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Experimental investigation and kinetic modeling of adsorption behaviour of inexpensive *Ziziphus mauritiana* seeds

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The adsorption potential and equilibrium data modeling of a low cost biowaste adsorbent *Ziziphus mauritiana* seed powder (ZMSP) without any pretreatment as pretreatment of a biowaste also add to the wastewater treatment cost has been investigated. Batch adsorption studies have been carried out to determine adsorption potential using cationic dye methylene blue (MB) as adsorbate. Equilibrium is achieved in 180 min. It is found that adsorption increased with the increase in amount of adsorbent as well as increase in *p*H value. The experimental data for the ZMSP is fitted well to the Langmuir adsorption isotherm followed by Freundlich, Temkin and Dubinin-Raduskevich. On the basis of parameter E of Dubinin-Raduskevich isotherm it has been found that chemisorption is the phenomenon involved in the removal of dye. Pseudo second order and Elovich model fitted better than Pseudo first order kinetic model. Surface properties of the adsorbent have been characterized by SEM, EDX, BET analysis, and FTIR. It has been found from the experimental investigation that *Ziziphus mauritiana* seeds have a potential to be used as a cost effective adsorbent. Its adsorption capacity has been found to be comparable with other low cost adsorbents reported in the literature.

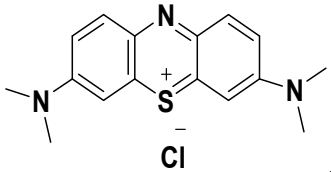
Keywords: Adsorption, Biowaste, Kinetics, Isotherms, Methylene blue

Coloured wastewater is expected to be highly toxic due to the existence of organic contaminants and chemicals. Most of these chemicals are very harmful for humans and cause sensitivity, dermatitis as well as skin irritation problems. The water polluted with dyes represent serious toxicity problems and are of grave concern which needs to be dealt with on priority basis[1]. It is therefore, an important and challenging area of wastewater treatment.

Various physical, chemical and biological methods are adopted for the removal of dyes from industrial effluents. A number of methods have been reported in the literature for the removal of dyes like aerobic microbial degradation, membrane separation, coagulation and chemical oxidation, filtration, reverse osmosis etc. However these methods have certain limitation such as high cost and disposal problems, which do not make them a favorable option for color removal at larger scale[2]. Adsorption system required less initial cost and is a superior mean for the removing organic waste from wastewater[3]. After many years of research, the investigators found that the use of cheap and non-conventional adsorbents are very useful to remove dyes from polluted water[2].

Methylene Blue is a cationic dye and is very toxic in nature. It is used widely for the dyeing of nylon, wool, silk and acrylic in textile industries. About 10 to 15% of the dye is lost in the effluents of textile unit. MB can cause cancer, skin irritation, and mutation and eye burns[4].

The physical and chemical properties of the cationic dye i.e. Methylene Blue (MB) are given below:-

Standard name	Methylene Blue
Form	Blue
Commercial name	Basic blue 9
Molecular formula	$C_{16}H_{18}N_3SCL.3H_2O$
Molecular weight	319.86
Molecular structure	 **$3H_2O$**
IUPAC Name	IUPAC name: 3, 7-bis (Dimethyl-amino)-Phenazathiionium chloride-tetramethylthionine chloride

Colour index number	52015
λ_{max} (nm)	661

A number of researchers have worked on the low cost adsorbents for the removal of methylene blue. Table 1 presents a summary of the related work for the adsorption of methylene blue using low cost adsorbents and highlights key findings. This literature survey served as basis for the present work and adsorption potential is also compared with this literature.

Although lot of research work is done to prepare adsorbents by some chemical or physical treatment, however not much was explored in the area of using biowaste material without any pre-treatment. This can bring down the cost of wastewater treatment. So, there is a need to explore the potential of a waste as adsorbent without giving it any pre-treatment. Present study is an endeavor to explore the potential of *Ziziphus mauritiana* seed powder as a low cost adsorbent without giving it any pretreatment. Adsorption potential is measured by using a basic dye methylene blue in batch isotherm studies. *Ziziphus mauritiana* was not been explored for its adsorption potential till date.

Experimental Section

Preparation of adsorbent

The seeds of *Ziziphus mauritiana* were collected from the local area of Jalandhar, Punjab. To remove the dust particles and remaining pulp, the seeds were thoroughly washed and dried appropriately in the oven at a temperature of 70°C for 3 h. Seeds so obtained were powdered to nearly uniform size. No chemical treatment was given to adsorbent.

