Kinetics and equilibrium studies for methylene blue removal from simulated wastewater effluents using agricultural waste, *Parthenium hysterophorus* L.

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Batch adsorption experiments have been carried out for the removal of cationic dye, methylene blue from aqueous solutions by using *Parthenium hystrophorous L.* as biosorbent. The effect of major variables such as *p*H, initial concentration, adsorbent dose and contact time has been investigated for the sorption of methylene blue on the low cost adsorbent. Equilibrium data were fitted in Freundlich, Langmuir and Temkin isotherm models and their constants are determined. The data could best be explained by Freundlich isotherm with maximum adsorption capacity (q_o) of 40.79mgg^{-1}. Kinetic modeling for methylene blue adsorption is done using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. It is found that the pseudo-second-order kinetic model most appropriately described the adsorption kinetics. The result indicates that the weed biomass can effectively be used for methylene blue removal from simulated aqueous solutions.

Keywords: Adsorption, Methylene blue, Equilibrium studies, Pseudo-second-order kinetics

Colours have always attracted the attention of humankind. This has led to the discovery and development of different dyes and pigments which give attractive color to the fabric materials as desired. But the natural colors used earlier for dyeing had many problems including lack of colour fastness, fast degradation and unstability. In order to solve these problems, synthetic dyes replaced the natural ones.According to an estimate, about 100000 dyes of different classesare available commercially with the annual production of 7×10^5 tonnes dyestuffs.These dyesare used in different industries including textiles, plastic, dyeing, leather, along with paper and pulp industry[1,2]. Methylene blue (MB), used as a model dye for the study, is used as colorant for paper, hair along with dyeing cottons, wools, and coating for paper stock. But the colored effluents along with the large quantities of suspended organic materials discharged from these industries have posed a threat to the environment and the aquatic life. The resultant effluents obstruct the passage of sunlight through the water surface thus leading to inhibition of photosynthesis with adverse effects on aquatic ecosystem[3]. The dyes and their metabolites have also been found to be mutagenic as well as carcinogenic to the aquatic life[4]. Therefore there is an urgent need to remove dyes from aqueous effluents to handle the problem of environmental pollution efficiently.

Different physico-chemical methods have been used for removing color from the effluents which include the usage of oxidizing/ reducing agents[5], photo catalysis[6], solar photo- Fenton process[7], electro-chemical degradation[8] and adsorption[9]. Amongst different methods used so far, adsorption has been found to be the most suitable one, both in terms of efficiency and economics to remove dyes from the effluents. Different adsorbents derived from agricultural waste like coconut husk[10], jujuba seeds[11], pumpkin seed hull[12], Dika nut[13] spent fennel seed[14], walnut shell[15] have been explored to develop an economic alternative of activated carbon for efficient removal of dyes.

Parthenium hysterophorus L. is an aggressive prolific weed that can grow anywhere. It is also known as Congress grass, star weed, bitter weed, white top, the 'Scourge of India' and gajar ghas[16]. The weed has been found to be responsible for reducing pasture productivity up to 90% by affecting vegetation and the amount of nutrient content[17,18]. It is being estimated that in India this invasive weed has infested about two million hectares of land. So there is a need to look for solutions to manage this

notorious weed. For the purpose, the study was conducted to understand the kinetics and adsorption behavior of methylene blue on the weed biomass. The work was carried with a dual purpose of managing the weed population along with the assessment of its dye removal efficiency from simulated aqueous solutions.

Experimental Section

Adsorbate

The work was carried outusing methylene blue(MB), a basic dye since it has been found to be adsorbed strongly onto solids[19]. The dye was supplied by Merck Co. (M) Germany. Its chemical structure and physicochemical properties are listed in Table 1

Adsorbent

Whole plant material of *Parthenium hysterophorus* L. (PH) was collected from the sides of the Indian Agricultural Research Institute (IARI) fields. The biomass was washed thoroughly to remove adhered dust and then air-dried. The moisture from the plant material was removed completely by drying it in an oven (IIC 101, India) at 105°C overnight. The dried adsorbent was then ground and sieved through a sieve of BSS 30 and kept in an air tight container. The material was used as such for adsorption experiments without doing any physical or chemical treatment. Prior to its use in the experiments, the sample was mixed thoroughly so as to ensure uniformity.

