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Biosorption of methylene blue dye by chemically modified *Aspergillus japonicus* MG183814: kinetics, thermodynamic and equilibrium studies

Ramakrishnan Gnanasekaran[a], Balaji Dhandapani[b,*], Anbalagan Saravanan[c]

[a] *Department of Biotechnology, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Avadi, Chennai 600 062, India*
[b] *Department of Chemical Engineering, SSN College of Engineering, Chennai 603 110, India, Tel. +91 9443637244;*
Fax: +91 44 27469772; emails: dbalajii@yahoo.com, balajid@ssn.edu.in (Balaji Dhandapani)
[c] *Department of Biotechnology, Rajalakshmi Engineering College, Chennai 602 105, India*

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ABSTRACT

The biosorption of methylene blue (MB) dye from aqueous solutions by raw *Aspergillus japonicus* (RAJ) and sulphuric acid-treated *A. japonicus* (SMAJ) was explored to recognize the dye evacuation productivity of adsorbent. Retaining in mind the end purpose to upgrade the adsorption capacity of *A. japonicus* and enhance the application execution, surface modification of *A. japonicus* was examined in this work. The characterization studies of newly prepared biosorbent material were performed by scanning electron microscope and Fourier-transform infrared spectroscopic analysis. The influencing parameters such as initial MB dye concentration, contact time, solution pH, temperature and biosorbent dosage were examined. The optimum conditions for the maximum removal of MB dye for an initial MB dye concentration of 25 mg/L were measured as follows: pH of 7.0, adsorbent dose of 0.6 g/L for RAJ and 0.3 g/L for SMAJ, contact time of 60 min for RAJ and 30 min for SMAJ, and temperature of 30°C. From the kinetic and equilibrium studies, the results demonstrated that biosorption process was portrayed by pseudo-second order and Freundlich isotherm model. The maximum adsorption capacity (q_m) was calculated 45.78 mg/g using Langmuir equation. The results of the thermodynamic study showed that present biosorption process was exothermic and spontaneous in nature. The information from the above findings recommending that chemically modified microbial biosorbent could turn into a potential biosorbent for the removal of organic contaminants from wastewater.

Keywords: Wastewater treatment; Surface modification; *A. japonicus*, Isotherm; Kinetics

1. Introduction

Water contamination and pollution are much considerable in degradation of water bodies including rivers, lake, reservoir, aquifers, groundwater, etc. Among all water pollutants, the textile industrial effluent draws more attention in causing natural corruption in the water body environment. The textile dyeing industry uses lots of available water and thereby expels destructive organic and inorganic components without satisfied pretreatment [1]. Chemical dye mixed with the affluent is much hazardous and is a carcinogen in nature. Because of its destructive impact on the animals and other good beings, some special measures are to be demanded [2,3].

Moreover, all dyes are deficiently biodegradable or impenetrable to environmental conditions and, therefore, make huge issues in the treatment of wastewater originating from the textile dyeing industries [4,5]. For the most part, expanding natural mindfulness combined with more stringent control measures has activated different ventures to move them in looking for suitable wastewater treatment innovations [6]. Specialists have announced associations between

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* Corresponding author.

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water contamination and intense water-borne illnesses which incorporate loose bowels, typhoid, cholera, dysentery, kidney impairment and headache [7–10] and furthermore, the expanding antagonistic effects of water contamination have put more individuals in danger of cancer-causing maladies, conceivably adding to malignancy towns [11,12].

Dyes are for the most part used as a basic unrefined material in plastics, elastics, paper, cowhide, pharmaceuticals, printing, nutrition and beautifiers businesses. Around 8%–10% of the colour essence as waste was released as hued mechanical profluent in the wake of assembling forms and different modern activities. The arrival of untreated dye spouting into the water bodies causes biological issues, for instance, oxygen content weariness in water and diminished light invasion, which put the life of maritime animals and plants in the hazard. Also, the wastewater containing dyes is by and large associated with unsafe and disease making sway the general population.

Methylene blue (MB) has a place with the order of cationic shading and has a heterocyclic fragrant structure. Being the business colouration with excessive extent introduction, MB unearths its plug-ins in shading paper, hair colourant, shading cotton, wools, paper inventory masking, and so on. MB causes headache, eye maladies, breathing difficulties, extended heart rate, chest torment, expending sensation in the mouth, ailment, heaving, free guts, gastritis, extra sweating, paralysis, mental confusion, jaundice, Heinz body game plan, cyanosis, quadriplegia and tissue debasement [13,14].

Advances in physiochemical techniques such as ion exchange, coagulation, chemical oxidation, membrane separation, adsorption and electrochemical procedures have been examined to remove dye from wastewater [15–17]. Every one of these techniques has its own particular points of interest and hindrances. Subsequently, the adsorption is a standout among the best strategies for colours expulsion water. To include, adsorption gives an appealing alternative treatment, particularly if the adsorbent is cheap and promptly accessible [16–18].

