sites. So, when saturation value reached, no more adsorption occurs. It is also assumed that it is not interactions between molecules adsorbed on neighbouring molecular site.

Freundlich isotherm- Freundlich isotherm describes a physical type of adsorption in which the adsorption occurs in several layers (multilayer) and the bonds are not strong.

Temkin isotherm- Temkin isotherm assumes that the adsorption heat decreases linearly with increasing surface adsorbent coverage, the adsorption process assumes a uniform binding energy distribution on the adsorbent surface, and the adsorption interaction involves the interaction between adsorbate and adsorbent.

Jovanovic isotherm- Jovanovic isotherm is based on the assumptions found in the Langmuir model, without allowing some mechanical contact between the adsorbate and the adsorbent.

Table 2 — Isotherm parameters for methylene blue adsorption

Isotherms	Parameters
Langmuir	R^2= 0.8932, Qmax = 19.88, KL = 4.9803, RL = 0.16 [from graph 6(a)]
Freundlich	R^2= 0.9856, KF = 14.2934, n = 4.1999, 1/n = 0.2381 [from graph 6(b)]
Temkin	R^2= 0.9399, BT = 3.6418[from graph 6(c)]
Jovanovic	R^2= 0.9009 [from graph 6(d)]

A separation factor R_L calculated for Langmuir isotherm represents model fitness for a particular system. If value of R_L falls between 0 and 1, the system is considered appropriate for adsorption purpose and Table 2 shows result which is in this range. The low value of R_L indicates high and favourable adsorption of MB onto biosorbent's surface. Since the value of '*n*' calculated from Freundlich isotherm is greater than 1 and the adsorption heat constant BT calculated from Temkin equation is less than 8 kJ/mol, it indicates that physical interactions are present. The result shows that the value of 1/n is less than unity indicating that the dye is favourably adsorbed by biosorbent. Table 2 show R^2 values calculated for each isotherms from the graphs as shown in Fig. 6. It is found that Freundlich Adsorption Isotherm has higher R^2 value than that of others. So adsorption follows Freundlich Adsorption Isotherm model[14, 15].

Adsorption kinetics

In batch adsorption process, kinetic studies provide information about optimum conditions, mechanism of sorption and possible rate controlling step. For this purpose, pseudo-first- and pseudo-second- order kinetics is applied on adsorption data. For this study 50 mL MB dye of 10 mg/L concentration was taken and 0.05 g of sorbent was added for a contact time of 10 to 60 min.

The equations for pseudo-first-order and pseudo-second-order kinetic model and calculated results are noted in Table 3. R^2 value calculated from graph (Fig. 7b) for pseudo-second-order kinetic model is