Characterization of the Adsorbent

The point of zero charge (pH_{pzc}) for the PH biomass was determined using 0.1 M KNO_3 solutionas per the method followed by Lim *et al.*[20]. 0.05g of the PH was added to 25 mL of potassium nitrate solution and the desired *p*H (3, 4, 6, 7, 8 and 10) was maintainedusing 0.1M HCl and/or 0.1M NaOH (pH_i). The solutions of different *p*H were shaken on a mechanical shaker at 250 rpm for 2 h after which the final (pH_f) was recorded. The change in *p*H ($\Delta pH=pH_i-pH_f$) was recorded for each solution and the graph of ΔpH against pH_i was plotted. The point of zero charge of PH is that point which passes through the X-axis. *p*H of the adsorbent was determined through the standard test methodASTMD 3838-80. An amount of 1g of the dried PH material was taken in a beaker to which distilled water (100 mL) was added. The mixture was then stirred for 1h. After the mixture was allowed to equilibrate, the *p*H of the solution was recordedusing *p*H meter (HI 96107, Italy).

CHNS analyzer (Euro vector) was used for the elemental analysis of the PH adsorbent material. Scanning Electron Microscope (SEM, Model-Tescan Vega3) was utilized to study the surface morphology of the PH biomass before and after dye adsorption. The changes in the dye concentration in aqueous solutions before and after adsorption were recorded at maximum absorbance wavelength of 667 nm (λ_{max}) using UV/visible SmartSpec Plus spectrophotometer.
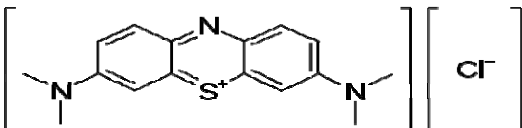
Batch adsorption studies

The experiments in batch mode were carried out in order to assess the influence of initial *p*H, initial dyeconcentrations, contact time and dosage of PH material on the removal of methylene blue by adsorption.

Effect of pH

In order to assess the effect of *p*H on the adsorption behavior of the adsorbent, values of *p*H were varied from 3 to 10. The experiment was carried out in

Table 1 — Properties of Methylene Blue

Dye name	Methylene blue (Syn. aizen methylene blue, basic blue 9, schultz No. 1038, calcozine blue ZF, chromosmon)
IUPAC name	3,7-Bis-(dimethylamino)phenazathionium chloride / 3,9- bis(dimethyl amino)phenazothioniumchloride
Chemical formula	$C_{16}H_{18}N_3SCl$
Molecular weight	319.88 g/mol
Colour Index Number (CI No.)	52015
Color	Dark green-blue
λ_{max}	667 nm
Solubility	Water: 2.5 g/100mL Ethanol: 1.5 g/100mL Acetone: 0.5 g/100mL
Structure	

triplicate with 0.25 g of the adsorbent in 50 mL dye solution with initial concentration of 25 mgL^{-1}. The solutions were shaken on mechanical shaker at 30°C for 180 min. The desired pH of the aqueous solution was maintained by using 0.1M HCl and 0.1M NaOH solution. The dye concentration in the supernatant of different aqueous solutions after the defined time interval was measured by UV-Vis spectrophotometer at appropriate λ$_{max}$ value.

Effect of **PH** *adsorbent dosage*

To study the effect of adsorbent dose on the dye adsorption, the amount of PH biomass was varied from 75-625 mg in the definite volume (50 mL) of fixed initial dye concentration (25 mgL^{-1}). The aqueous solutions were shaken for 180 min keeping the pH of the solution constant at 30°C. After the predefined time interval, dye concentration of the aqueous solution was measured at λ$_{max}$ using UV-Vis spectrophotometer.

Equilibrium studies

The batch adsorption studies were carried out by taking 0.375 g of the PH adsorbent in the Erlenmeyer flask with 50 mL of the aqueous solution of different initial dye concentrations (25-250 mgL^{-1}) at pH of 8 and temperature 30°C. The flasks were shaken for 180 min at a constant speed throughout the experiment to achieve equilibrium. The amount of dye adsorbed after attaining equilibrium, q$_e$ (mgg^{-1}) was calculated by using the following equation[21].

$$q_e = \frac{(C_o - C_e)W}{W} \quad \text{... (1)}$$

C$_o$ and C$_e$ (mgL^{-1}) are initial and concentration of dyeat equilibrium, respectively; V is the volume of solution (L) and W is the mass of adsorbent (g). The removal percentage was calculated as[22]

$$\text{Removal percentage} = \frac{(C_o - C_e)}{C_o} \times 100 \quad \text{... (2)}$$