Adsorption is a procedure of gathering of materials at the interphase of the two phases, viz., gas–liquid, gas–solid, liquid–liquid and liquid–solid. Adsorption technique has been a promising strategy for treating colour wastewater, attributable to its operational straightforwardness and accessibility in treating a greater part of pollutants [19–23]. Financially activated carbon is a good adsorbent material with a broad number of applications in the restorative of tainted groundwater and industrial effluents. Because activated carbon is a costly adsorbent due of its high expenses of assembling and recovery, much consideration has been centred on different normally happening adsorbents, for example, chitosan, zeolites, fly fiery debris, coal, paper mill muck and different earth minerals. In view of starting cost, less complex outline and activity, obtuseness to lethal ingredients and insignificant sludge production, biosorption have been appeared to be a successful strategy in the expulsion of contaminated dye from watery arrangements [24,25]. Generally, the low-cost adsorbents were originated from the industrial solid waste, natural materials, agricultural byproducts, biological organisms, etc., which behave as good and powerful adsorbents for the removal of heavy metal ions from the wastewater [26–28].

In this study, the interest was to appraise the general adsorption potential of fungi biomass *Aspergillus japonicus* based on MB dye adsorption experiments. These parts have different capacities, including attachment and macromolecular authoritative, particularly the fibrillar system of teichoic acids and nonpartisan polysaccharides. Adsorption on the cell divider surface is an association between the poisons and utilitarian gatherings of the phone surface, in light of physical adsorption, particle trade and complexation. The cell dividers harbouring polysaccharides (glucan, mannan), proteins and lipids show various extraordinary and effectively available adsorption focuses and in addition distinctive restricting components including hydrogen bonds, ionic or hydrophobic collaborations. Studies on the adsorption of MB dye onto the *A. japonicus* are somewhat inferior due to its low porosity, surface territory and crystallinity. As a result of these drawbacks, *A. japonicus* adsorbent material was treated with sulphuric acid which in turn will enhance the adsorbent surface properties. The raw *A. japonicus* (RAJ) and sulphuric acid-treated *A. japonicus* (SMAJ) were characterized by scanning electron microscope (SEM) and Fourier-transform infrared spectroscopic (FTIR) analysis. The influence of operational parameters, such as solution pH, initial MB dye concentration, biosorbent dosage, temperature and contact time was contemplated. The equilibrium study of the adsorption process was used to consider the adsorption mechanism of the MB dye. This considers likewise intended to check the adsorption conduct of *A. japonicus*. In correlation of every one of the strategies, biosorption generously diminishes the costs associated with capital speculation, operational and add up to treatment.

2. Materials and methods

2.1. Preparation and characterization of fungus A. japonicus

The isolated biomass – *A. japonicus* was collected and utilized for adsorption study. The collected biomass was dried in sunlight to remove the moisture content for about 24 h. The dried material was pounded as a fine powder utilizing mortar and pestle and stockpile in a plastic container. The obtained raw powder is referred as RAJ. The newly prepared RAJ was further used for surface modification process. The surface properties of RAJ were modified by treating RAJ with concentrated H_2SO_4 in the ratio of 1:2 for about 24 h. The dried out material was evacuated by washing it with refined water until the point when the pH of the supernatants stays steady (pH = 7.0). Then, the adsorbent material was allowed to dry in the hot air oven at the temperature of 80°C for about 60 min. The obtained material is referred as SMAJ. The characterization of the newly prepared biosorbent was subjected to SEM and FTIR analysis. The SEM examination can be utilized to decide the surface morphology and permeable structure of the RAJ and SMAJ. The FTIR studies reveal the presence of functional groups in the RAJ and SMAJ.

2.2. Batch sorption studies

The batch experimental study was performed for adsorption study to investigate the MB dye removal from the synthetic wastewater by using RAJ and SMAJ. This experiment was conducted in 250 mL of Erlenmeyer flask and performed in shaking incubator at 150 rpm. Batch adsorption studies were investigated by changing the influencing parameters such as solution pH, initial MB dye concentration, adsorbent dosage, temperature and contact time. In 250 mL of Erlenmeyer flask, 100 mL of different concentration (25–150 mg/L) of MB dye solution was added. The pH of the MB dye solution was maintained by utilizing either 0.1 M NaOH or 0.1 M HCl. In that, an ideal measure of biosorbent was included and kept in the temperature-controlled shaking hatchery for the predetermined time interval. On coming to the pre-decided time interim, the flasks were pulled back from the shaker and filtered using Whatman filter paper. The gathered supernatants (MB colour fixation) were investigated by using UV–visible spectrophotometer. The concentration of the MB dye in the solution was calculated by using the following formula:

$$\%\,\text{Removal of MB dye} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{1}$$

where C_o and C_e are the initial and final MB dye concentrations (mg/L) in the solution, respectively.