Characterization of ZMSP

Average diameter of adsorbent particle was determined using sieve method[4]. Further characterization was done with the help of scanning electron microscopy (SEM) to characterize surface morphology and particle size, energy dispersive X-ray spectroscopy (EDX) to find the elemental composition, BET analysis to measure surface area, pore volume etc. and FT-IR spectroscopy to determine the functional groups present on the surface of the adsorbent.

Batch mode adsorption studies

All the chemicals used in this study were of analytical grade and used without any further purification. For batch adsorption study 50 mL aqueous solution of known concentration of methylene blue, was taken in a conical flask which contained a known mass of the adsorbent (ZMSP). These flasks were placed in the thermostatic shaker at 150 rpm at a desired temperature. The effect of various parameters like *p*H (2-10), adsorbent dose (0.1-0.8 g/50 mL), initial concentration of dye (30-150 mg/L), temperature (303-313K) and contact time on the adsorption of methylene blue was determined by keeping one of the parameter varying and others at a constant value. To separate the adsorbent from adsorbate, aliquot of the sample withdrawn was centrifuged at 2000±100 rpm. Residual dye concentration was measured by recording optical density in a spectrophotometer at 661 nm.

Kinetic studies were performed first, in which all the parameters like *p*H, temperature, concentration of dye, adsorbent dose, shaking speed were maintained at constant fixed value and removing the aliquot of sample at a fixed interval of time. Equilibrium time for adsorption was determined from this experiment. All other experiments were conducted at an equilibrium time of 180 min. Each experiment was conducted at 3 different temperatures i.e. 303 K, 308K and 313 K. Each experiment was repeated for at least two times and error bars have been shown at 95% confidence level in the relevant figures in this paper.

Percentage removal of dye, amount of dye adsorbed in mg per gram of the ZMSP at time t (Q_t) and at equilibrium (Q_e) have been calculated using following Equations:

$$\% \text{ removal} = \frac{C_o - C_t}{C_o} \times 100$$

$$Q_t = \frac{C_o - C_t}{m} \times v$$

$$Q_e = \frac{C_o - C_e}{m} \times v$$

where

Q_e= solid phase concentration of dye afterequilibrium, mg adsorbate/ g adsorbent.

Q_t = solid phase concentration of dye at time t, mg adsorbate/ g adsorbent.

C_O= initial concentration of adsorbate, mg/L

C_t= concentration of dye in aqueous solution at time t after adsorption, mg/L

C_e= concentration of dye in aqueous solution at equilibrium, mg/L

v= volume of liquid in the reactor, L

m =mass of adsorbent, g

Table 1 — Represents review of low cost adsorbents used for the removed of methylene blue

Adsorbent	Functional group present	BET analysis	Optimum initial *p*H	Best fit adsorption isotherm	Best Fit kinetic model	Adsorption capacity
Water Hyacinth [5]	-	-	-	Langmuir isotherm	Pseudo 2nd order	0.187 kg kg^{-1}
Pine sawdust (*Pinustabulaeformis*) [6]	COOH, NH_2, OH	-	6.5	Langmuir isotherm	Elovich equation	111.46 mg g^{-1}
Raw pine cone biomass of *Pinus radiate*[7]	OH, C=O, C=C, C-N, -C-C-, -CN	-	6.16	Langmuir isotherm and Freundlich isotherm	Pseudo 2nd order kinetics	109.89 mg/g
Tea seed shells (*Camellia sinensis* L.) [8]	C=C, R-OH, C=C, C-O, OH, C-H	Surface area = 1530 m^2/g, average pore diameter =2.045nm, total pore volume = 0.7826 cm3/g, micropore volume = 0.5989 cm^3/g, mesopore volume = 0.1837cm^3/g	-	Langmuir isotherm	Pseudo 2nd order kinetics	324.7mg/g
Loofah [9]	-	-	7	Langmuir isotherm and Temkin	Pseudo 2nd order kinetics	Modified Loofah= 85.5 mg/g and unmodified=33.7mg/g
Rice husk ash [10]	OH, O-Si-O, C-O	-	7	Freundlich isotherm	Pseudo 2nd order kinetics	~690 mg/g
Papaya (*Carica papaya* L.) leaf powder [11]	-	-	6.8	Langmuir isotherm	Pseudo 2nd order kinetics	512.55 mg/g
Green pea peels (Pisumsativum) [4]	OH,C=O, C-H, Carbonyl stretch, amine group, CH_3 bending, C-O and $-SO_3$ stretching,	Surface area= 316.20 m^2/g, specific pore volume= 0.2717cm^3/g and average pore diameter= 34.95Å	7	Langmuir isotherm	-	163.94 mg/g
Hen feather [12]	-	Surface area=557.9 m^2/ g	7.0	Langmuir isotherm	Pseudo 2nd order kinetics	134.76 mg/ g
Sawdust [13]	-	-	6 (SD), 12 (PPy/SD)	Langmuir isotherm	-	SD=19.41 and PPy/SD= 34.36 mg g-1
Buffalo dung and mustard waste [14]	-	-	6.0	Langmuir isotherm, Freundlich isotherm	-	245.76 (MWA), 294.11(BDA)
Lemon grass ash [15]	-OH stretching vibrations, C=C stretching and CH3 bending, C-O stretching.	-	10	Langmuir isotherm	Pseudo 2nd order kinetics	413.22 mg/g
Hazelnut shell [16]	-	-		Langmuir isotherm	-	2.14 × 10 − 4 (25°C), 2.17 × 10 − 4 (35°C), 2.20 × 10 − 4(45°C) and 2.31 × 10 − 4 (55°C)mol /g