Kinetic studies

Batch kinetic studies were also carried out in a similar manneras that of the equilibrium studies. The samples were withdrawn at pre-defined time intervals and the concentration of the basic dye remaining in the supernatant was measured at 667 nm (λ$_{max}$) using UV-Vis spectrophotometer. The amount of sorption at any time t, q$_t$ (mgg^{-1}) is given as

$$q_t = \frac{(C_o - C_t)v}{w} \quad \text{... (3)}$$

where C$_t$ (mgL^{-1}) is the concentration of MB dye at known time-interval.

Results and Discussion

Adsorbent characterization

Point zero charge of the adsorbent

It can be seen from Fig. 1 that the pH$_{pzc}$ of PH biomass was 7.1 approximately which suggests that at pH = 7.1, thecharge on the adsorbent surface is zero. At the pH below 7.1, the adsorbent surface will be positively charged that can be utilized for the adsorption of anionic dyes. If the pH is more than the pH$_{pzc}$ the surface of the adsorbent will be negatively charged which will enhance the sorption of cationic dyes. The pH$_{pzc}$ of breadnut peel was reported to be 4.819 while the pH$_{pzc}$ for carrot stem and leave powder was found to be 6.12 and 6.1, respectively[15].

Analysis of the adsorbent

The elemental analysis of the PH biomass showed that it contained C(%): 35.47, N(%): 2.16, S(%): 0.162, H(%): 6.26. Figure 2 illustrates SEM image of PH biomass before and after adsorption of the dye.It can be clearly seen from the images that before dye sorption the surface of the PH material is rough but after dye adsorption the surface appears to be smooth. This pertains to the coverage of adsorbent with the respective MB dye molecules. The physicochemical properties of the adsorbent determined through standardized parameters are listed in Table 2.

Effect of pH

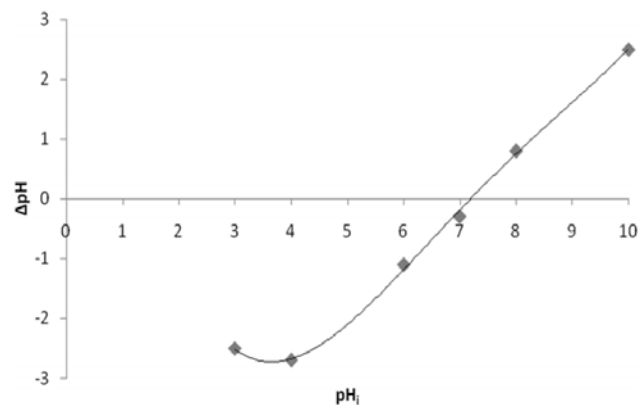As pH controls the degree of ionization of the chemical, it plays a key role in the adsorption process.

Fig. 1 — The point of zero charge of PH using 0.1M KNO$_3$ solution

Therefore to assess the effect of different *p*H on the sorption of MB dye on PH adsorbent, *p*H was varied from 3-10. The desired *p*H of the solution was obtained with the help of 0.1MHCl or 0.1MNaOH solutions. It was found that MB was sorbed a

Fig. 2 — SEM images of PH biomass a) before adsorption b) after adsorption

Table 2 — Physico-chemical properties of PH biomass

Moisture content (%)	8.08
Ash Content (%)	17.2
Volatile matter (%)	42.32
Fixed carbon (%)	32.4
Bulk density (%)	0.39
*p*H	6.9

minimum at *p*H 3 with the percent sorption of 78. The percent sorption then increased up to *p*H 8 and became constant though *p*H variation was done up to 10. This behavior can be ascribed to the fact that as the *p*H increases availability of negative charges at adsorbent surface becomes more which leads to more electrostatic interaction between negatively charged PH adsorbent and MB, the cationic dye. It is also confirmed from the value of pH_{pzc}. As the pH_{pzc} of PH biomass is 7.1 (Figure 1), it revealsthat the PH surface will be negatively charged and the adsorption of cationic dye will increase as the *p*H increases beyond 7.1.But as the *p*H further increasedfrom 8 to 10, not much change in percent sorption was observed therefore *p*H 8 was chosento investigate the effect of adsorbent dosage and other experiments.