2.3. *Adsorption isotherm studies*

Isotherm studies were performed for various MB dye concentration (25–150 mg/L) with the adsorbent quantity of 0.6 and 0.3 g for RAJ and SMAJ, respectively, and with the pH of the solution 7.0 at 30°C temperature for around 60 and 30 min for RAJ and SMAJ, respectively, in a shaker. After the incubation period, the treated mixture was filtered, and the supernatant was collected for further investigation by the assistance of spectroscopy. Entirely, the analyses of adsorption process were triplicated, and results were expressed as an average of three values. The equilibrium adsorption limit (q_e) (mg/g) was assessed by the succeeding equation:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where V is the volume of wastewater (L), q_e is the equilibrium adsorption capacity (mg/g) and m is mass of adsorbent (g). Adsorption equilibrium data were tested with Langmuir, Freundlich, Redlich–Peterson and Toth models.

Langmuir isotherm model can be described as follows [29]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where K_L is the Langmuir constant related to the affinity of dye molecules to the adsorbent (L/mg) and q_m is the maximum monolayer adsorption capacity (mg/g).

Freundlich isotherm model can be described as follows [30]:

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F is the Freundlich constant ([mg/g] [L/mg]$^{1/n}$) used to measure the adsorption capacity and n is the Freundlich exponent which is used to measure the intensity of adsorption. The consequence of n is given as follows: $n < 1$ (chemical process); $n > 1$ (physical process); $n = 1$ (linear).

Redlich–Peterson model can be described as follows [31]:

$$q_e = \frac{K_{\text{RP}} C_e}{1 + \alpha_{\text{RP}} C_e^{\beta} RP} \tag{5}$$

where α_{RP} is the Redlich–Peterson isotherm constant $(\text{L/mg})^{1/\beta}{}_{\text{RP}}$, K_{RP} is Redlich–Peterson isotherm constant (L/g) and β_{RP} is the exponent which lies between 0 and 1. The significance of β is given by as follows: $\beta = 0$ (Freundlich adsorption isotherm model is the preferable adsorption isotherm model) and $\beta = 1$ (Langmuir adsorption isotherm model is the preferable adsorption isotherm model).

Toth isotherm model can be described as follows [32]:

$$q_e = \frac{q_{\text{mT}} C_e}{\left(\frac{1}{K_T} + C_e^{\text{mT}}\right)^{\frac{1}{\text{mT}}}} \tag{6}$$

where q_{mT} is the Toth maximum adsorption capacity (mg/g), K_T is the Toth equilibrium constant and mT is the Toth model exponent.

2.4. *Adsorption kinetic studies*

The batch adsorption kinetic studies reveal the rate of adsorption of MB dye on the solid adsorbent. Trails were performed for the constant quantity of adsorbent material in temperature-controlled vibrating shaker for variable contact time in the range of 10 to 90 min for RAJ and 5 to 45 min for SMAJ at defined condition (initial MB dye concentration = 25 mg/L; pH = 7.0; temperature = 30°C; biosorbent dosage = 0.6 g for RAJ and 0.3 g for SMAJ). On reaching the pre-determined time interval, the flasks were withdrawn from the shaker and filtered using Whatman filter paper to collect the supernatant. The collected supernatants (MB dye concentration) were analyzed by using UV–visible spectrophotometer. The adsorption capacity of the adsorbent at a time (t) was assessed by using the trailing formula:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{7}$$

where q_t is the amount of MB dye adsorbed per gram of adsorbent at a known time.

Pseudo-first-order kinetic model can be described as follows [33]:

$$q_t = q_e\left(1 - \exp\left(-k_1 t\right)\right) \tag{8}$$

where k_1 is the pseudo-first-order kinetic rate constant (1/min) and t is the time (min).

Pseudo-second-order kinetic model can be described as follows [34]:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{9}$$

where t is the time (min) and k_2 is the pseudo-second-order kinetic rate constant (g/mg.min).

Elovich kinetic model can be described as follows [35]:

$$q_t = \left(1 + \beta_E\right)\ln\left(1 + \alpha_E \beta_E t\right) \tag{10}$$

where α_E (mg/g.min) is the initial adsorption rate and β_E (g/mg) is the desorption constant related to the activation energy of chemisorption.