(Contd.)

Table 1 — Represents review of low cost adsorbents used for the removed of methylene blue (*Contd*.)

Adsorbent	Functional group present	BET analysis	Optimum initial *p*H	Best fit adsorption isotherm	Best Fit kinetic model	Adsorption capacity
Tobacco stem ash [17]	Si-O asymmetric stretching, Si-O symmetric vibrations,carbonate (CO32−) and asymmetric stretching vibration of carbonate (CO32−).	-	10.38	Langmiur isotherm	Pseudo 2nd order kinetics	35.7 mg /g
Feather Keratin Deposits [18]	-OH stretching vibrations, C=C stretching and CH3 bending, C-O stretching.	-	7.0	Langmiur isotherm	Pseudo 2nd order kinetics	156.5 mg/g
Rice husk , Peanut shell , Activated carbon [19]	-OH Stretching vibrations, (C=O) Stretching vibrations	surface area ,NPS = (585m2/g) , PPS=(430 m2/g) and NRH= (330 m2/g).	10.0	Langmuir Isotherm	-	(18.7 mg/g) for PRH100
cashew nut shell [20]	-OH stretching vibrations, -O-CH3 stretching , CH3 bending, C=O stretching.	surface area = 984m2/g, average pore diameter=, 2.52nm and pore volume=0.552 cm3/g.	9.0	Redlich-Peterson Isotherm	Pseudo 2nd order kinetics	-
Waste coffee-grounds [21]	-	-	6.0	Freundlich Isotherms.	Pseudo 2nd order kinetics	18mg/g

Results and Discussion

Fourier Transform Infrared (FT- IR) spectroscopy

FTIR was performed to identify functional groups present on the surface of the adsorbent which can potentially favour the adsorption of dye ions[22]. To analyze the possible interaction of ions of dye with these functional group, FTIR spectra of pure adsorbent and FTIR spectra of the adsorption after the adsorption process was taken. As visible in the Fig. 1 (Red colour), the broad and intense peak is positioned at 3354 cm^{-1} recognized the bonded OH group in lignin and cellulose. The peaks located at 2929 cm^{-1} is associted with the alkene streching. The bands at 1649 cm^{-1} and 1738 cm^{-1} corresponds to C=O peak in ketones and aldehyde[23]. Peak at 1427 cm^{-1} can be assigned to C-O with carboxyl group. A peak at 1030 cm^{-1} which is asociated with C-O is particularly associated to the lignin present in the ZMSP. Hydroxyl and carbonyl groups can act as proton donor and consequently coordination is possible with the positively charged dye ions with deprotonated carbonyl and hydroxyl group[6]. Therefore, it can be infered that ZMSP have an anionic structure which can attract positively chraged dye molecules.

It can be deduced from FTIR spectrum (Blue colour) that there is significant difference in the functional gropus detected in ZMSP after the adsoprtion process. An absorption peak at 2880 cm^{-1} corresponds to the alkene streching. Changes were also observed in the intensity of OH peak and shifting of carbonyl group position. This clearly indiacted that ions of MB dye have interacted with these groups. These two groups are known to be favourable for the adsorption process as reported elsewhere[6].