Effect of PH dosage

The effect of adsorbent dosage on the adsorption of MB is depicted in Fig. 3. In this experiment, the dose of *p*H biomass was varied from 1.5 gL^{-1} to 12.5 gL^{-1} keeping *p*H and concentration of the dye solution fixed at 8 and 25 mgL^{-1}, respectively. It can be clearly inferred from the Fig. 4 that as the dosage of
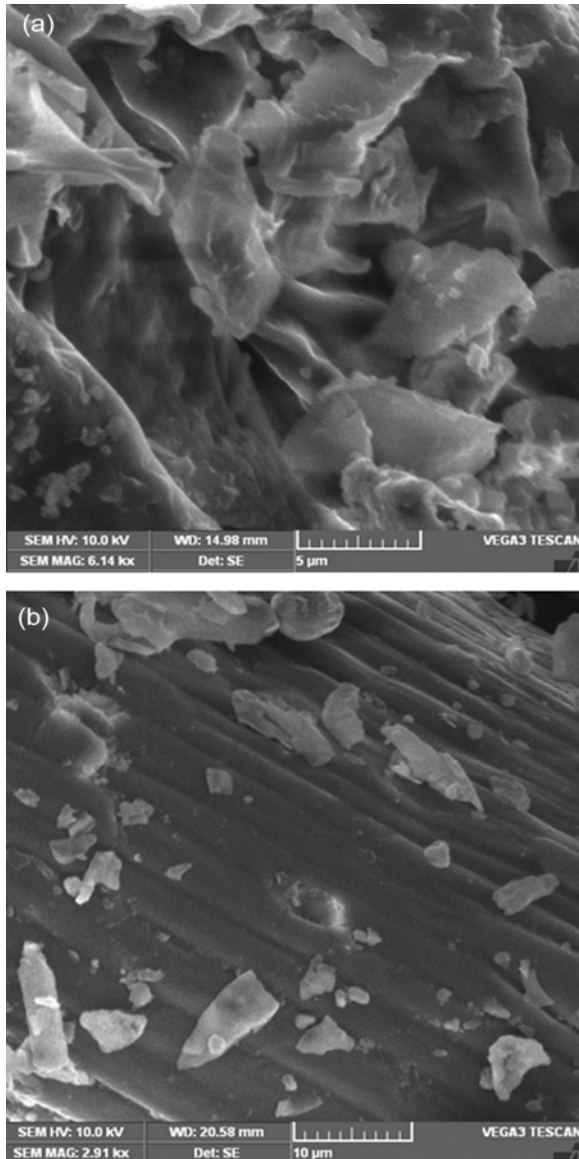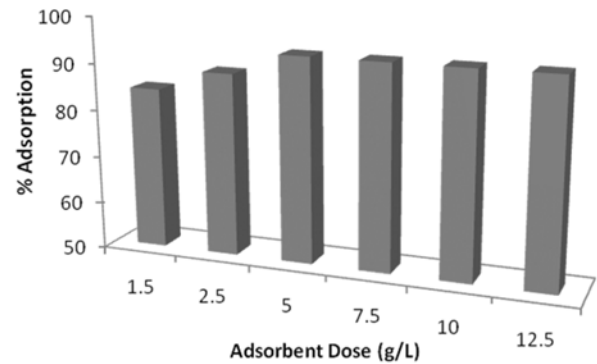

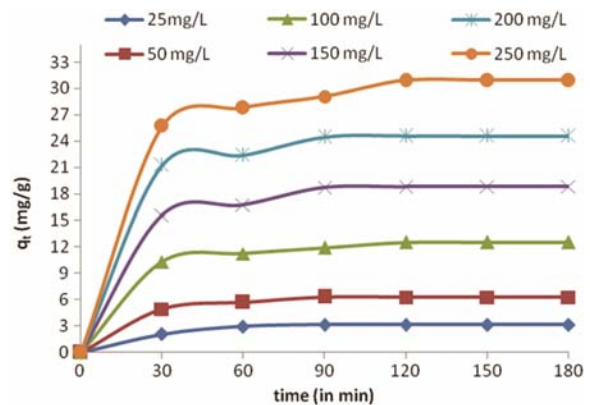Fig. 3 — Effect of adsorbent dosage on removal of MB by PH biomass at 30°C

Fig. 4 — Methylene blue adsorption on PH biomass at 30°C

PH biomass increased from 1.5 to 7.5 gL^{-1}, the removal efficiency of the sorbent material increased from 75% to 87%. There was a decrease in equilibrium adsorption capacity as the dose of the adsorbent increased. It is due to the fact that at a lower dose of the adsorbent, the dye molecules can be accessed easily resulting inan increase in the removal of the adsorbate molecules per unit weight of the adsorbent[23]. But as the dose increased from 7.5 to 12.5 gL^{-1}, the change in the adsorption is insignificant with a slight decrease in adsorption from 87.86 to 87.73%. It can be due to split in the flux between concentration of adsorbate molecules present in the solution and surface of the adsorbent[24].