2.5. Thermodynamic studies

Thermodynamic studies reveal the influence of temperature on the rate of binding of adsorbent–MB dye onto the biosorbent (RAJ and SMAJ). Trails were performed for the constant quantity of adsorbent material in temperature-controlled vibrating shaker for variable incubation temperature in the range of 30°C–60°C at defined condition (initial MB dye concentration = 25 mg/L; pH = 7.0; biosorbent quantity = 0.6 g for RAJ and 0.3 g for SMAJ; contact time = 60 min for RAJ and 30 min for SMAJ). On reaching the pre-determined time interval, the flasks were withdrawn from the shaker and filtered using Whatman filter paper to collect supernatant and were analyzed by using UV–visible spectrophotometer. The binding of the dye molecules is quantified and controlled by the thermodynamic parameters, such as Gibbs free energy ($\Delta G°$, kJ mol^{-1}), enthalpy ($\Delta H°$, kJ mol^{-1}) and entropy ($\Delta S°$, kJ mol^{-1}). The thermodynamic parameters can be estimated by using the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{11}$$

$$\Delta G° = -RT \ln K_c \tag{12}$$

$$\log K_c = -\left[\frac{\Delta H°}{2.303RT}\right] + \frac{\Delta S°}{2.303R} \tag{13}$$

where K_c is the equilibrium constant, C_{Ae} is the amount of MB dye adsorbed onto the adsorbent per litre of solution (mg/L), T is the temperature and R is the universal gas constant (8.314 J/mol. K).

3. Results and discussion

3.1. Adsorbent material – characterization study

The external structure and morphology of present adsorbent material – RAJ and SMAJ – were known by SEM analysis. Generally, surface assimilation is absolutely relying upon the surface properties of adsorbent. SEM images reveal the porous network structures of RAJ and SMAJ. Figs. 1(a) and (b) show that SEM image of RAJ and SMAJ, severally at completely different magnifications of 500 x (50 µm), 2 kx (20 µm) and 10 kx (2 µm) and therefore the fast voltage of 10 kV. The SEM pictures validated that RAJ and SMAJ have littler scale porous void spaces and significant cavities. SEM analysis implied that SMAJ has an irregular surface with huge openings and macro pores compared with RAJ. These macropores and large cavities are important for dye adsorption. The dimension and state of the pores are sporadic and interrelated. The accessible pores on the SMAJ could shape the grid layer with a cross-connected system. These properties demonstrated that SMAJ has superior adsorption qualities for the removal of MB dye from industrial wastewater.

FTIR investigation can be used to decide the proximity of vital functional groups on the surface of the biosorbent [36,37]. Adsorption process depends upon the surface interaction between the biosorbent material and the adsorbate MB dye in the liquid. FTIR analysis of RAJ and SMAJ is shown in Fig. 2. The FTIR spectroscopy of the biosorbent has been investigated for the frequency in the range of 400–4,000 cm^{-1}. The intense peak at 3,613 and 3,572 cm^{-1} in the RAJ is corresponding to the presence of alcohol and hydroxyl compound group frequencies of the tertiary alcohol, OH stretch. The band vibrations at 2,992 and 2,852 cm^{-1} in RAJ relate to aliphatic group frequencies of methyl C–H symmetric stretch. The peak vibrations at 1,640, 1,459 and 1,203 cm^{-1} indicate that aromatic ring frequency of aromatic ring stretch and aromatic C–H in the plane bend. The FTIR spectrum of SMAJ shows that the strong peaks at 2,920 and 2,136 cm^{-1} correspond to aliphatic group frequencies of methyl asymmetric C–H stretch and alkyne group frequencies of the terminal alkyne. The adsorption peaks at 1,737 and 1,428 cm^{-1} relate to the presence of carbonyl group frequencies of aldehyde and carboxylate. FTIR results illustrated that MB dye can be interfaced with the aliphatic, hydroxyl, aromatic and alcoholic functional groups which are interconnected and cross-linked network present in the biosorbent [38]. These ionic groups form the covalent bond between the surface of the adsorbent material and the MB dye. The FTIR peaks show that the presence of hydroxyl, ether groups, covalent bridge and matrix formation confirms that adsorbent material (RAJ and SMAJ) has superior potential for the adsorption of MB dye from the wastewater. Hence, it can be concluded that RAJ and SMAJ had good potential for the removal of MB dye from wastewater by adsorption.

3.2. Influence of process influencing parameter–adsorption studies

3.2.1. Influence of biosorbent loading

Biosorbent charging is a significant part of the adsorption procedure. Batch adsorption study was carried out by adding the biosorbent in the range of 0.1 to 0.8 g for RAJ and 0.05 to 0.4 g for SMAJ. The batch experimental data for biosorbent loading was shown in Fig. 3. As the adsorbent loading increases from 0.1 to 0.6 g for RAJ and 0.05 to 0.3 g for SMAJ, the amount of MB dye concentration in wastewater decreases. The reason for this behaviour might be due to that