Surface morphology analyses using SEM images

Scanning electron micrographs of ZMSP were taken at three different magnification to analyze detailed surface morphology of the adsorbent used. Figures 1a and 1b represents SEM images of ZMSP at 500 x and 15K x magnifications. Surface of the adsorbent was found to be irregular and rough as can be oberved in Figure 1a, which may be due to the presence of lignin content. At higher magnifications (Figure 1b), surface was found to be consisted of flakes with overlapping layers with irregualr surface spots on it. The average size of the flakes was 180 μm and average diameter of the spots was found to be 0.43 μm. This type of

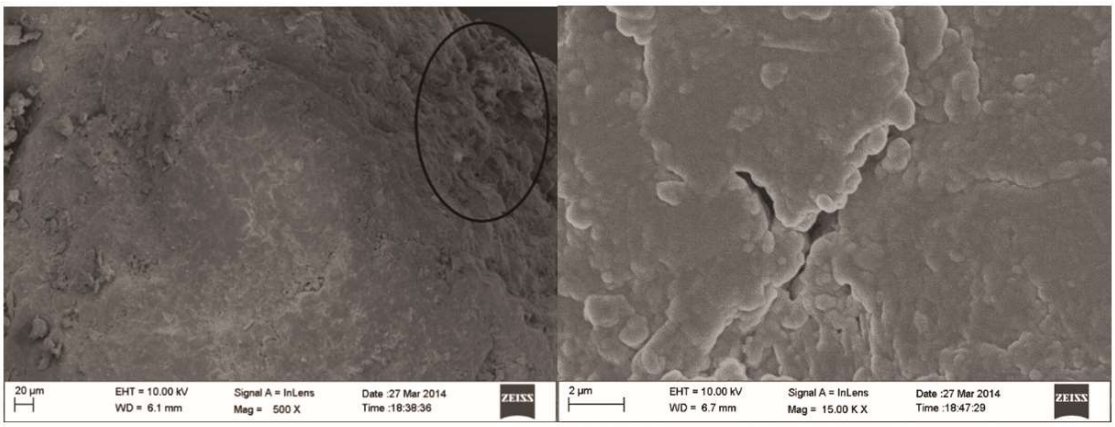


Fig. 1a — SEM of ZMSP at 500x; 1b — SEM of ZMSP at 15K

irregularity can make the adsorption feasible in different parts of the adsorbent[6].

Partical size

The partical size of the adsorbent ZMSP was examined using sieve method and mean diameter of adsorbent was found to be 686.17µm.

BET Analysis

Table 2 represents the results of of BET analysis with respect to surface area, pore volume and pore width. It is evident from the values of surface area and pore volume that it is extremely minute in comparison to activated carbons (>500 m^2/g). Therefore it can be inferred that surface of the adsorbent is not favourable for the physical adsorption as it provides less surface area.

Energy dispersive X-ray Spectroscopy

Figure 2 and Table 3 represents the results of EDX analysis. It is clear from the analysis that ZMSP contains high amount of carbon and oxygen followed by smaller percentage of copper and calcium. High oxygen content is reported to be favourable for adsorption[15].

Batch adsoprtion studies

Effect of contact time with respect to tempearture

Adsorption as a function oftime for the initial dye concentration 150 mg/L at *p*H=7.2 is shown below in Fig. 3. The figure clearly indicate that the uptake of adsorbent species is fast at the initial stages of the contact,after that it becomes slow as approached towards the equilibrium. A large number of vacant surface sites were available for adsorption initially which, later on gradually occupied by the dye molecules and trend tend to be almost constant. After a

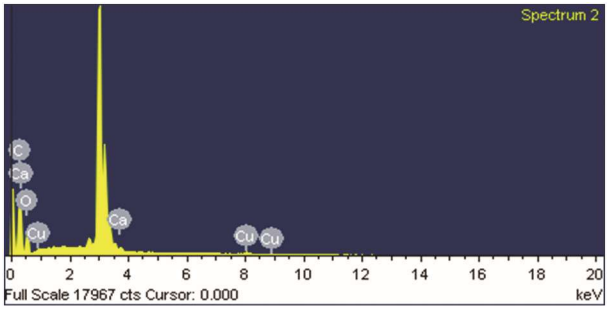


Fig. 2 — EDX spectrum for ZMSP

Table 2 — Results of BET analysis

BET surface area	0.3455 m^2/g
Langmuir surface area	0.3838 m^2/g
t-Plot micropore area	21.4406 m^2/g
Single point adsorption total pore volume of pores	0.014698 cm^3/g
t-Plot micropore volume:	0.008845 cm^3/g
Adsorption average pore width (4V/A by BET):	1701.6206 Å

Table 3 — Elemental composition for ZMSP

Element	Series	Normalized composition (Wt %)	Atomic composition (At %)
C	K	54.95	63.87
O	K	39.97	34.87
Ca	K	1.13	0.39
Cu	K	3.96	0.87

definite time, the vacant sites are difficult to be occupied due to the repulsive forces between the solute molecules available on the solid and bulk phase. ZMSP have a number of binding sites, and the dye adsorption showed a dispersion inclination at 180 min at three different temperature chosen for the study of ZMSP.

