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Biosorption of Malachite Green, Safranine T and Methylene Blue onto Spent Substrate of *Flammulina Velutiper*

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Abstract: Spent substrate of *Flammulina velutipes* (SSFV) was firstly used as a bio-adsorbent to adsorb malachite green, safranine T and methylene blue in aqueous solution, and the adsorption thermodynamics and kinetics were also studied. Langmuir and Freundlich isotherm models fit well the adsorption data, and the maximum adsorption capacity of SSFV for malachite green was 30.77 mg/g. Adsorption of the dyes onto SSFV was a spontaneous exothermic process based on adsorption thermodynamics model. SSFV could absorb the dyes rapidly and achieve equilibrium in a short time, and the data fit well with second-order kinetics model. The results suggest that SSFV should be an economical and efficient bio-adsorbent for the three dyes.

Key words: biosprption, spent substrate of *flammulina velutiper*, dyes, adsorption isotherm, thermodynamics, kinetics

1. Introduction

According to statistical results, dye species for commercial use have more than 100 000 kinds, and the world's annual yield is about 80 million to 90 million tons. With the rapid development of dye industry and the widely use of dyes, there are about 10 percent to 15 percent of the dyes to be released into the environment, which results in the problem of dye waste water pollution. The treatment methods of dye wastewater include mainly physical, chemical and biological methods [1-4]. In recent years, the agriculture and food industry waste, such as orange peel, sawdust, rice husk as a bio-adsorbent for the removal of dye wastewater has attracted a lot of attention [5, 6].

China is a big country of edible fungus production. In 2012, the total amount of edible fungus production was about 3,100 tons, and the total amount of spent mushroom substrate (SMS) was about 800 tons. SMS had become one of the major municipal wastes. The vast majority of SMS were abandoned or burned in situ, which not only wasted the resources but also polluted the environment. Because of the abundant surface hydroxyl, carbonyl, carboxyl, amide, phosphate group in SMS [7], SMS could be considered as an appreciable low-cost bio-adsorbent for wastewater treatment. Nevertheless, only a few studies have examined its potential as a bio-adsorbent [8, 9].

Flammulina velutipes, one of the most popular edible fungi, has been widely cultivated in the world [10]. However, there was not an economic and effective technology to utilize the spent substrate of *F. velutipes* (SSFV). In this study, SSFV was firstly used as a new type of bio-adsorbent for the removal of triarylmethane dye malachite green, azine dye safranine T and thiazine dye methylene blue, and the adsorption thermodynamics and kinetics were also studied.

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2. Materials and Methods

2.1 Biomass

SSFV was purchased from Huai'an Taishengyuan Agricultural Science and Technology Co., Ltd., Jiangsu, China and washed with tap water followed by washing with distilled water, and then oven dried at 60°C for 72 hours followed by milled, sieved and the particles (diameter ≤ 0.25 mm) were selected for use as bio-adsorbent.

2.2 Preparation of Synthetic Dye Solution

Three stock solutions of 200mg/Lwere prepared by dissolving the accurate amount of malachite green, safranine T or methylene blue in 200 ml and completed to 500ml with distilled water. All the chemicals used throughout this study were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. The initial pH was adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH. All the adsorption experiments were carried out in the shaker controlled by a thermostat (uncertainty of ±0.5 K).

2.3 Batch Bio-adsorption Studies

To study the effect of pH, initial dyes concentrations, temperature and time on the adsorption of malachite green, safranine T and methylene blue onto SSFV, bio-adsorption studies were conducted in 250 ml conical flasks with 100mL aqueous solution of malachite green, safranine T or methylene blue (10, 20, 50, 80, 100 and 120 mg/L of concentration) mixed individually with 1 g of SSFV under the conditions of pH (2.0, 4.0, 6.0, 8.0, 10.0 and 12.0) and absolute temperature (288, 293, 298, 303, 308, 313, 318, 328, and 338 K) for (1, 3, 5, 7, 10, 20, and 30) min or 4 hours equilibrium time.

2.4 Determination of Concentration of Dyes

The equilibrium suspensions were centrifuged with a speed (5000 r/min) for 10 min, and the concentrations of dyes were measured by using a direct UV–vis spectrophotometric method using UV–vis spectrophotometer (754, Shanghai Sunny Hengping Instrument Co., Ltd., China) with silica cells of path length 1cm at wavelength $\lambda_{\text{malachite green}}$ 617 nm, $\lambda_{\text{safranine T}}$530 nm and $\lambda_{\text{methylene blue}}$ 664 nm. All data were five times replicated determinations.

