

Adsorption of methylene blue and malachite green dyes from aqueous solution by soya bean seed powder-equilibrium isothermal modeling

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ABSTRACT

This study was aimed at using soya bean seed powder (SSP) as a potential adsorbent to remove methylene blue (MB) and malachite green (MG) dyes from aqueous solution. The SSP powder was used without any modification. In a batch adsorption system as a function of pH, contact time, adsorbent dose, and initial concentration of dyes was evaluated. Maximum removal of MB and MG dyes were observed at pH 6.0 and 5.0 respectively. The equilibrium uptake was increased with an increase in the initial dye concentration in the solution. Adsorption kinetic data were properly fitted with the pseudo second order kinetic model. The experimental isotherms data were analysed using Langmuir and Freundlich isotherm equations. The best fit was obtained by the Langmuir model with high correlation coefficient $R^2 = 0.9962$, $R^2 = 0.9998$ with a maximum monolayer adsorption capacity of 149.25 mg/g for Methylene Blue and 232.55 mg/g for Malachite Green. The adsorbent was analysed by using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) for determination of functional groups and surface morphology respectively.

Keywords: Methylene blue; Malachite green; Soya bean seed powder; Isotherms; Kinetics

1 INTRODUCTION

Many dyeing industries give rise to dye-bearing effluents in the production process and these problematic waste waters have to be treated to accord with discharge limit before discharge not only for their high chemical and biological oxygen demand but also for suspended solids of toxic properties to aquatic life and reduce in light penetration [1]. Methylene Blue is a toxic dye and causes several health risks in humans upon exposure such as nausea, vomiting, eye injury and methemoglobinemia [2]. Contact of malachite green with skin causes irritation with redness and pain. Dyes are also major component of the laboratory wastes, which are then led into the soil and water bodies [3]. So, these dyes need to be removed. Most of these dyes are synthetic and exhibit complex aromatic structure, thus being stable and difficult to be biodegraded. Several techniques have been developed to treat dye effluents such as microbial degradation, chemical oxidation, membrane separation, bioaccumulation, electrochemical treatment, adsorption and reverse osmosis [4], and among these techniques, adsorption is generally preferred due to easy handling, high efficiency, low energy input and availability of different adsorbents [5,6].

Although the activated carbon [7] is most effective for adsorption of dyes, but it is quite expensive and hence there is an increasing need for equally effective but cheaper sorbents. Recently, there have been several reports of the economic removal of dyes using different adsorbents such as rice husk, cotton, bark, hair and coal [8], perlite [9], sewage sludge-based activated carbons [10], apple pomace and wheat straw [11], banana and orange peel [12], organobentonite [13], pearl millet husk [14], peat particles [15], wood [16], fly ash and coal [17].

In the present study, the Soya bean seed powder (SSP) has been used as an adsorbent for the removal of Methylene blue [MB] and Malachite green (MG) from aqueous solution. MB and MG were selected as a model dyes for evaluating the potential of the Soya bean seed powder to remove dyes from waters.

Methylene blue (MB) is a basic aniline dye, $C_{16}H_{18}N_3S$ that forms a deep blue solution when dissolved in water. Methylene blue is a water-soluble thiazine dye, which is widely used in the textile, paper, printing, pharmaceutical, food industries and also in research laboratories. Malachite green (MG) is an N-methylated diaminotriphenylmethane dye. Malachite green dye is a green crystal powder with a metallic luster. Malachite green is toxic and must be removed before discharged into receiving streams. MG is one such dye used extensively in textile industry for dyeing silk, leather, cotton, wool and jute. It also extensively used as bactericide, fungicide and parasiticide in aquaculture industries worldwide. MG is highly toxic to mammalian cells and causes kidney tumours in mice and reproductive problems in rabbit and fish.

The objective of this research is to study the comparison and percentage of dye removal of Soya bean seed powder towards the adsorption of methylene blue and malachite green dyes. Adsorption process

was optimized by investigating pH, dye concentration, contact time and adsorbent dosage. The equilibrium adsorption data were evaluated by Langmuir and Freundlich isotherm models. The First order, Pseudo-second order and Weber Morris kinetic models were used for determining of the adsorption kinetics.