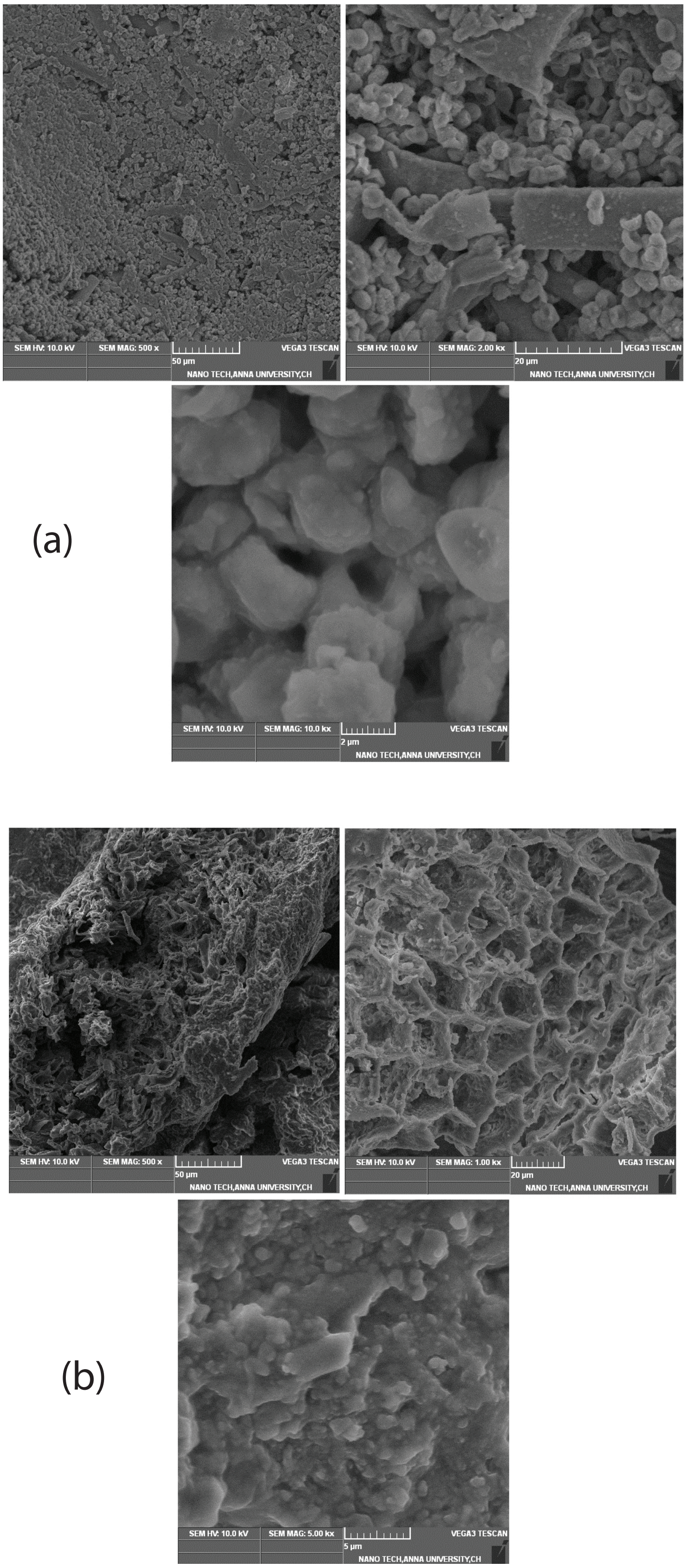

Fig. 1. (a) SEM images of RAJ and (b) SEM images of SMAJ.

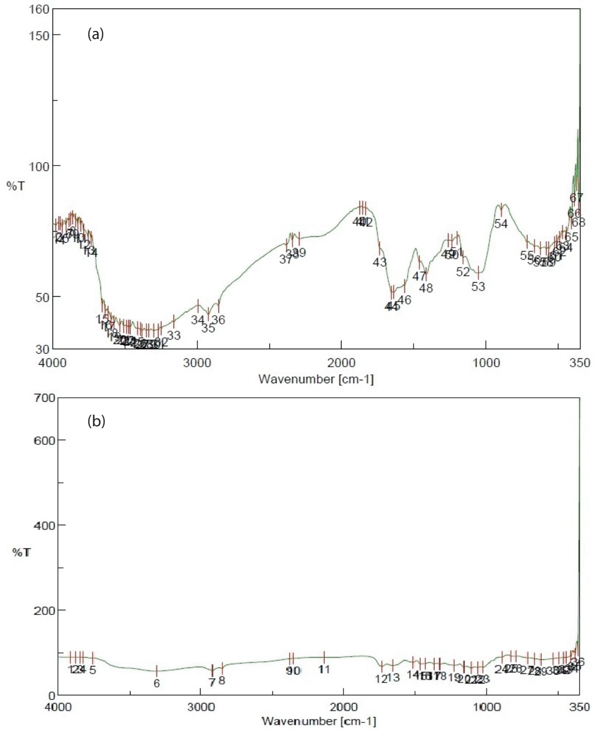

Fig. 2. FTIR images of (a) RAJ and (b) SMAJ.