Adsorption rate (R%) of dye onto SSFV was calculated by the Eq. (1), and equilibrium adsorption quantity of SSFV for dye, *Qe*(mg/g), was calculated by Eq. (2).

$$R(\%) = \frac{C_0 - Ce}{C_0} \times 100\% \tag{1}$$

$$Qe = (C_0 - Ce) \times \frac{V}{W} \tag{2}$$

where C_0 and Ce is the initial and equilibrium liquid-phase concentrations of the dyes respectively (mg/L), V is the volume of the experiment solution (L), and W is the weight of the SSFV used (g).

3. Results and Discussion

3.1 Effect of pH on Dyes Uptake

The effect of pH on the removal of malachite green, safranine T and methylene blue from aqueous solutions as showed in Fig. 1. When initial pH of the dyes solutions was increased from 2 to 12, the adsorption rate of malachite green and methylene blue but safranine T onto SSFV remained stable at about 96%. With increase in pH from 2 to 4, the adsorption rate of safranine T onto SSFV increased from 88.5 to 93%. With further increased in pH to 8, there was a very slight increase in percent removal from 93 to 94%, while increase of the pH from 8 to 12, the adsorption rate of safranine T decreased from 94 to 88%. Malachite green, safranine T and methylene blue were all basic dyes, and SMS was rich in functioning groups such as –OH, -COOH and –NH, which indicated that the adsorption process mainly depended on the chemical adsorption onto the substrate surface through electrostatic attraction, complexation and coordination reaction [11]. SSFV was also used to adsorb acid dye amaranth in this study, but it was found that amaranth was very hard to be adsorbed by SSFV. Consequently, SSFV should be a good bio-adsorbent for basic dyes malachite green, safranine T and methylene blue, and have a relatively wide optimal adsorption pH value. The adsorption rate was more than 93% in 100 mg/L dyes solution with 1g of SSFV at pH 6.0.

3.2 Effect of Initial Dyes Concentration and Evaluations of Adsorption Isotherm

Adsorption efficiency of three dyes malachite green, safranine T and methylene blue onto SSFV generally decreased with increase in initial dyes concentration as shown in Fig. 2. The adsorption rates of malachite green and methylene blue onto SSFV had little effect with the initial dyes concentration between 10 mg/L to 120 mg/L, and the adsorption rates of malachite green and methylene blue were decreased only from 97.5% to 96%, and from 98.9% to 97.5%, respectively. Initial safranine T concentration affected the adsorption rate of SSFV. Nevertheless, the adsorption rate was still up to 89.5%. Therefore, SSFV could be a good bio-adsorption for malachite green, safranine T and methylene blue.

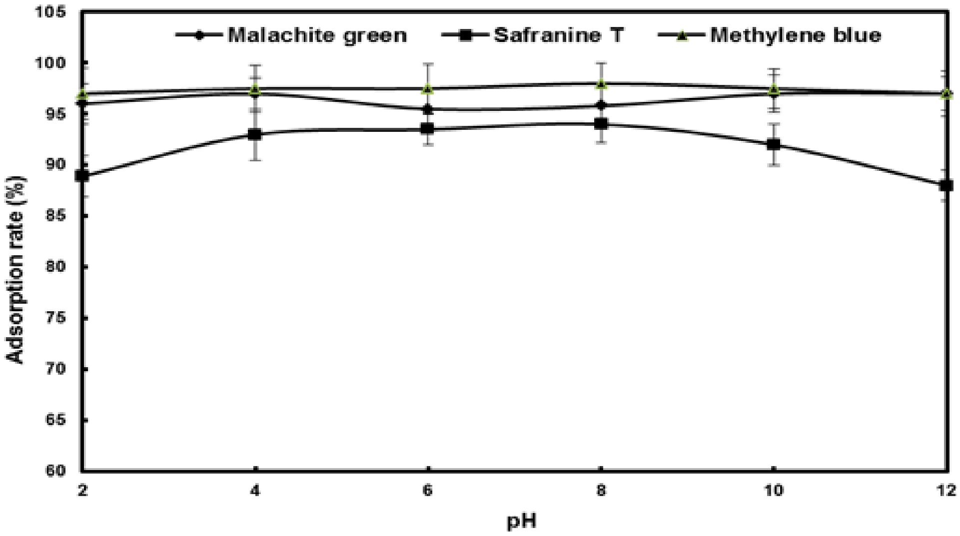


Fig. 1 Adsorption efficiencies of malachite green, safranine T and methylene blue onto SSFV as bio-adsorbent with different system pH at 100 mg/L of initial dyes concentration, 1g of SSFV and 303 K of temperature.