2. EXPERIMENTAL SECTION

2.1. Materials

Methylene blue (MB) and Malachite green (MG) dyes were used in this study as adsorbates. The methylene blue, MB (C.I.52015, C₁₆H₁₈N₃SCl), malachite green, MG (C.I.42000, C₂₃H₂₅N₂Cl) HCl and NaOH were obtained from Merck with analytical grade. MB and MG are cationic dyes and Chemical structures were shown in Fig. 1 and 2. MB dye was purchased from Merck and was used as adsorbates and was not purified prior to use.

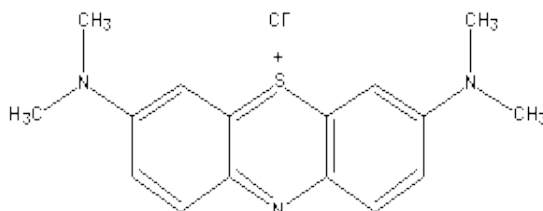


Fig. 1. Chemical structure of methylene blue

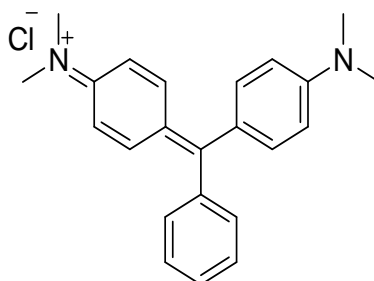


Fig. 2. Chemical structure of malachite green

2.2. Preparation of biosorbent

The seeds of Soya bean were purchased from local market of Nellore (A.P.). They were washed and dried in sunlight for 3 to 5 days. Then, they were dried in oven at 70 ° C for 2h to remove moisture completely and then ground into fine powder. After that, the seed powder was sieved to separate 60 mesh particle size powder and large size particles were grinded again. This powder was stored in air tight plastic bottles till further use.

2.3. Preparation of Methylene Blue and Malachite Green Dye standards

The stock solutions of MB and MG were prepared by dissolving 1.22 g and 1.111 g in 1L of distilled water respectively. The experimental solutions of desired concentration were prepared by diluting stock solution with distilled water. The concentration of MB and MG dyes were measured at $\lambda_{max} = 665\text{nm}$ and $\lambda_{max} = 619\text{ nm}$ using UV-Visible spectro photometer (JASCO, Model V-750, SERIAL NO.A 055361799 made in Japan). The pH of solutions was adjusted with 0.1 M concentrations of HCl and NaOH, using a pH meter (Hanna, pH211).

2.4. Batch adsorption experiments

The batch adsorption studies were carried out at various pH (2-11), dye concentration (20-100 mg/L), contact time (10-240 min), adsorbent concentration (0.1-1.0 g/ 0.1L) with 100 mL methylene blue and malachite green solutions in water bath to elucidate the optimum conditions of biosorption. After each adsorption process, the dye solution was separated from the adsorbent by centrifugation at 3000 rpm for 10 min. Then, supernatants were analyzed for remaining dye concentration by UV-visible spectrophotometer (GBC, Cintra 202) monitoring the changes in the absorbance values at 665 and 619 nm. The amount of methylene blue and malachite green adsorbed on the seed, q (mg/ g), was obtained by the following equation

$$q = \frac{(C_o - C_e)V}{M} \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations of dye (mg/ L), respectively. V is the volume of the solution (L) and M is the amount of adsorbent used (g).

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

FTIR spectra are commonly used to identify the groups involved in the reaction process and thus the FTIR spectra of soya bean seed powder are investigated and shown in Fig. 3. The peak around 3329 cm^{-1} represented the OH stretching vibration that showed the presence of free hydroxyl group on the surface of SSP powder. This vibration corresponded to inter and intra molecular hydrogen bonding among the constituents of biomass before treatment. The band at 1645 cm^{-1} may correspond to C=O stretching (Amide) and it had almost no change after treatment.