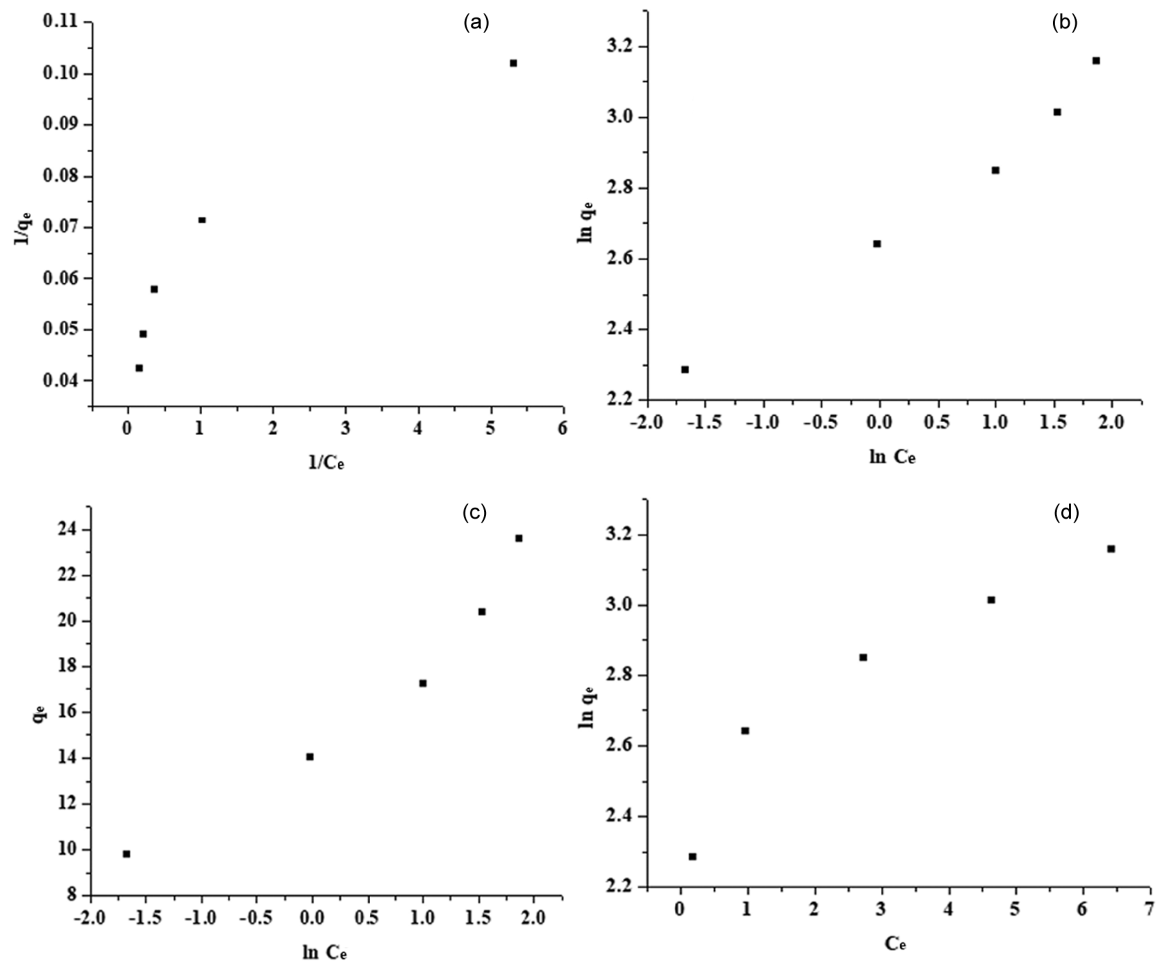

Fig. 6 — Different adsorption isotherm models: (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Jovanovic applied to adsorption system

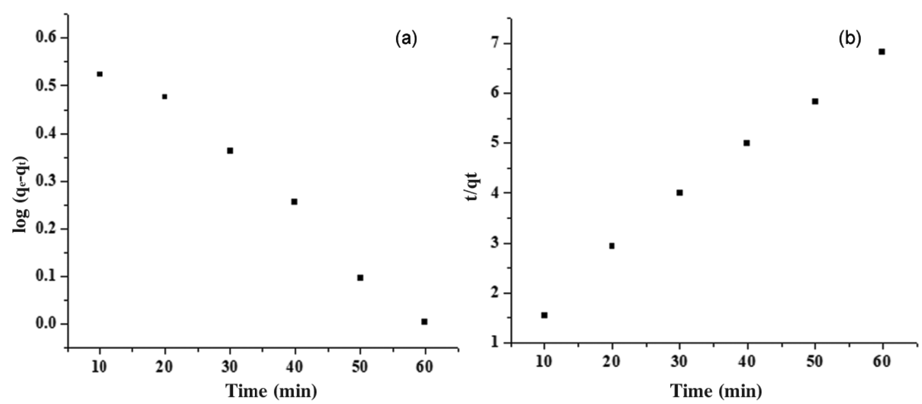

Fig. 7 — Kinetic data for adsorption (a) pseudo-first-order and (b) pseudo-second-order applied to adsorption system

Table 3 — Kinetic models tested in this study

Kinetic Model	Equation	Meaning of terms involved	k min^{-1}	Qe	R2
pseudo-first-order	$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t$	Qt is the amount adsorbed at time t, Qe is the equilibrium amount, t is time in min, and k1 & k2 are the rate constants.	0.02533	4.6900	0.9820
pseudo-second- order	$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \left(\frac{1}{Q_e}\right)t$		0.01420	9.7087	0.9932

Table 4 — Thermodynamic study carried out

Equations	Meaning of terms involved	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° kJ/mol/K
$\Delta G^0 = -RT\ln(K_0)$ $\ln K_0 = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	ΔG° Gibbs free energy change ΔH° enthalpy change ΔS° entropy change K equilibrium constant	- 0.04682	20.75	0.078