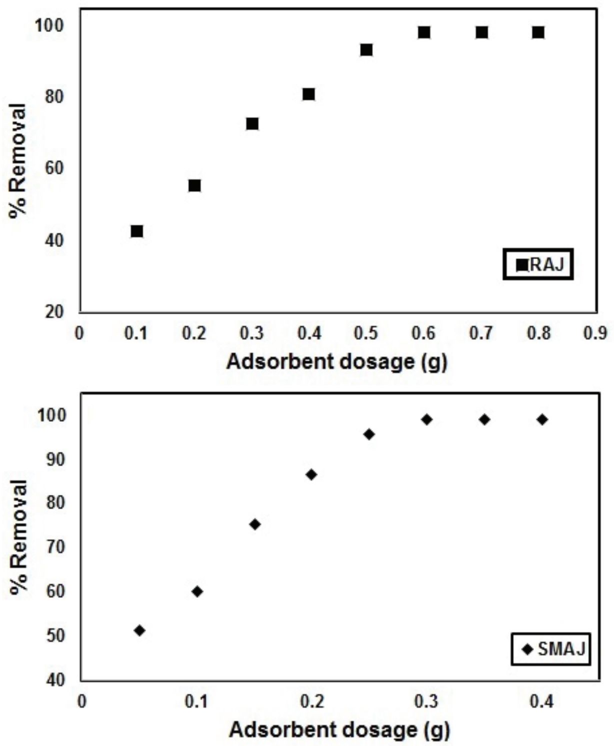

Fig. 3. Effect of adsorbent dose on removal of MB dye onto the RAJ and SMAJ (initial MB dye concentration = 25 mg/L, pH = 7.0, contact time = 60 min for RAJ and 30 min for SMAJ, temperature = 30°C and volume = 100 mL).

availability of adsorption sites is increased while increasing the dosage. The expansion in adsorption capacity was credited to bring up in the number of adsorption sites present at first. Nonetheless, on further addition, the MB dye adsorption remains genuinely steady beyond the quantity of 0.6 g for RAJ and 0.3 g for SMAJ. This is because of the moderately low equilibrium fixation, availability of adsorption sites was gradually decreased and low driving force.

3.2.2. Influence of solution pH

The influence of pH for the removal of MB dye using RAJ and SMAJ was carried out by changing the pH from 3.0 to 9.0 which was shown in Fig. 4. The pH of the adsorbate liquid is one of the essential factors which impacts the adsorption procedure. In this manner, it is essential imperative to discover the ideal pH for the removal of MB dye from the fluid arrangement. The MB dye removal was gradually increased from pH 3.0 to 7.0. The adsorption was constant at pH of 8.0 and 9.0. The adsorption of MB dye was lower at acidic pH condition which might be possibly due to electrostatic repulsion, that is, at lower pH, positively charged adsorption sites of RAJ and SMAJ tend to contend the cationic dye molecules. On increasing the pH of the acidic medium to the base, the adsorption sites of RAJ and SMAJ turn into negatively charged which may attract the opposite charge of MB dye in the liquid medium, that is, electrostatic interaction. Point of zero charge (pH_{pzc}) of the biosorbent is another parameter to clarify the impact of arrangement pH on the expulsion of MB dye by the biosorbent. pH_{pzc} of the biosorbent material was observed to be underneath 7.0 which demonstrates that the biosorbent surface procured positive charge beneath this pH esteem. At arrangement pH < pH_{pzc}, the majority of the metal species will be decidedly charged which demonstrates the expulsion of MB dye beneath pH_{pzc} esteem is a particle trade process. In the event that the arrangement pH was expanded over the pH_{pzc} of the biosorbent then the adsorption procedure was expanded till the pH estimation of 7.0 and after that there is a slight abatement in the evacuation of MB dye. After specific pH, the charge on the metal species and the biosorbent surface turns out to be adversely charged which shows that the adsorption procedure diminished essentially. For the

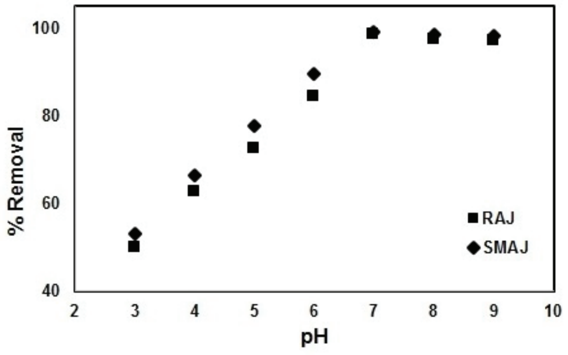

Fig. 4. Effect of pH on removal of MB dye onto the RAJ and SMAJ (initial MB dye concentration = 25 mg/L, contact time = 60 min for RAJ and 30 min for SMAJ, adsorbent dosage = 0.6 and 0.3 g for RAJ and SMAJ, temperature = 30°C and volume = 100 mL).

present adsorption framework, the ideal pH was settled as 7.0, and it was kept up to facilitate exploratory investigations.