Temperature plays a significant role in the adsorption process. It was observed that equilibrium was achieved earlier at higher temperature than at lower temperature values. Moreover, greater percentage

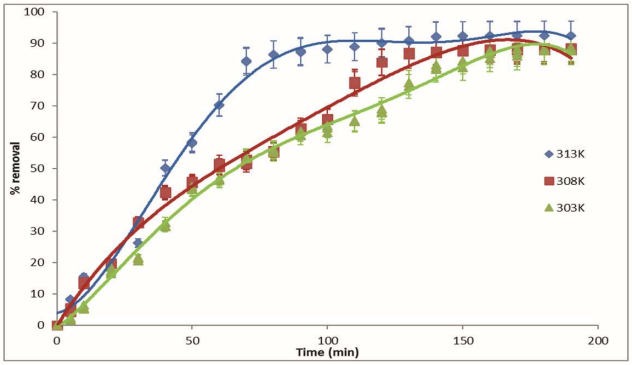


Fig. 3 — Effect of contact time on the process of adsorption for methylene blue with ZMSP (RPM= 150, Adsorbent dose= 0.2 g, *p*H= 7.2, Equilibrium time = 180 min and concentration 150 mg/L)

of dye removal was observed upon increasing the temerature from 303K to 3013 K. Increase in temperature causes decrease in the density and viscosity of the dye which can result in the enhanced diffusion rates. It also increases the mobilty of dye molecules. This result also signifies that the process of the adsorption of methylene blue to ZMSP was endothermic in nature[24,25]

Effect of adsorbent dosage

Amount of the adsorbent at a particular concentration is very significant as it determines the adsorption capacity of the adsorbent[26]. Effect of adsorbent dose studied for the initial concentration of the dye of 150 mg/L, with the varying amount of ZMSP ranging from 0.1 g to 0.8 g/50 mL keeping all other parameters constant. Result showed that percentage dye removal was increased with an increase in the adsorbent dose. For instance at 303K temperature percentage removal was increased from 15.5 to 64.1% when amount of adsorbent was increased from 0.1 to 0.8 g/50 mL. Upon increasing the adsorbent dose surface area also increases which lead to the increase in the active sites of adsorbent. This was the reason for greater removal of dye in terms of percentage (Fig. 4a). However the amount of MB adsorbed at equilibrium (Q_e) is decreased with the increase in the adsorbent dose as shown in Fig. 4b. This is due the reason that active sites remain uncovered as ratio of active size to that of dye molecules increases as we increase the adsorbent amount, which leads to the lower specific adsorption capacity. At lower adsorbent amount there is increase in the number of active sites saturated with methylene blue dye and hence the specific adsorption capacity. Similar results have been reported elsewhere[27,28].

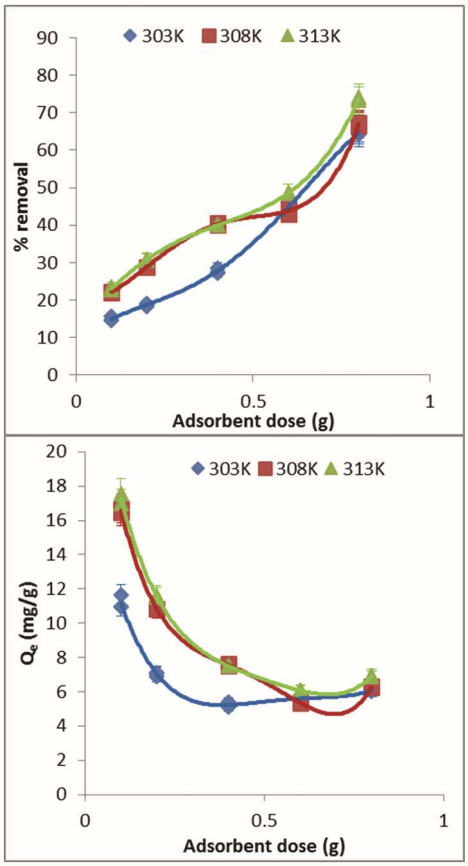


Fig. 4 — Effect of the adsorbent dose on (a) percentage of adsorption and (b) the amount of dye adsorbed (Q_e) of methylene blue with ZMSP (RPM = 150, concentration = 150 mg/L, *p*H = 7.2, equilibrium time = 180 min)

Effect of *p*H of the solution

The surface charge of the adsorbents as well as the degree of ionization of different pollutants is affected by the *p*H of the solution. In this paper, effect of initial *p*H was studied in the *p*H range of 2 to 10. It is clear from Fig. 5 that percentage removal of methylene blue increased for ZMSP with the increase of solution *p*H from 2 to 10. This behavior of dye removal with respect to *p*H may be credited to numerous reasons.