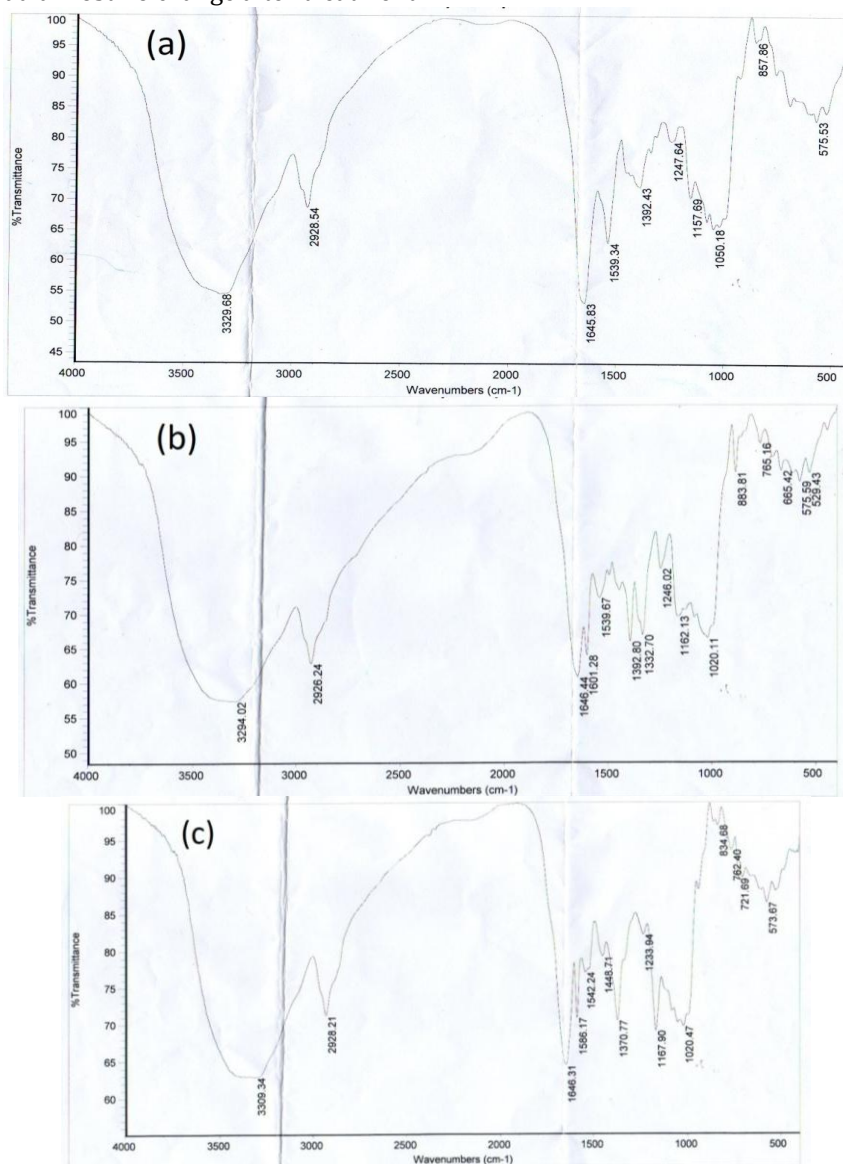


Fig. 3: FTIR Spectra of (a) Pure SSP (b) SSP loaded with MB and (c) SSP loaded with MG

3.2. Scanning Electron Microscopy (SEM) analysis

The SEM was used to observe the changes in the surface morphology of the materials. Scanning Electron Microscopy (SEM) analysis was carried out on the Soya bean seed powder to study its surface texture before and after adsorption (Fig. 4). The figures illustrate the surface texture and porosity of SSP with holes and small openings on the surface which increased the contact area. These will lead to pores diffusions during adsorption. Surface area is related to the adsorption capacity of an adsorbent. As the surface area increases, more binding sites are available for the adsorbate to be adsorbed.

The figures show the SEM micrographs of SSP sample before and after dye adsorption. It is clear that SSP has considerable numbers of heterogeneous layer of pores where there is a good possibility for dye

to be absorbed. The surface of dye-loaded adsorbent, however, clearly shows that the surface of SSP is covered with dye molecules.