3.2.3. Influence of initial MB dye concentration

The influence of the process parameter, initial concentration of MB dye was experimented by varying the dye concentration from 25 to 150 mg/L with solution pH of 7.0, temperature of 30°C and at an optimum adsorbent (0.6 g for RAJ and 0.3 g for SMAJ) quantity for the contact period of 60 min for RAJ and 30 min for SMAJ, respectively. Fig. 5(a) demonstrated that as the dye concentration increases from 25 to 150 mg/L, the removal of dye was declined from 98.85% to 85.23% for RAJ and 99.12% to 88.56% for SMAJ. Due to the reduction of active sites in the surface of the adsorbent material – RAJ and SMAJ – the amount of dye removal was reduced with an increase in initial dye concentration. The proportion of the measure of MB dye to the adsorbent dosage was expanded with the expansion in initial MB dye concentration. The framework is worked with a consistent adsorbent dosage of 0.6 g for RAJ and 0.3 g for SMAJ. Additionally, the (q_e) quantity was expanded along with a rising MB dye concentration. The explanation behind this conduct is that adsorption rate was higher and furthermore the dynamic locales were completely connected with the MB dye. Hence the optimum MB dye concentration is 25 mg/L for the better transfer process at the defined operational condition.

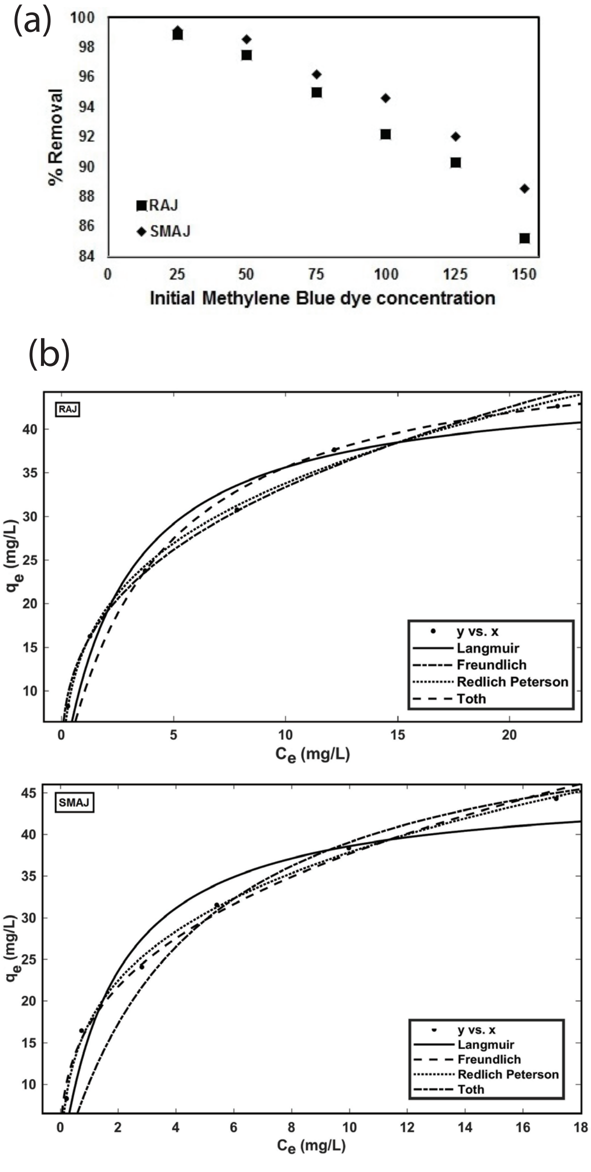

Fig. 5. (a) Effect of initial MB dye concentration on removal of MB dye onto the RAJ and SMAJ (pH = 7.0, contact time = 60 min for RAJ and 30 min for SMAJ, adsorbent dosage = 0.6 and 0.3 g for RAJ and SMAJ, temperature = 30°C and volume = 100 mL) and (b) adsorption isotherm study for the removal of MB dye onto RAJ and SMAJ.

3.2.4. Adsorption isotherm studies

Adsorption isotherm demonstrates the essential data about the point of confinement of the adsorbent in like manner, the portrayal of the adsorption methodology. Furthermore, this furnishes the data regarding the particular association linking the MB dye in the liquid medium and the adsorbate in the solid medium at balance. The adsorption isotherm contemplate was accomplished by utilizing the information from the impact of initial concentration studies of MB dye. The adsorption balance of MB dye on RAJ and SMAJ was studied with the following isotherm models: Freundlich, Langmuir, Redlich–Peterson and Toth. By plotting the graph between C_e and q_e, the equilibrium parameters, error values (sum of squared errors [SSE] and root mean square error [RMSE]) and R^2 were estimated and values are tabulated in Tables 1 and 2. The adsorption isotherm studies for the removal of MB dye onto RAJ and SMAJ were shown in Fig. 5(b). Model analysis infers that Freundlich model fits best because higher R^2 and lower RMSE and SSE compared with other isotherm models. Also, the MB dye in *A. japonicus* biosorbent adsorbs multilayer, and heterogeneous patches were accessible over the surface. The Freundlich model refers that the adsorption intensity is good at higher concentrations but worse at lower concentrations. This suggests that the heterogeneous nature of the adsorption surfaces onto the adsorbents. The highest Freundlich isotherm constant (K_F) value for MB dye is a sign of the higher adsorption capacity of the *A. japonicus*. The best applicability of a model to the experimental data was determined in terms of R^2 values. Based on n value, the quality of adsorption can be defined. For the present investigation, n esteem was observed to be greater than 1 which demonstrates the usefulness of the entire scope of dye particle fixation and profoundly good transfer processes.