Effect of contact time and initial concentration

The contact time between the dye molecule and adsorbent is important for waste water treatment by adsorption. The studies on *P*H biomass at various initial concentrations of methylene blue were carried out at 30°C in order to determine equilibrium time. From Fig. 4, it was observed that there was a rapid increase in the dye uptake initially which proceeded at a slow pace and finally reached an equilibrium where no more uptake could be observed. It could be ascribed to the availability of active sites available on the adsorbent which got covered gradually as the contact time and dye concentration increased. It was observed that with the increase in initial MB concentration from 25-250 mgL^{-1}, the equilibrium concentration increased from 3.13 to 30.92 mgg^{-1}. It was also observed that at low initial concentration (25-50 mgL^{-1}), the adsorption of MB reached equilibrium at 90 min while it took 120 min to reach equilibrium at higher dye concentrations taken initially. However, to ensure that full equilibrium has been attained, the readings were taken up to 180 min. The adsorption studies of different adsorbents have shown different adsorption rates for MB dye. Shahryari *et al.*[25] reported the equilibrium time of 60 min for MB adsorption on breadnut peel while removal of the same dye using walnut shell took 120 minutes to equilibrate[15].

Isotherm analysis

The isotherm helps to get the insight of the interactions between adsorbate molecules and the adsorbent under study. Adsorption data so obtained were fitted to Langmuir, Freundlich and Temkin isotherm models. Different isotherm parameters had also been calculated accordingly and reported.

According to Langmuir theory assumption, there is monolayer coverage by the adsorbate over the homogeneous surface of the adsorbent[26]. If an adsorbent site is occupied by the dye molecule, no further sorption can take place. The linear equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad \dots (4)$$

where q_m is the maximum monolayer adsorption capacity expressed as mgg^{-1} and b, Langmuir adsorption constant (mg^{-1}), is related to the free energy of adsorption. The plot of C_e/q_e against the equilibrium concentration was plotted to determine q_m and b from the slope and intercept (Fig. 5) as given in Table 3. Separation factor, a dimensionless constant, is an important property of Langmuir model and can be expressed as
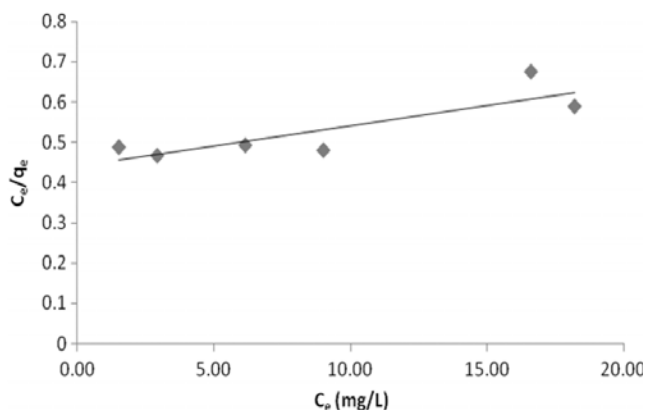

Fig. 5 — Langmuir isotherm for MB adsorption on PH biomass

Table 3 — Isotherm model parameters for MB adsorption on PH at 30°C

Isotherm	Parameters
Langmuir	
q_m (mgg^{-1})	99
K_l (Lmg^{-1})	0.023
R^2	0.722
Freundlich	
q_m(mgg^{-1})	40.79
K_f (mgg^{-1})(Lg^{-1})$^{1/n}$	2.34
n	1.12
R^2	0.987
Temkin	
K_t (Lg^{-1})	1.437
B	10.63
R^2	0.94

$$R_L = \frac{1}{1 + bC_o} \qquad \qquad \dots (5)$$

where C_o is the highest initial concentration of the dye (mgL^{-1}) and b is the adsorption constant (Lmg^{-1}). Nature of the shape of the isotherm is indicated by R_L values as following:

$R_L > 1$ unfavorable adsorption
$R_L < 1$ favorable adsorption
$R_L = 0$ irreversible adsorption
$R_L = 1$ linear adsorption

In the present study R_L value was found to be 0.148 which showed that the adsorption of methylene blue on PH biomass was favorable.It can be seen from Table 3 that maximum adsorption capacity $q_m$of PH biomassfor MBis 99.0 mgg^{-1}, as computed from Langmuir equation. The $q_m$value has also been compared with the maximum adsorption capacity of different adsorbents for MB dye adsorption (Table 4) which showed that performance of PH biomass for MB removal is higher.