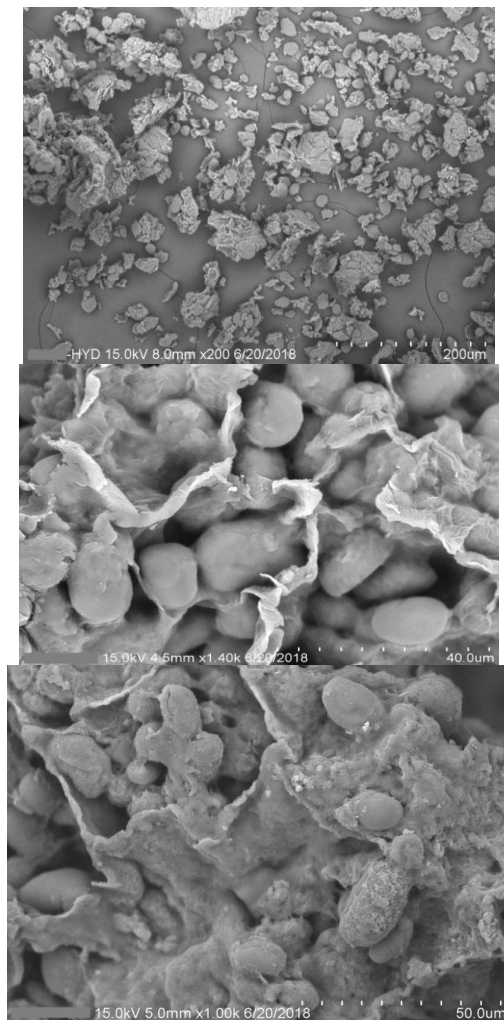


Fig. 4: SEM images of (a) Pure SSP (b) SSP loaded with MB and (c) SSP loaded with MG

3.4. Surface Area Analysis

The influence of the surface properties on the extent of adsorption is evaluated by measuring the Single point surface area ($4.0123 \text{ m}^2/\text{g}$), BET surface area ($3.825 \text{ m}^2/\text{g}$), total pore volume ($0.00071 \text{ cm}^3/\text{g}$) and the average pore diameter (36.48 \AA). The BET surface area, pore volume and pore structure of soya bean seed powder were obtained from nitrogen adsorption data at 77 K using a gas adsorption analyser (BELSORP, BEL Japan). Each sample was degassed at 323 K for 12 h to obtain a residual pressure $< 10^{-6} \text{ mmHg}$. The specific surface areas and micro pore volume of the samples were calculated by the BET equation. The amounts of N_2 adsorbed at relative pressure ($P/P_0 = 0.9966$) were used to investigate the total pore volumes, which correspond to the sum of the micropore and mesopore volumes.

3.5. Effect of pH

pH is one of the most important factors affecting the process. In order to investigate the influence of pH on the MG and MB removal by SSP, experiments were carried out over a pH range of 2.0-11 at dye concentration 100 mg/L , adsorbent dosage $0.1\text{g}/0.1 \text{ L}$. As shown in Fig. 5, the maximum removal efficiency, approximately 90.93% at pH 6.0 for MB and 91.56% for MG at pH 5.0.

The effect of initial pH on biosorption percentage of MB and MG dyes were examined over a range of pH values from 2 to 11 and the results are presented in Fig. 5. As elucidated in Fig. 5, the dye removal was minimum at the initial pH 2. The dye adsorbed increased as the pH was increased from pH 2 to 6. Incremental dye removal was not significant beyond pH 6 and 5 for MB and MG. For this reason, pH 6 and 5 were selected for MB and MG for future equilibrium studies.

After adsorption experiments, it was found that at low pH, the dyes become protonated, the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites results in

decreased adsorption. Higher adsorption at increased pH may be due to increased protonation by the neutralization of the negative charges at the surface of the adsorbent; which facilitates the diffusion process and provides more active sites for the adsorbent.

Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes the percentage of dye removal will increase. In contrast, at a high pH solution the percentage of dye removal will increase for cationic dye adsorption and decrease for anionic dye adsorption [18]. For cationic dyes, lower adsorption of dye at acidic pH is probably due to the presence of excess H⁺ ions competing with the cationic groups on the dye for adsorption sites.