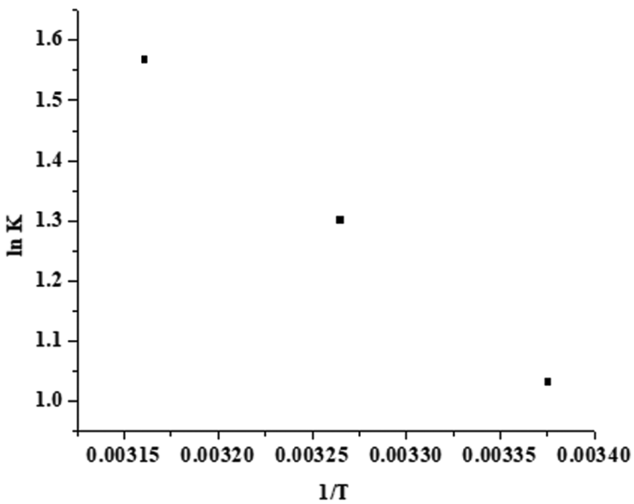

Fig. 8 — Plot of ln K vs. 1/T for adsorption of MB on GPW

higher than that for pseudo-first-order kinetic model calculated from graph (Fig. 7a). Also calculated (9.7087) and experimental (9.8129) values of *Qe* are in good agreement in case of pseudo-second-order kinetics. This indicates that adsorption follows pseudo-second-order kinetics[16].

Thermodynamics studies

Thermodynamic calculations of adsorption process are necessary to conclude whether the process is spontaneous or not. Thermodynamic studies reflect the feasibility and spontaneity of adsorption process and its exothermic or endothermic nature[17]. van't Hoff equation was used to know about the thermodynamic parameters[18].

The values of $\Delta H^0$and $\Delta S^0$are calculated from the plot of ln K vs. 1/T (Fig. 8) and ΔG^0 from van't Hoff equation (Table 4). The negative value of the ΔG^0 at the studied temperature range indicated that the sorption of MB on sorbent was thermodynamically feasible and spontaneous. The increase in the value of ΔG^0 with temperature further showed the increase in feasibility of sorption at the elevated temperature. The positive value of ΔH^0 showed that the sorption was endothermic. The positive value of ΔS^0 showed an increased randomness at the solid-solution interface during the adsorption, reflecting the affinity of sorbent towards dye[19]. ΔG^0 values for physisorption are in the range –20 to 0 kJ/mol. The observed value is in this range indicating physical adsorption[13].

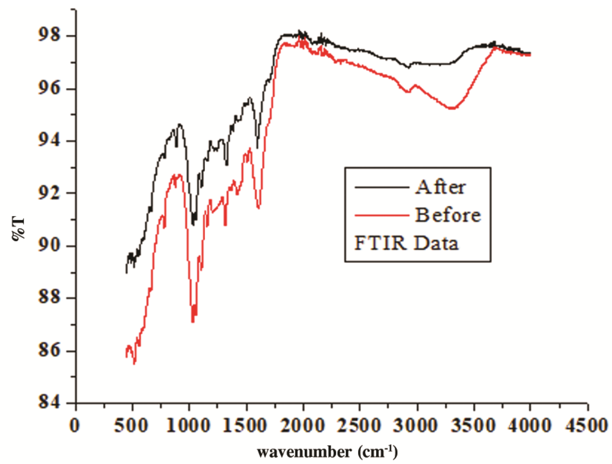

Fig. 9 — FTIR spectra of GPW before and after adsorption of MB dye

FTIR analysis

The FTIR (Perkin Elmer Spectrum Version 10.5.3) spectra (Fig. 9) of GPW was recorded before (red line) and after (black line) the adsorption of MB dye. Before adsorption the peak at 3316 cm^{-1} is observed due to –OH, peak at 1606 is observed due to C=C, peak at 1304 is observed due to $=CH_2$ and peak at 1030 is observed due to C-H. After the adsorption of MB dye the peak at 3316 cm^{-1} is disappeared and slight shift in other peaks is observed (1596, 1331 and 1032 cm^{-1}). A shift in frequency, disappearing of peak or formation of new peak indicates that the functional groups are involved in the adsorption process[20].