Another isotherm model, Freundlich isotherm is an empirical equation which assumes that there is multilayer coverage by the adsorbate molecules on the heterogeneous surface of the adsorbent[27]. The linear equation can be expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \qquad \dots (6)$$

where q_e and C_e are variables as the amount adsorbed at equilibrium (mgg^{-1}) and equilibrium concentration of the dye, respectively. K_f and n are the Freundlich constants which are indicators of adsorption capacity and adsorption intensity, respectively. The values of the constants can be calculated from plot of ln q_e vs ln C_e (Figure 6). The values of n represent whether the adsorption is favorable or not[28,29]. The results showed that the value of n is greater than 1 which indicated that the basic dye has been adsorbed favorably on the PH biomass used as adsorbent in the study. According to Halsey[30], the maximum adsorption capacity for Freundlich isotherm can be calculated from equation 7 as following:

$$K_f = \frac{qo}{c_o^{1/n}} \qquad \qquad \dots (7)$$

where q_o is the maximum adsorption capacity (mgg^{-1}). To calculate q_o, it is necessary to operate with constant initial concentration (C_o, mgL^{-1}) and variable weights of the adsorbent. The values of Freundlich constants (K_f, n) and linear regression coefficient (R^2) of Freundlich isotherm model are given in Table 3.The coefficient of correlation ($R^2 = 0.987$) was also found to be high which showed good linearity. The maximum adsorption capacity q_o, calculated from Freundlich equation was found to be 40.79 mgg^{-1}.

Temkin and Pyzhev[31] considered that indirect adsorbate – adsorbent interactions also have effect on the adsorption isotherms. It had been suggested that as a result of these interactions, the heat of adsorption of molecules present in the layer decreases with coveragein a linear mode. The isotherm can be expressed by the following equation

$$qe = \frac{RT}{b} \ln (K_t \cdot C_e) \qquad \qquad \dots (8)$$

Table 4 — Comparison of maximum adsorption capacity for the removal of dye on different adsorbents

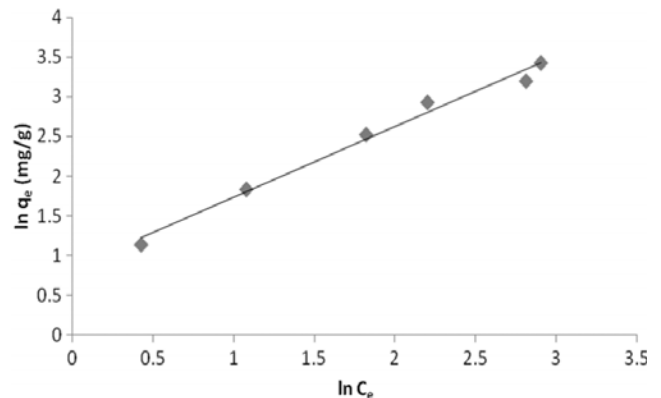| Adsorbent	Adsorption capacity (mg/g)	Reference
Parthenium hysterophorus L. (PH)	99	Present work
Walnut shell	51.55	15
Leaves of *Solanum tuberosum*	52.6	35
Stem of *Solanum tuberosum*	41.6	
Activated banana peel	19.7	36
Garlic peel	82.64	37
Metal-organic framework Uio-66	91	38
Leaf-shaped ZIF-8	205	39
TiO$_2$ /montmorillonite-albumin Nanocomposite	18.18	40

Fig. 6 — Freundlich isotherm for MB adsorption on PH biomass

In the linear form, equation 8 can be written as

$$q_e = B \ln K_t + B \ln C_e \qquad \ldots (9)$$

where,
B=RT/b $\ldots (10)$

The adsorption data was analyzed using equation (9). The plot of q_e versus $\ln C_e$ (Fig. 7)can be used to find the values of the constants K_t and B. The constants K_t and B along with R^2 value are mentioned in Table 3.The data presented in Table 3 shows that amongst three isotherm models, the equilibrium data fitted best in Freundlich isotherm model.