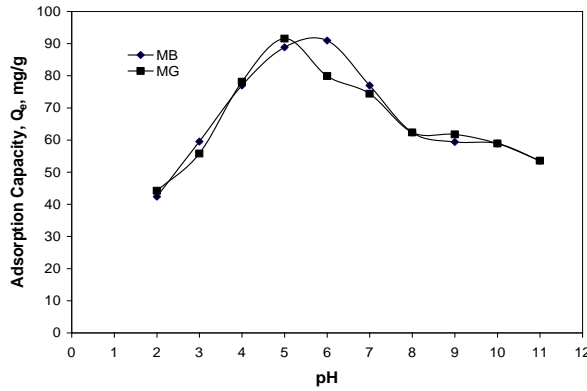


Fig. 5: Effect of pH on biosorption of MB and MG on SSP

3.6. Effect of contact time

Time has significant influence on the adsorption of dye. It can be observed from the figure that adsorption of MB and MG was quite rapid in the first 60 min, and then gradually increased with the prolongation of contact time (Fig. 6 and 7). After 210 min of contact time equilibrium was observed and with further increase in contact time there is no additional enhancement in sorption capacity. Based on these results, 210 min was taken as the equilibrium time in batch adsorption experiments.

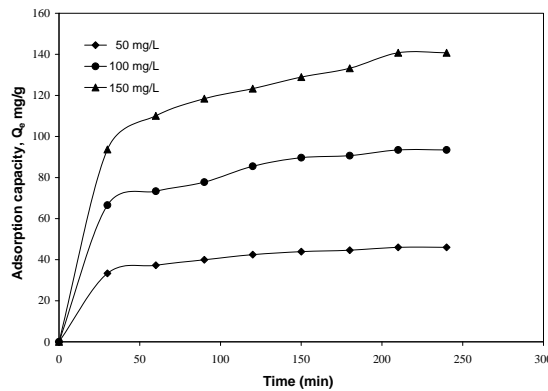


Fig. 6: Effect of contact time on adsorption of MB on SSP

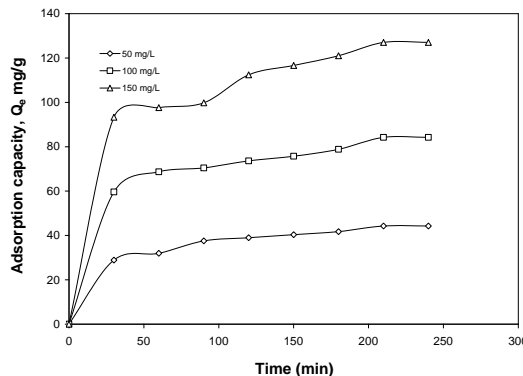


Fig. 7: Effect of contact time on adsorption of MG on SSP

3.7. Sorption Dynamics

Successful application of the adsorption technique demands development of inexpensive, non-toxic, readily available adsorbents of known kinetic parameters and sorption characteristics. Therefore, kinetic studies of adsorption are carried out at initial concentrations of 50-150 mg/L.

Reaction based models

In order to investigate the mechanism of the adsorption process pseudo-first and second order kinetic models were used to fit the kinetic experimental data. The pseudo-first order equation assumes the adsorption is of one adsorbent surface while in pseudo-second-order model one adsorbate molecule is adsorbed onto two active sites. The non-linear form of Pseudo-first-order [19] and pseudo-second-order [20] kinetic rate equations are given as (Eqs. (2) and (3):

Pseudo- first-order model

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{2}$$

Pseudo-second-order model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e and q_t are the amount of dye adsorbed per unit mass of adsorbent (mg/g) at equilibrium and any time t (min), k_1 (1/min) and k_2 (g/mg. Min) are the rate constants of first and second order sorption respectively. K_1 is calculated according to the linear plot of $\log (q_e - q_t)$ versus t and k_2 is determined by plotting t/q_t against t .

The estimated kinetic parameters and coefficient of determination (R^2) from the pseudo-first-order and pseudo-second-order models are summarised in Table 1 and 2. The low R^2 value and the difference between experimental q_e and theoretical q_1 indicate that the pseudo-first-order was not well suited to describe the adsorption of MB and MG by SSP. On the other hand, the R^2 value for the pseudo-second-order model was relatively higher than that of the pseudo-first-order model. Moreover, the q_2 value calculated by the pseudo-second-order model was close to the experimental q_e value. Thus, these results suggest that the pseudo-second-order model provided a good correlation for the adsorption of MB and MG onto SSP.