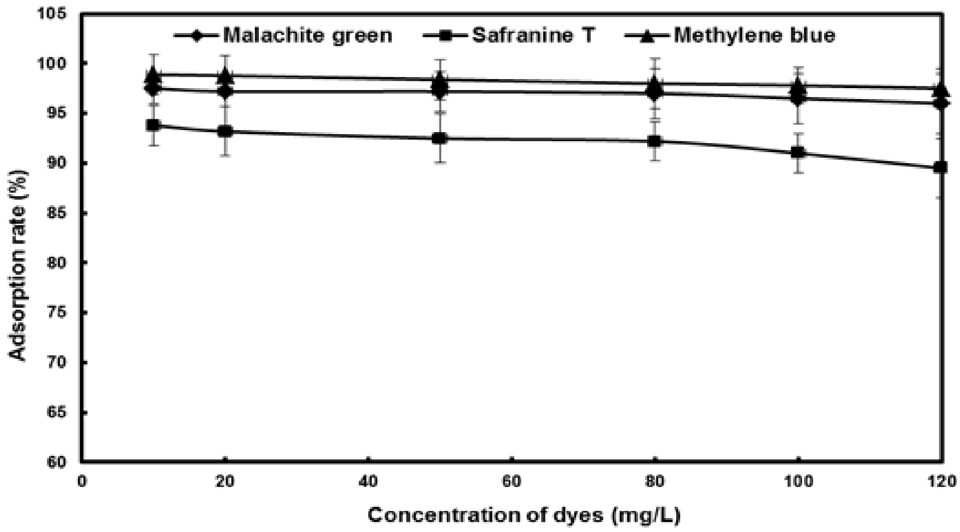


Fig. 2 Adsorption efficiencies of malachite green, safranine T and methylene blue onto SSFV as bio-adsorbent with different initial dyes concentration at 1g of SSFV, 6.0 of pH and 303 K of temperature.

To evaluate the adsorption isotherm of dyes onto adsorbent, Langmuir and Freundlich models are used widely. Langmuir model are suitable for single molecule adsorption, and can be expressed linearly in Eq. (3) as followed.

$$\frac{Ce}{Qe}=\frac{Ce}{Qm}+\frac{1}{K_L \times Qm} \tag{3}$$

Freundlich model provides an empirical description of the single component adsorption equilibrium, and is applicable within a broader scope. Freundlich model can be expressed as Eq. (4).

$$Qe = K_F (Ce)^{1/n} \tag{4}$$

Logarithm to Eq. (4), linearly Eq. (5) is obtained as followed.

$$\ln Qe = \ln K_F + \frac{1}{n}\ln Ce \tag{5}$$

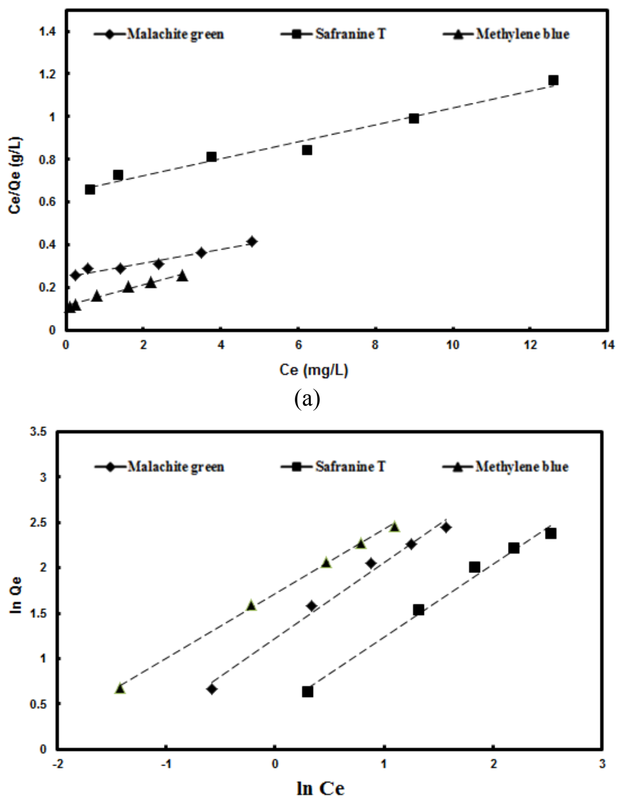
where C_e is the equilibrium liquid-phase concentrations of the dye (mg/L), Q_e and Q_m are the equilibrium and maximum adsorbed amount of dye per mass of SSFV respectively (mg/g), K_L is the Langmuir equilibrium adsorption constant (L/mg) related to the free energy of adsorption, K_F is the Freundlich constant [(mg/g) (L/mg)$^{1/n}$] related to the strength of the adsorptive bond, and $1/n$ is the adsorption intensity factor or surface heterogeneity[12].