SEM analysis

The surface morphology of GPW was studied using Scanning Electron Microscopy (Instrument Model JEOL JSM IT 200), before [Fig. 10 (a), (b)] and after [Fig. 10 (c), (d)] adsorption of MB dye. The surface morphology of adsorbent was not so porous before adsorption but became very porous and rough after adsorption[21]. This confirms that the MB dye was strongly adsorbed on the surface of GPW.

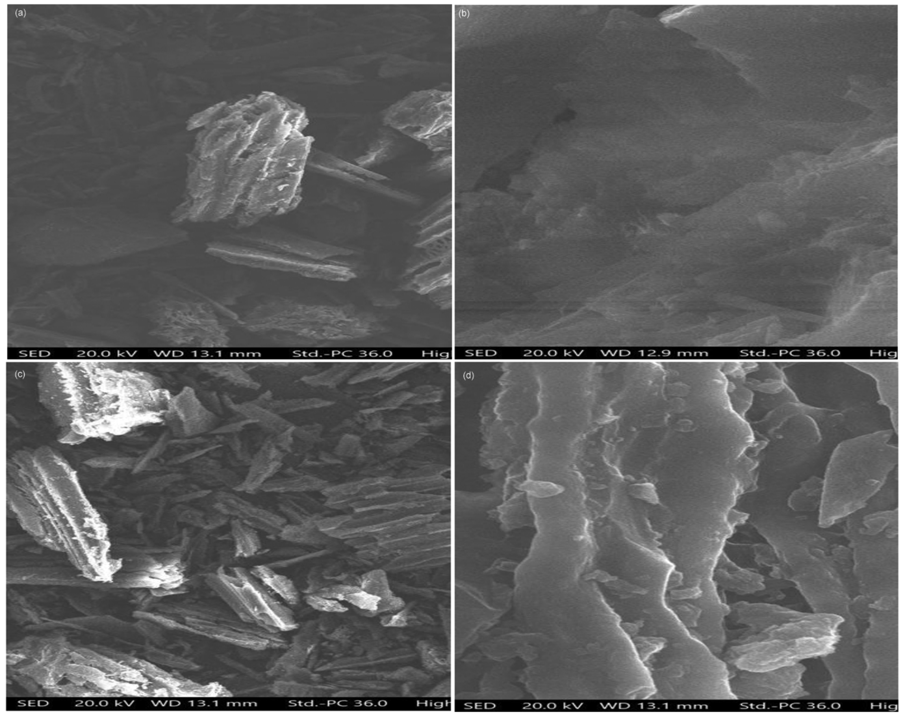

Fig. 10 — SEM images of GPW before (a), (b) and after (c), (d) adsorption of MB dye

Proposed adsorption mechanism

The functional groups, size, and charge of biosorbents influence the determination of the adsorption mechanism. There are various mechanisms for methylene blue adsorption, including π-π interactions, hydrophobicity, electrostatic hydrogen bonding, cation exchange, etc. Plant material includes lignocellulosic materials such as cellulose, hemicellulose, and lignin, which are composed of functional groups such as –CO, -OH and -COOH are good candidates for adsorption processes.

Column adsorption experiment

Column experiment was conducted in a glass column of diameter 2.5 cm and length of 35 cm. A 0.05 g of GPW was packed into the glass column with quartz sand at the top of the packed bed to hold the GPW biosorbent. MB dye solution of 10 ppm concentration was flowed from the top of the column and flow rate of 1 mL/min was maintained[22-23]. The effluent samples at the outlet of the column were collected at regular time intervals between 10 to 60 min and absorbance were measured at 665 nm using Systronics UV-visible double beam spectrophotometer. The experiments were performed in triplicate at room temperature. For a contact time of 10 min, the adsorption was found to be 58.58%, while it increases with increase in contact time of 60 min to about 83.93% as shown Fig. 11.