Diffusion based model

The results are also analyzed in terms intraparticle diffusion model to investigate whether the intraparticle diffusion is the rate controlling step in adsorption of MG and MB on SSP. The mathematical expression for Weber-Morris intraparticle diffusion model [21] is

$$q_e = k_{id} t^{0.5} + C \tag{4}$$

where k_{id} is the intraparticle diffusion rate constant (mg/g min^{-0.5}) and C is the intercept. It can be seen that all the plots have an initial curved portion, followed by a linear portion and a plateau regions. The initial curve of the plot is due to the diffusion of MB and MG through the solution to the external surface of SSP. The linear portion of curves describes the gradual adsorption stage, where intraparticle diffusion of MB and MG on SSP takes place and final plateau region indicates equilibrium uptake. The rate constants of Weber-Morris intraparticle diffusion model are shown in Table 3. Based on the results it may be concluded that intra particle diffusion is not only the rate determining factor.

Table 1: Legergren first-order rate constants for MB and MG adsorption on SSP

Initial concentration (mg/L)	Methylene Blue		Malachite Green	
	K_1	R^2	K_1	R^2
50	0.0149	0.9979	0.0124	0.9964
100	0.015	0.969	0.0112	0.9941
150	0.0117	0.9926	0.0105	0.9891

Table 2: Pseudo second-order rate constants for MB and MG adsorption

Initial concentration (mg/L)	Methylene Blue				Malachite Green			
	Q_e exp. (mg/g)	Q_e cal. (mg/g)	K_2	R^2	Q_e exp. (mg/g)	Q_e cal. (mg/g)	K_2	R^2
50	45.97	50	0.00107	0.9991	44.24	49.01	0.00073	0.9974
100	93.45	102.04	0.00044	0.9977	84.18	90.09	0.00050	0.9963
150	140.80	153.84	0.00026	0.9968	127.01	138.88	0.00028	0.9928

exp. = experimental; cal. = calculated

Table 3: Weber-Morris rate constants for MB and MG adsorption on SSP

Initial concentration (mg/L)	MB			MG		
	K _{id}	C	R ²	K _{id}	C	R ²
50	2.688	10.376	0.8296	2.6524	7.89111	0.8889
100	5.527	19.636	0.851	4.8283	18.216	0.836
150	8.318	27.36	0.8699	7.3615	26.358	0.8482s

3.8. Effect of Adsorbent dose

The effect of biosorbent dosage on the biosorption of Methylene blue and Malachite green dyes were studied using different biosorbent dosage in the range of 0.1-1.0 g results showed that the biosorption efficiency increased with highly dependent on the increase in biomass dosage of solutions up to 0.7 g where the maximum biosorption (90%) of the dye ions was attained. This can be expected because at higher dose of biosorbent in the solution, availability of exchangeable sites for the ions is high. However, the biosorption efficiency remained nearly constant at biosorbent dosage higher than 0.8 g. This could be attributed to a partial aggregation of biosorbent which reduces effective surface area of the biosorption. Therefore, the optimum biosorbent dosage was selected as 0.8 g for further experiment.

3.9. Adsorption isotherm models

In order to study the effect of initial dye concentration on the adsorption uptake, Both MG and MB solutions with initial concentrations of 20 - 100 mg/L with the adsorbent dose 0.1g/100 mL of SSP. The biosorption capacity of the SSP increased with increase in initial dye ion concentration. Increase in the initial concentration of dye ion provides more sorption sites and increases sorption sites and increases sorption

Successful application of the adsorption technique demands the studies based on various adsorption isotherm models, because adsorption isotherm models clearly depict the relationship between the concentration of dye in solution and the amount of dye adsorbed on the solid phase when both phases are in equilibrium [22]. In this study, the two adsorption isotherm models, Langmuir and Freundlich isotherm equations were used to describe the experimental sorption date.

Langmuir isotherm

The Langmuir isotherm [23] assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The non - linear form of Langmuir adsorption isotherm is given below.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_e is the amount of adsorption at equilibrium (mg/g), q_m is the maximum adsorption capacity of adsorbate per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and K_L is the Langmuir constant which is related to the energy of adsorption (L/mg).