The adsorption of positively charged dye groups on the adsorbent surface is influenced by the charge on the surface of the adsorbent which in turn is affected by the solution *p*H. From the result, it was concluded that the negatively charged groups at the surface of adsorbent are required for the basic dye adsorption. At lower *p*H, there was a net positive charge on the surface of the adsorbent due to the presence of the H_3O^+. Moreover, carboxyl and hydroxyl group were also present in the protonated form which result in the poor electrostatic interaction between the dye ions and the adsorbent

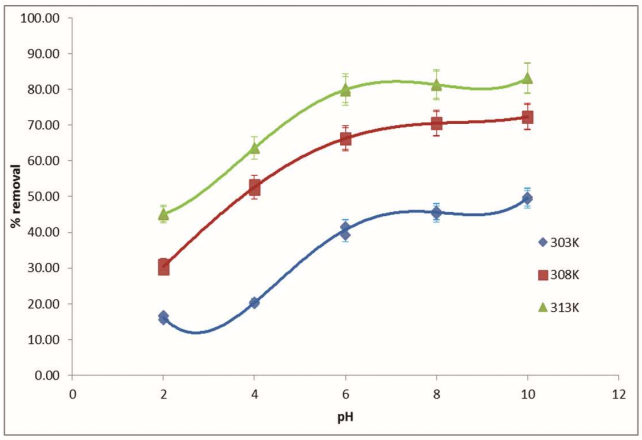


Fig. 5 — Effect of *p*H on the adsorption process onto methylene blue with ZMSP (RPM= 150, adsorbent dose = 0.2 g, concentration = 150 mg/L, equilibrium time = 180 min)

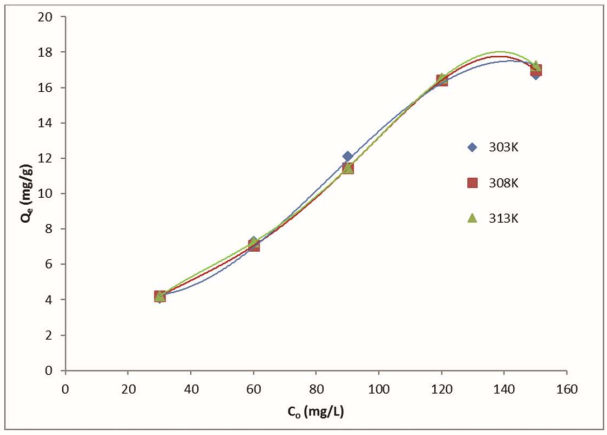


Fig. 6 — Effect of the initial concentration on the process of adsorption of methylene blue with ZMSP (RPM= 150, *p*H = 7.2, adsorbent dose = 0.2 g, equilibrium time = 180 min)

surface. This leads to lower percentage adsorption of the dye. As *p*H was increased, surface of the adsorbent became more negatively charged due to deprotonation of hydroxyl and carboxyl groups which favoured the adsorption of positively charged dye ions. Hence, as the *p*H was increased, the dye removal was also observed to be increased. Similar results have been reported elsewhere for treated biowaste based adsorbents like green pea peels, sawdust[4,6].

Effect of initial dye concentration on adsorption

To study the effect of initial concentration of dye on the adsorption process experiments were conducted by varying initial dye concentration in the range of 30 to 150 mg/L by keeping all other experimental conditions at a fixed value. Concentration of the dye offers a significant driving force to overcome the mass transfer resistance of the methylene blue between the aqueous and solid phases[29]. With the increase in initial concentration, the amount of methylene blue adsorbed per unit mass of adsorbent increased as shown in the Fig. 6. The amount MB adsorbed at equilibrium (Q_e) increased from 4.07 to 16.74, 4.2 to 16.99 and 4.2 to 17.23 for ZMSP as initial concentration increased from 30 to 150 mg/L at different temperatures i.e. 303K, 308K and 313K respectively. Loading of adsorbent with increasing initial dye concentration may also be due to higher interaction between dye and adsorbent, which increased the number of collisions between the ZMSP and dye ions. Similar results have been found in the literature[4,6].

Develoment of adsorption isotherms

Equilibrium data analyis is significant for the development of an equation which can be used for the optimum designing of an adsorption system as well as can accurately represents the results obtained. In this paper Langmuir, Freundlich, Temkin, and Dubnin-Raduskevich isotherms have been used to charachterize adsorption process. Experimental data was fitted at three different temperatures in these isotherms.

Langmuir isotherm

This isotherm is published by Irving Langmuir in 1916, and developed on a number of assumptions[30]:

i) All the sites available on the adsorbent surface have the same energy.
ii) Adsorption is a reversible process.
iii) A particular site can hold only one molecule.
iv) The rate at which adsorption proceeds is proportional to the driving force.