Adsorption kinetics

The adsorption data was investigated by two common models *viz.*Lagergren pseudo-first-order and pseudo-second-order models. The pseudo-first-order kinetic equation by Lagergren can be expressed as[32]:

$$\ln(q_e - q_t) = \ln q_e - K_f t \qquad \ldots (11)$$

where k_f is the pseudo-first-order rate constant (min^{-1}). Plot of $\ln q_e$-q_t *vs* t (Fig. 8) can be used to calculate values of k_f and q_e for different initial concentrations of dye from the slope and intercept, respectively. The values along with their corresponding correlation coefficients are presented in Table 5 which suggests that the pseudo-first-order model has not fitted well for MB adsorption. It was also found that there was variation in the calculated q_e values and the experimental q_e values which confirmed that MB adsorption did not follow pseudo-first-order-kinetics.

Pseudo-second-order kinetic equation in linear form can be expressed as:

$$\frac{t}{q_t} = \frac{1}{K_s q_f^2} + \left(\frac{1}{qe}\right)t \qquad \ldots (12)$$

where the value of equilibrium adsorption capacity (q_e) and second order constant, k_s (gmg^{-1} min^{-1}) can be determined from the slope and intercept after plotting the graph of t/q_t versus t (Fig. 9). As it can be seen from the values of coefficient of pseudo-second-order kinetics (Table 5) that R^2 values exceeded 0.99 and $q_{e, cal}$ (calculated equilibrium adsorption capacity, mgg^{-1}) values were more consistent with the experimental values ($q_{e,exp}$). Hence the adsorption behavior of MB dye on PH followed pseudo-second-order kinetics suggesting that the adsorption process is controlled by chemical process.
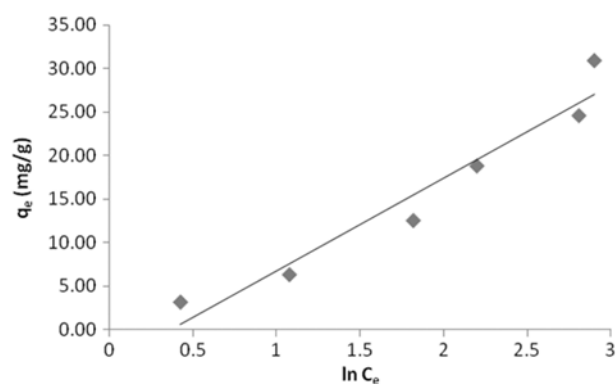

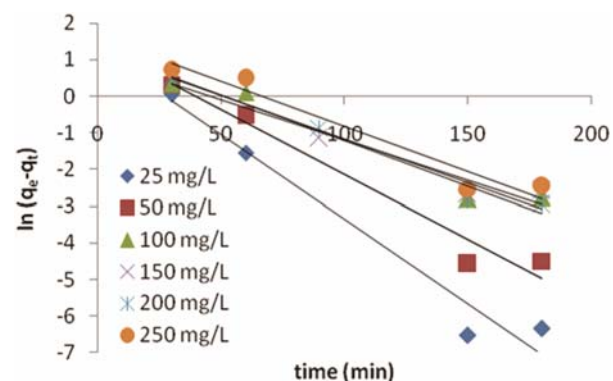Fig. 7 — Temkin isotherm for MB adsorption on PH biomass

Fig. 8 — Pseudo-first-order kinetics for MB adsorption on PH biomass at different dye concentrations

Table 5 — Comparison of adsorption rate constants of pseudo-first-order and pseudo-second-order kinetic models and calculated and experimental q_e values obtained at different initial concentrations of Methylene Blue

Initial concentration (mgL^{-1})	$q_{e, exp}$ (mgg^{-1})	Pseudo first order kinetic model			Pseudo second order kinetic model		
		k_f	$q_{e, cal}$ (mgg^{-1})	R^2	k_s	$q_{e, cal}$ (mgg^{-1})	R^2
25	3.13	0.105938	3.462532	0.961	0.044425	3.278689	0.993
50	6.29	0.080605	4.100053	0.964	0.033169	6.493506	0.997
100	12.51	0.052969	3.36356	0.954	0.016578	12.82051	0.998
150	18.8	0.048363	2.680491	0.95	0.011931	19.60784	0.997
200	24.58	0.055272	3.528949	0.976	0.011611	25.64103	0.998
250	30.92	0.055272	5.068272	0.949	0.006407	32.25806	0.997