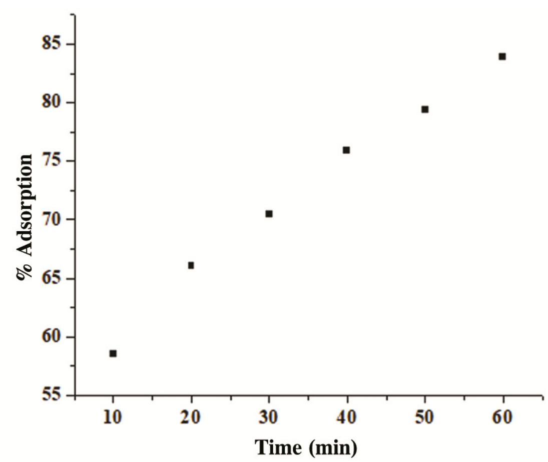

Fig. 11 — Column study (Dose=0.05 g Conc. = 10 ppm pH = 7 Temp = 25 °C)

Application for real wastewater sample

About 0.5 L of wastewater sample was collected from laboratory wastewater. The sample was stored before testing as per the method reported by Ramutshatsha-Makhwedzha *et al.*[24]. The prepared GPW biosorbent was used to remove MB from real wastewater sample. Result showed that the initial concentration of MB in real wastewater was 18 ppm. The prepared GPW biosorbent showed potential to remove MB in real wastewater sample up to about 85.7% after 2 h of contact time.

Regenerative capacity of adsorbent

One of the most important variables that determines how long the adsorbent can be employed is regeneration. In other words, the maximum number of times we can use the prepared adsorbent in adsorption while retaining its original adsorption capability. The mixture of 1 M HCl and 1 M Butanol in 1:3 proportion was used in batch experiment[25] to measure changes in the percentage adsorption-desorption over time in order to determine the reusability and stability of GPW biosorbent. It has been discovered that GPW biosorbent performs consistently, exhibiting about 85-88% removal efficiencies and similar adsorption capacities for up to five cycles as shown in Fig. 12. The results show that the biosorbent is stable and may be utilized repeatedly on the chosen samples without losing its affinity. The decrease in adsorption of MB dye during repeated use might due to protonation of some active sites or functional groups present on the surface and decomposition of adsorbent material because of consecutive adsorption-desorption cycles[33].

Cost analysis of biosorbent preparation

An analysis of the specific costs related to the adsorbents in the batch adsorption process has been attempted. Given the prevalence of cost analysis in decision making, it is noteworthy to remark that it is a crucial factor to take into account while selecting a treatment strategy to eliminate pollutants. The cost of the adsorbent used to remove the dye largely determines the cost of adsorption. Activated carbon is the most widely used adsorbent for any dye removal method, yet it is too costly on the market. This makes it unfeasible for any colour removal method when activated carbon is a viable adsorbent economically. Therefore, there is a great demand for a variety of inexpensive materials that have an uptake capability and economic viability similar to activated carbon.

The cost for the preparation of GPW biosorbent was calculated based on the procedure reported in the literature [26-27]. One of the main factors influencing biosorbent's industrial application and marketing is the cost of processing. On the other hand, the price of biosorbent includes all operating costs, such as those associated with production, upkeep, feedstock, transportation, labor and distribution. The detailed break-up of the cost analysis of biochars preparation as biosorbents was calculated based on the method reported by Akom *et al.*[28]. The estimation and costing of per kg of GPW derived biochars production are given in Table 5.

From the analysis, it was found that the cost for GPW per kg of MB removal is Rs.29.00 as compare to the cost of commercial activated charcoal available in market which ranges from Rs.250 to Rs.1000 per kg. The prepared GPW biosorbent and commercial activated charcoal (CAC) was tested in the removal of MB dye from aqueous solution. A 0.05 g of GPW and CAC was mixed in 50 mL of 10 ppm of MB dye

Table 5 — Cost analysis of GPW derived biochar production

Material/Process	GPW
Feedstock cost	Rs.2/kg
Feedstock Transport	Rs.2/kg/km
Drying cost	1 kWh
Pyrolysis cost	3 kWh
Grinding cost	1 kWh
Net Cost	*Rs. 29/kg*