Langmuir equation in linear form is represented as follows:

$$\frac{1}{Q_e} = \frac{1}{Q} + \frac{1}{bQC_e}$$

Q = Langmuir adsorption capacity (mg/g)

b =energy of adsorption (L/gm).

The plot of $1/Q_e$ vs. $1/C_e$ gives a straight line of slope 1/bQ and intercepts 1/Q.

$$R_L = \frac{1}{1 + bC_o}$$

where C_o represents the maximum initial concentration of the dye in mg/L and b is the Langmuir constant. R_L value indicate the process feasibility. If R_L is greater than 1 then process is unfavourable, R_L equal to 1

indicate a linear process, if R_L value lies between 0 to 1 then process is supposed to be favourable and if R_L is equal to 0 then process is irreversible[31,32]. Results obtained (Table 4) clearly indicate that adsorption is favourable in this case.

Freundlich isotherm

Freundlich isotherm is widely used for the description of adsorption characteristics which is used in water or wastewater treatment[30].

The derived equation for the Freundlich isotherm is defined below in its linear form:-

$$\mathrm{LogQ_e} = \mathrm{LogK_f} + \frac{1}{\mathrm{n}}\mathrm{LogC_e}$$

This isotherm is suitable for describing reversible adsorption on heterogeneous systems and is not limited to monolayer adsorption only. The plot of Log $Q_e$vs. Log C_e gives a straight line. Freundlich constant K_f and exponent 1/n will be determined from the intercept and slope of the graph respectively and indicate the affinity of adsorbent for adsorbate and adsorption intensity respectively. If value of 1/n lies between 0.1 to 1 then process is said to be favourable[33]. Freundlich parameter were calculated and are given in Table 4 and found to be satisfactory with respect to 1/n values.

Temkin isotherm

The Temkin isotherm[34] incorporate the factor of adsorbent-adsorbate dealings. Its assumptions are as follows[35]:

Table 4 — Values of various parameters associated with Langmuir, Freundlich, Temkin and Dubinin-Raduskevich adsorption isotherm

Temperature →		303K	308K	313K
Langmuir	Q	68.493	40.766	45.290
isotherm	b	0.005	0.008	0.008
constants	R^2	0.974	0.955	0.967
	SD	0.015	0.018	0.016
	R_L	0.594	0.440	0.468
Freundlich	K_f	0.434	0.466	0.459
isotherm	1/n	0.862	0.837	0.847
constants	R^2	0.936	0.937	0.947
	SD	0.076	0.075	0.069
Temkin	b_T	321.104	329.083	322.640
isotherm	A	0.112	0.113	0.112
constants	R^2	0.903	0.875	0.886
	SD	2.010	2.298	2.212
Dubinin-	Q_m	14.625	13.977	14.235
Raduskevich	K	0.00004282	0.00003634	0.00003572
isotherm	R^2	0.825	0.768	0.786
constants	SD	0.291	0.331	0.319
	E	108.06	117.30	118.31

1 Adsorption causes a uniform distribution of biniding energy, and
2 Heat of adsorption in the layer of adsorbent decreases linearly beacuase of the adsorbate-adsorbate repulsionss.

Linear form of Temkin can be represented as follows

$$Q_e = B \ln A + B \ln C_e$$

where, $B = RT / b_T$, a constant associated to the heat of adsorption. A corresponds to the maximum binding energy (L/g), T is the temperature in Kelvin and b_T is the Temkin constant associated to heat of adsorption (J/mg). Temkin isotherm and constants, which are given in Table 4.

Dubinin-Raduskevich (D-R) Isotherm

Dubnin and Radushkevich had given an isotherm for the analysis of equilibrium data of adsorption[36]. This isotherm determines porosity apparent free energy and behaviour of adsorption instead of assuming a homogeneous surface or uniform adsorption potential. D-R isotherm can be represented as follows:

$$Q_e = Q_m \exp(-K\varepsilon^2) \text{(Non-linear form)}$$

$$\ln Q_e = \ln Q_m - K\varepsilon^2 \text{(Linear form)}$$

$$\varepsilon = \mathrm{RTln}\left(1 + \frac{1}{\mathrm{C_e}}\right)$$

where, Q_m represents adsorption capacity in mg/g, K is Dubinin-Raduskevich [D-R] Isotherm constant andε isPolanyi potential.

The data calculated from D-R isotherm is representated in Table 4. Values for the parameter Q_m (mg/g) and K (mol^2/kJ^2) were calculated from the intercept and the slope of the plot, respectively.