Intraparticle diffusion

Weber and Morris intraparticle diffusion model[33] is an empirical functional relationship which helps to get the insight of diffusion mechanism. It is expressed as:

$$q_t = k_t t^{1/2} + C \qquad \qquad \dots (13)$$

where k_i (mg/gmin$^{1/2}$) is intraparticle diffusion rate constant. If the adsorbate uptake q_t *vs* $t^{1/2}$ is linear then
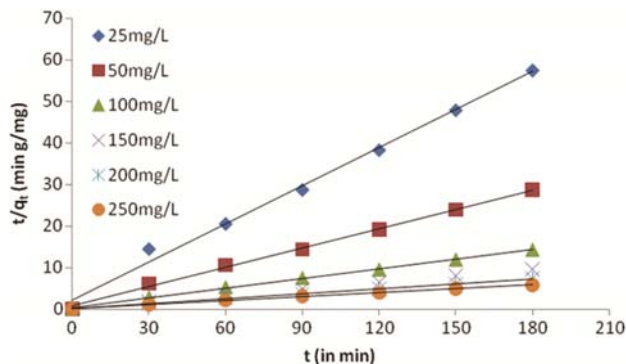

Fig. 9 ― Pseudo-second-order kinetics for MB adsorption on PH biomass at different dye concentrations
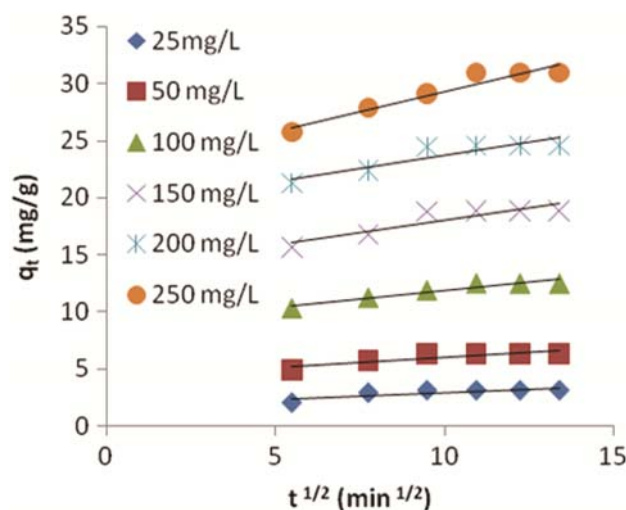

Fig. 10 ―Weber-Morris Intraparticle Diffusion models for MB sorption on PH biomass at different dye concentrations

Table 6 ― Intra-diffusion model parameters for MB adsorption on PH at 30°C

Initial concentration (mgL^{-1})	k	C	R^2
25	0.118	1.75	0.673
50	0.167	4.296	0.77
100	0.291	8.959	0.912
150	0.428	13.67	0.813
200	0.45	19.17	0.823
250	0.699	22.31	0.925

it shows that intraparticle diffusion is the only rate controlling step. But the linear plot (Fig. 10) of each concentration did not pass through the origin.So it can be concluded that intraparticle diffusion in not the sole rate limiting step[34] The values of different parameters of IPD were calculated from the slope and intercept of the linear plots (Table 6)..

Conclusion

The results obtained in the study show that *Parthenium hysterophorus* L., a notorious weed, can be utilized to remove methylene blue from aqueous solutions in an effective manner. The data are fitted and analyzed through different isotherm models viz. Langmuir, Freundlich and Temkin. It is found that the equilibrium data fitt best in Freundlich isotherm equation. The maximum monolayer adsorption capacity (q_o) for methylene blue on *P*H biomass is found to be 40.79 mgg^{-1}. The kinetic modeling of the dye adsorption on PH showed that the process follow pseudo-second-order kinetics. It suggests that the adsorption process is controlled by chemisorption. The intraparticle diffusion plots suggest that adsorption is affected by more than one process. The PH biomass used in the study is abundantly available round the year which needs a way out to get it disposed appropriately. Therefore, the adsorbent can be expected to be a good opportunity and a low cost alternative for the removal of methylene blue from the aqueous solutions.

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