To effectively evaluate the Langmuir isotherm, the values of C_e/Q_e were plotted against C_e as shown in Fig. 3a, and the values of K_L and Q_m were calculated as shown in Table 1 using the slope and intercept of the best fit line, respectively. Furthermore, the values of lnQe and lnCe were plotted to evaluate the Freundlich isotherm parameters of $1/n$and$K_F$as shown in Fig. 3b and Table 1. The regression coefficients (R^2) values were used to evaluate the fit of the Langmuir and Freundlich isotherms to the experimental data.

From Table 1, the order of maximum adsorption capacity (Q_m) of dyes onto SSFV was malachite green > safranine T > methylene blue based on Langmuir model. Values of "n" obtained from Freundlich isotherm were all above 1, which indicated a potential good adsorption of dyes onto SSFV. Based on the alignment of the experimental data with the model lines in Fig. 3, together with the regression coefficient (R^2), it was clear that the adsorption data of malachite green, safranine T and methylene blue onto SSFV all fit the Langmuir and Freundlich model, but Freundlich model fit better with R^2 of 0.9861, 0.9886, and 0.9984, as compared to Langmuir model with R^2 of 0.9471, 0.9744, and 0.9809, respectively. The suitability of Freundlich model could be interpreted to mean that the adsorption of dyes took place on monolayer surface of SSFV and interacted with each other during the adsorption process.

3.3 Adsorption Thermodynamics and Evaluation of Thermodynamics Coefficients

Adsorption efficiency of three dyes malachite green, safranine T and methylene blue onto SSFV decreased



(b)

Fig. 3 Plots of Langmuir (a) and Freundlich (b) isotherms for dyes sorption onto SSFV. The dashed lines were the linearized Langmuir and Freundlich models.

Table 1 Coefficients of langmuir and Freundlich models.

Dye	Langmuir model			Freundlich model		
	Q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)(L/mg)$^{1/n}$	R^2
Malachitc green	30.77	0.1298	0.9471	1.195	3.398	0.9861
Safranine T	25.19	0.0615	0.9744	1.243	1.535	0.9886
Methylene blue	19.92	0.4419	0.9809	1.412	5.554	0.9984

with increase of adsorption temperature as shown in Fig. 4. The adsorption rates of malachite green and methylene blue decreased slower than that of safranine T with temperature increasing from 288 K to 338 K. No matter what, increase of temperature was unfavourable to the adsorption of the dyes onto SSFV.

To evaluate the adsorption thermodynamics of dyes onto the adsorbent, modified Gibbs-Helm holtz equation was used as Eq. (6).

$$\ln\frac{C_{Be}}{C_{Ae}} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (6)$$

where C_{Be} and C_{Ae} represent the equilibrium concentrations of the dye in adsorbent and solution (mg/L), $\Delta H$is adsorption enthalpy change (kJ.mol^{-1}), ΔS is adsorption entropy change (J.mol^{-1}.K^{-1}), R is the molar gas constant (8.314 J.mol^{-1}.K^{-1}), and T is absolute temperature (K) [13].

The adsorption thermodynamics model was established by plotting the value of $\ln\frac{C_{Be}}{C_{Ae}}$ vs temperature (T) to determine the values ofΔH, ΔS and R^2 as shown in Fig. 4 and Table 2. The regression coefficients (R^2) of the adsorption thermodynamics model of the dyes onto SSFV all exceeded 0.98, which indicated that the model was suitable for the dyes adsorption onto SSFV. Adsorption included physical adsorption and chemical adsorption with endothermic or exothermic phenomenon. $\Delta H$and ΔS were all negative, which indicated that the adsorption of dyes onto SSFV were spontaneous, and the SSFV's adsorption for malachite green, safranine T and methylene blue were mainly chemical adsorption [13].