Another parameter named as energy of adsorption (E) in in KJ/mol is describing the free energy change when one mole of ion transferred from infinity in solution to the surface of the adsorbent. E can be calculated using following Equation,

$$E = \frac{1}{\sqrt{(2K)}}$$

If E < 8 KJ/mol then adsorption can be termed as physical

E > 8 KJ/mol then adsorption can be termed as chemisorption[37]

Value of E in the present study was found to be well beyond 8 KJ/mol, therefore adsortion can be designated as chemisorption.

Table 5 — Value of various parameters calculated for kinetics of adsorption

Lagergren pseudo-first order				Lagergren pseudo-second order				Elovich kinetic Model			
	303K	308K	313K		303K	308K	313K		303K	308K	313K
				Q_e	50.659	55.432	63.492				
Q_e	36.961	34.719	36.288	h	0.791	0.505	0.391	α	2.085	1.047	0.820
k_{1ads}	0.021	0.016	0.014	k_2	0.00031	0.00016	0.00010	β	0.095	0.079	0.072
R^2	0.962	0.916	0.968	R^2	0.962	0.940	0.960	R^2	0.941	0.963	0.985
SD	0.094	0.077	0.049	SD	0.214	0.242	0.171	SD	2.940	1.698	0.981

Adsorption kinetics

Adsorption kinetics was studied using various kinetic models reported in literature for adsorption like Lagergren Pseudo first order, Lagergren Pseudo second order and Elovich model. Adsorption data obtained at various time intervals was fitted to these kinetic models to analyze the adsorption kinetics.

The linear form of Lagergren pseudo-first order given as

$$\mathrm{Log}(Q_e - Q_t) = \mathrm{Log}Q_e - \frac{k_{1,ads}}{2.303}t$$

and Lagergren pseudo-second order model is

$$\frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_e}t$$

where,

$Q_e$is the amount of dye (mg) adsorbed on the surface of adsorbent (g) at equilibrium (mg/g), Q_t is the amount of dye adsorbed at time t (mg/g), k_{1ads} is the reaction rate constant for pseudo first-order in minute, h is $k_2 Q_e^2$ and k_2 = reaction rate constant of adsorption the for pseudo-second-order in mg/g/min[38,39].

Linear form of Elovich model can be represented as follows[40]:

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$$

α represents the rate of chemisorption at zero coverage and β is associated to the amount of surface coverage and the activation energy of chemisorption.

A series of experiments were conducted at taking time as independent variable and keeping all other parameters constant. The straight line plots of log (Q_e-Q_t) against time (t) for pseudo 1st order reaction and Q_t/t against t for the pseudo 2nd order kinetics. The rate parameter K_1, K_2, Q_e and R_1^2 and R_2^2 of MB under different conditions were calculated from the plots given in Table 5. Constants α and β can be calculated from the slope and intercept of the plot between ln (t) and Q_t. It is evident from the Table 5 that Lagergren Pseudo second order and Elovich model fitted better than Lagergren Pseudo first order kinetic model.

Conclusion

The present study shows that the low cost biowaste ZMSP has appreciable adsorption ability and it can be used for the removal of basic dye methylene blue (MB) without any pretreatment. Following conclusions are drawn from this study:

- ZMSP has irregular flakes type of surface morphology at lower magnification and at higher magnification flakes structure with few small spots are observed through SEM. The average size of flakes is 180 μm and diameter of the spots is 0.43μm.
- FTIR results show that there are certain functional groups like OH and CO which are reported as favourable for the process of adsorption in the existing literature.
- Mean diameter of powdered adsorbent is found to be 686.17μm.
- Optimum contact time for the equilibrium to be achieved is found to be 180 min for ZMSP.
- Effect of adsorbent dose is studied for the dye in the range of 0.1 to 0.8g/50mL which show that with the increase in amount of active sites, the adsorption of dye increase which cause an increase in the removal efficiency.
- Optimum *p*H for the adsorption process is found to be around 6. The adsorption of positively charged dye on the adsorbent surface mainly influenced by the surface charge on the adsorbent which in turn by the *p*H solution.
- The experimental data for the ZMSP has fitted well to the Langmuir adsorption isotherm followed by Freundlich, Temkin and Dubinin-Raduskevich. On the basis of parameter E of Dubinin-Raduskevich isotherm, it is found that chemisorption is the phenomenon followed in this study.
- Temperature effects show that the process is found to be endothermic.

- Kinetic modelling of the data show that Pseudo second order and Elovich model fitted better than Pseudo first order kinetic model.

At last it may be concluded that *Ziziphus mauritiana* seeds has potential to be used as a low cost adsorbent. Its adsorption capacity is found to be comparable with other biowaste materials reported in the literature.

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