The essential characteristics of Langmuir isotherm may be expressed in terms of a dimensionless constant called separation factor (R_L) and is given by the following equation;

$$R_L = \frac{1}{1 + K_L C_o} \quad (6)$$

where R_L is the equilibrium constant that indicates the type of adsorption, k_L is the Langmuir constant (L/mg) and C_o is the initial dye concentrations (mg/L). R_L values lies between 0 and 1 for favourable adsorption, $R_L = 1$ represents linear adsorption, $R_L = 0$ indicates the irreversible adsorption process and $R_L > 1$ represents unfavourable adsorption. The values of R_L are all in the range of 0-1, which indicate the favourable adsorption of MB and MG onto SSP. This means that the equilibrium isotherms can be well described by the Langmuir isotherm model, and the adsorption process is monolayer adsorption onto a surface with finite number of identical sites, which are homogeneously distributed over the adsorbents surface.

On the other hand Table 4 represents the comparison between the results obtained in this work with the similar data from literature [24-29]. The value of MB and MG uptake found in this work is significantly higher than reported for other adsorbents. Thus, the comparison of adsorption capacities shows that the SSP is an efficient adsorbent for the uptake of MB and MG.

Table 4: comparison of MB and MG adsorption capacity with some environmental-friendly adsorbents

Adsorbent	Dye name		Adsorption capacity (mg/g)	Reference
	MB	MG		
Orange peel	√	-	18.6	[24]
Walnut shell	√	-	51.55	[25]
Neem sawdust	-	√	4.354	[26]
Cherry Sawdust	√	-	39.84	[27]
<i>Parthenium hypstrophorous</i> weed	√	-	23.8	[28]
Degreased coffee bean	-	√	55.3	[29]
<i>Soyabean</i> seed	√	√	-	Present

Freundlich isotherms

Freundlich isotherm [30] can be applied to an adsorption system when the number of adsorption sites exceeds the number of contaminant molecules/ion. The isotherm thus describes multilayer and physical adsorption over the heterogeneous surface. According Freundlich isotherm, each adsorbing site has specific bond energy and stronger binding site is occupied first and adsorption energy decrease exponentially upon the completion of the process. The non-linear form of Freundlich isotherm is given by the following equation:

$$q_e = K_f C_e^{1/n} \quad (7)$$

where K_f (mg/g) and n are the Freundlich constants which represent adsorption capacity at unit concentration and adsorption intensity, respectively. Both K_f and n predict the feasibility of adsorption process. Freundlich constants, n , is exponent which is measure of adsorption intensity or surface heterogeneity, whose values lies in the range 1-10 for favourable adsorption phenomenon. K_f values for MB and MG come out to be 4.911 and 2.311 mg/g. Then n values were 1.3509, 1.1518, thus n values in the range 1-10, provided information about favourability of MB and MG adsorption onto SSP.

The parameters of isotherms models, R^2 values are summarized in Table 5. On the basis of higher R^2 values for the Langmuir isotherm model indicate that the adsorption of MB and MG onto SSP follows the Langmuir model. The excellent fit of the Langmuir isotherm to the experimental adsorption data confirms that the adsorption is monolayer; adsorption of each molecule has equal activation energy and that sorbate-sorbate interaction is negligible.

Table 5: Parameters of Langmuir and Freundlich isotherms for adsorption of MB and MG onto SSP

Dye	Langmuir			Freundlich			
	q_m (mg/g)	b (L/mg)	R^2	K_f	$1/n$	n	R^2
Methylene blue	149.25	0.022	0.996	4.911	0.740	1.350	0.988
Malachite green	232.55	0.007	0.999	2.311	0.868	1.151	0.997

4. CONCLUSIONS

The study is focused on the adsorption of MB and MG onto SSP powder from aqueous solution. The effect of operating parameters such as pH of solution, adsorbent dosage, contact time and initial dye concentration on the uptake of MB and MG. Equilibrium data were fitted to Langmuir and Freundlich isotherm models and the equilibrium data were best described by the Langmuir isotherm model, with maximum adsorption capacity of 149.25 and 232.55 mg/g for MB and MG respectively. The kinetics of the adsorption process was found to follow the pseudo-second order kinetic model. By second order model to study the mechanism of adsorption, calculated Q_e value agreed well with the Q_e experimental values. Based on all results, it can be concluded that the SSP is an effective and alternative adsorbent for the removal of MB and MG from aqueous solutions in terms of high adsorption capacity, available in natural and abundant with low cost.

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