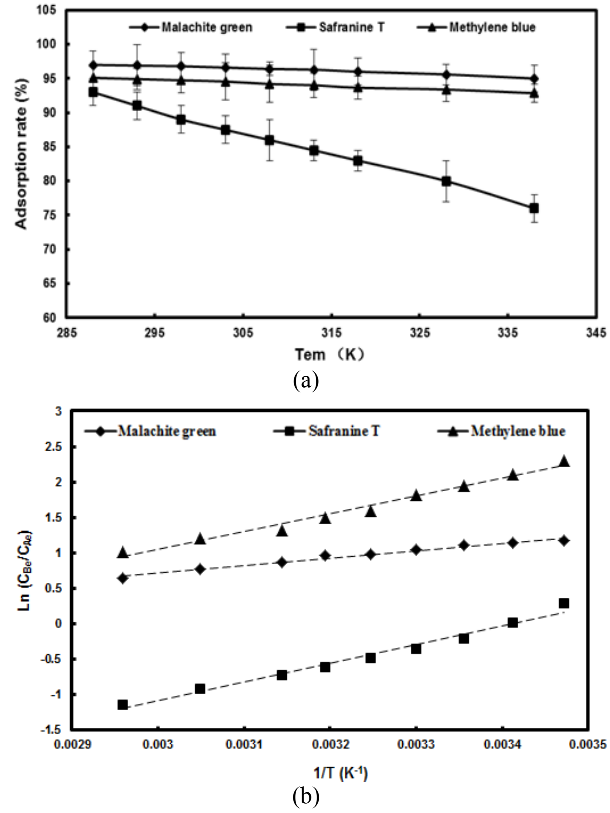


Fig. 4 Adsorption efficiencies (a) and adsorption thermodynamics (b) of malachite green, safranine T and methylene blue onto SSFV as bio-adsorbent with different temperature and at 100 mg/L of initial dyes concentration, 1g of SSFV and 6.0 of pH, The dashed lines were the linearized adsorption thermodynamics model (b)

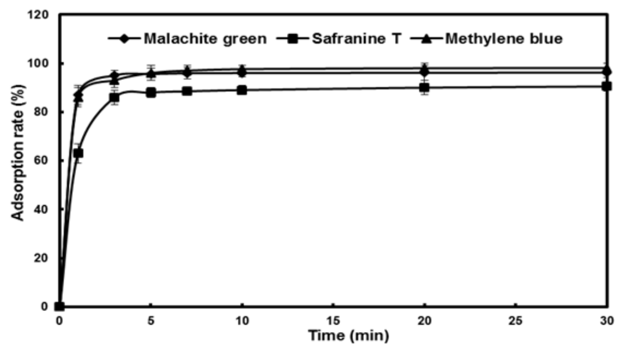


Fig. 5 Adsorption efficiencies of malachite green, safranine T and methylene blue onto SSFV as bio-adsorbent with different adsorption time at 100 mg/L of the dyes concentration, 1g of SSFV, 6.0 of pH and 303 K of temperature.

Table 2 Coefficients of adsorption thermodynamics.

Dye	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})	R^2
Malachitc green	-8.62	-19.9	0.9822
Safranine T	-21.96	-74.9	0.9806
Methylene blue	-20.98	-54.3	0.9817

3.4 Adsorption Kinetics and Evaluation of Kinetics Coefficients

Adsorption efficiency of three dyes malachite green, safranine T and methylene blue onto SSFV increased with increase of adsorption time as shown in Fig. 5. The adsorption rate of three dyes all exceeded 85% in initial three minutes, and then increased slower till to 30 minutes. Therefore, SSFV could adsorb malachite green, safranine T and methylene blue rapidly.

To evaluate the adsorption kinetics of dye onto adsorbent, the pseudo first-order (Eq. (7)) and second-order kinetics (Eq. (8)) shown below were used widely.