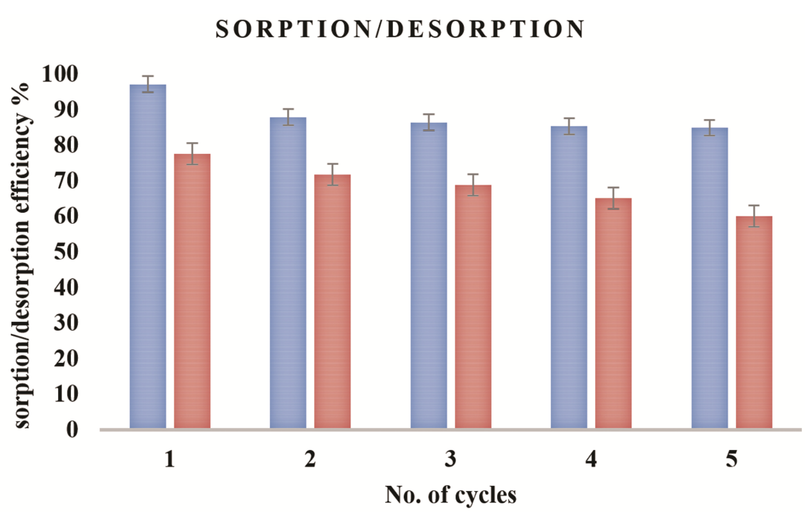

Fig. 12 — Adsorption/Desorption study

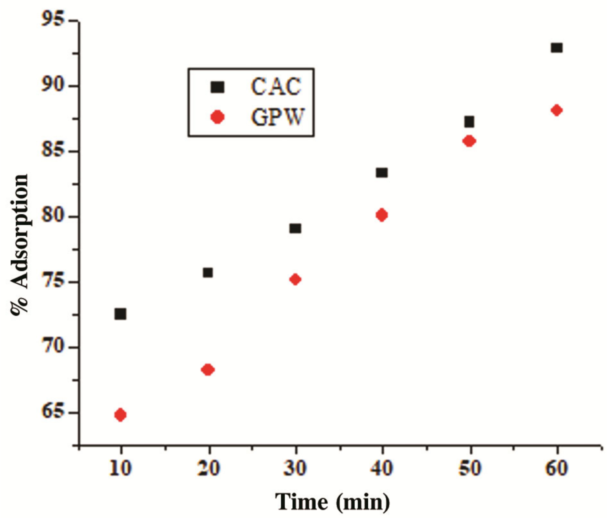

Fig. 13 — Comparison of CAC and GPW as adsorbent for MB dye

Table 6 — Comparison of adsorption capacity and efficiency

Material	Adsorption Capacity	Adsorption Efficiency
CAC	9.28mg/g	92.81%
GPW	8.80 mg/g	88.05%

solution separately maintaining pH=7 at normal temperature. Stirred well for 10 min and each solution was then filtered and the absorbance was measured at 665 nm using Systronics UV-visible double beam spectrophotometer. It was found that GPW and CAC showed percentage adsorption of about 88% and 93%, respectively. Fig. 13 shows the comparison of CAC and GPW as adsorbent for MB dye. So the prepared biosorbent GPW can be successfully employed for the dye adsorption technique from waste water. Table 6 shows comparison of adsorption capacity and efficiency between CAC and GPW for the adsorption of MB dye from its aqueous solution.

Disposal of Biosorbent

Prior to widespread commercial application, biosorbents must be carefully disposed of in the end. Incineration is one method which be used to dispose the used biosorbent. During incineration of waste biomass there is significant reduction in its bulk and volume because the biosorbents are rich in biomolecules like cellulose and lignin[29]. The regeneration and reuse of biosorbents in multiple biosorption cycles is also the most used biosorbent final disposal method. This will increase the life of adsorbent material and reduce the generation of biosorbent wastes from source[30]. The waste biosorbents can be used to make bricks, in landfill, similar to domestic waste landfill[31] after desorption of pollutants which is simple and inexpensive process and can also be used as fertilizer for poor soil[32].

Conclusion

In this work biosorbent prepared from Geranium plant waste shows promising adsorption capacity for methylene blue removal. The maximum sorption for MB solution concentration (10 mg/L), sorbent dosage (0.05 g), contact time (120 min) and temperature (43°C) were observed at pH 7. The equilibrium data was fitted well in Freundlich isotherm models. The rate of sorption was found to obey pseudo-second order kinetics. The negative ΔG^0 values indicated that the sorption of dye onto biosorbent was feasible and spontaneous. The positive ΔH^0 value depicted endothermic nature of the sorption. The interactions between sorbent and sorbate is found to be physical interactions. During regeneration and reuse it was found that the GPW biosorbent can be reused up to five cycles. The economic perspective of low cost synthesised biosorbent was also examined and found to be comparable to commercial activated charcoal. The findings of this cost will be useful for commercial purpose from small scale operation to large scale operation.

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