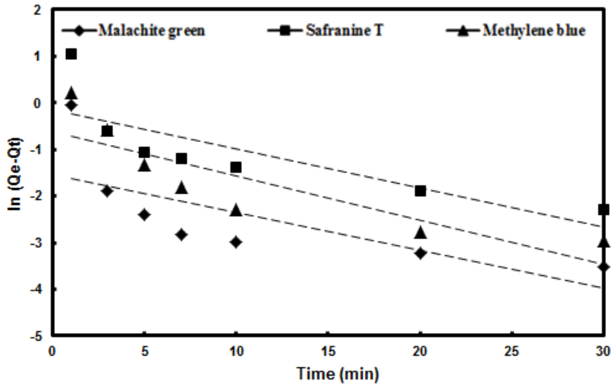
$$\ln(Qe - Qt) = \ln Qe - k_1 t \tag{7}$$

$$\frac{t}{Qt} = \frac{t}{Qe} + \frac{1}{k_2 Qe^2} \tag{8}$$

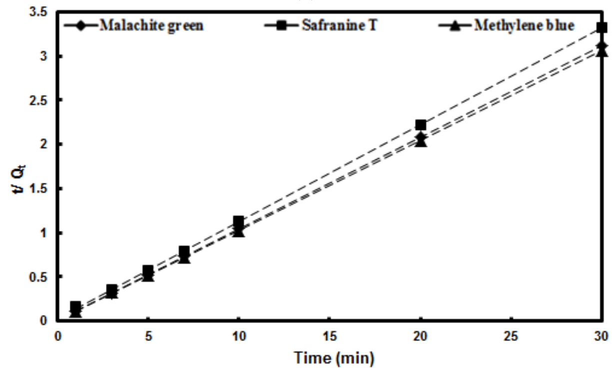
where Q_e and Q_t represent the adsorption capacities (mg/g) of SSFV at equilibrium and at a particular time t (min), respectively. The first-order and second-order kinetic rate constants are denoted by k_1 (1/min) and k_2 [(g/mg)(1/min)] [14].

The pseudo first order kinetic model was established by plotting the value of $\ln(Q_e – Q_t)$ vs time (t) to determine the values of k_1, Q_e, and R^2. However, the values of t/Q_t were plotted against time (t) in order to establish the pseudo second order kinetic model and to calculate the values of k_2, Q_e, and R^2. The regression coefficients (R^2) of the first and second order kinetic model were compared to obtain which of the models was suitable for the dyes adsorption onto SSFV.

The linear plot of t/Qtvs t as shown in Fig. 6b indicated the applicability of the second-order kinetic and good agreement with obtained experimental data. Adsorption capacities of malachite green, safranine T and methylene blue onto SSFV at equilibrium (Qe) were 9.643, 9.132 and 9.862 mg/g respectively. Regression coefficient (R^2) of second-order reaction kinetics was much better than that of first order reaction kinetics as shown in Table 3. The results indicated that the adsorption kinetics of the dyes



(a)



(b)

Fig. 6 Plots of first-order (a) and second-order (c) kinetics for dyes sorption onto SSFV. The dashed lines were the linearized first-order and second-order kinetics model.

Table 3 Coefficients of the first and second order kinetic models.

<table>
<tr><th rowspan="2">Dye</th><th colspan="3">First order kinetic model</th><th colspan="3">Second order kinetic model</th></tr>
<tr><th>Qe (mg/g)</th><th>k_1 (1/min)</th><th>R^2</th><th>Qe (mg/g)</th><th>k_2 (g/mg)(1/min)</th><th>R^2</th></tr>
<tr><td>Malachitc green</td><td>0.213</td><td>0.0814</td><td>0.533</td><td>9.643</td><td>1.792</td><td>1</td></tr>
<tr><td>Safranine T</td><td>0.862</td><td>0.0836</td><td>0.655</td><td>9.132</td><td>0.405</td><td>1</td></tr>
<tr><td>Methylene blue</td><td>0.544</td><td>0.0956</td><td>0.733</td><td>9.862</td><td>0.729</td><td>1</td></tr>
</table>

followed the second order kinetics well. However, no deviation was observed for the second-order kinetic model because the experimental value of the equilibrium adsorption capacity (Q_e) was similar to the value calculated from the second order kinetic model [12].

4. Conclusions

The results obtained in this study suggest that SSFV had the potential to be an economical and efficient bio-adsorbent for the three dyes removal from water and wastewater. The experimental data fit well with the Langmuir and Freundlich isotherm, adsorption thermodynamics, and second-order kinetics model. A filtration unit incorporating SSFV as adsorbent could be operated in a full-scale water and wastewater treatment plant for the removal of the dyes from the contaminated waters.

Acknowledgments

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