3.2.5. Influence of contact time

In batch adsorption study, contact time is the significant parameter which can be used to conclude the contact time required for attaining the equilibrium condition. The significance of contact time (10–90 min for RAJ and 5–45 min for SMAJ) for the removal of MB dye is shown in Fig. 6(a). The MB dye removal increases with an increase of contact time from 10 to 60 min for RAJ and from 5 to 30 min for SMAJ. This can be clarified by the way that, at introductory phase

Table 1
Adsorption isotherm study for the removal of MB dye onto RAJ

S. No.	Isotherm model	Parameters	Correlation coefficient	Error values	
				SSE	RMSE
1	Langmuir	$K_L = 0.3497$ (L/mg) $q_m = 45.78$ (mg/g)	0.9547	38.42	3.099
2	Freundlich	$K_F = 14.85$ ([mg/g][L/mg]$^{(1/n)}$) $n = 2.848$	0.9955	3.812	1.127
3	Redlich–Peterson	$K_{RP} = 78.52$ (L/g) $\alpha_{RP} = 4.338$ (L/mg)$^{1/\beta}{}_{RP}$ $\beta_{RP} = 0.71$	0.9912	7.485	1.368
4	Toth	$K_T = 0.235$ $q_{mT} = 50.76$ (mg/g) mT = 0.758	0.9399	50.59	3.191

Table 2
Adsorption isotherm study for the removal of MB dye onto SMAJ

S. No.	Isotherm model	Parameters	Correlation coefficient	Error values	
				SSE	RMSE
1	Langmuir	$K_L = 0.5262$ (L/mg) $q_m = 48.91$ (mg/g)	0.944	51.51	3.589
2	Freundlich	$K_F = 17.1$ ([mg/g][L/mg]$^{(1/n)}$) $n = 2.919$	0.9965	3.183	1.03
3	Redlich–Peterson	$K_{RP} = 117.2$ (L/g) $\alpha_{RP} = 5.751$ (L/mg)$^{1/\beta}{}_{RP}$ $\beta_{RP} = 0.7172$	0.992	7.25	1.356
4	Toth	$K_T = 0.2164$ $q_{mT} = 12.35$ (mg/g) mT = 1.025	0.8771	113	4.754

of adsorption process more number of adsorption sites was accessible on the adsorbent surface and motivating force could overwhelm the mass exchange protection of MB dye among the fluid and the strong stages. Along these lines, the removal of MB dye was increased gradually with an expansion of retention period. In addition to that, while over the long haul (60–90 min for RAJ and 30–45 min for SMAJ) the surface of the biosorbent reached threshold and further mass transfer process is restricted and ceases.

3.2.6. Adsorption kinetic studies

Adsorption kinetics is a basic apparatus for clarifying the rates of MB dye evacuation and its component. The adsorption dynamic information from the impact of various contact times was connected to the pseudo-first arrange, pseudo-second request and Elovich models, with the outcomes, appear in Figs. 6(b) and (c). By plotting the graph between time and q_t, the kinetic model parameters, error values (SSE and RMSE) and R^2 were estimated and values are tabulated in Tables 3 and 4. The adsorption kinetic studies for the removal of MB dye onto RAJ and SMAJ are shown in Figs. 6(b) and (c). The figured equilibrium adsorption limit estimations of the pseudo-second order demonstrate were near the tentatively observed equilibrium adsorption limit esteems as contrasted and the other dynamic show. Higher correlation coefficients and low error values were observed for the pseudo-second order show as contrasted and the pseudo-first order and Elovich kinetic models. The main reason for this performance can be recognized to the lower competition for the adsorbent sites at lower concentration. At higher concentration, the competition for the biosorption active sites will be high and accordingly lower biosorption rates were obtained. The dynamic comes about demonstrated that the pseudo-second-order display gave the elite result for MB dye biosorption. In this study, the initial concentration of MB dye was relatively high, and the change of concentration during the adsorption process was found to be small. This indicates that the pseudo-first-order kinetic equation may support the surface adsorption as a rate-controlling mechanism. Generally, the Elovich kinetic model explains the chemisorption mechanism on the heterogeneous surface. However no specific mechanism was given by Elovich kinetic equation but this can be used to confirm the chemisorption

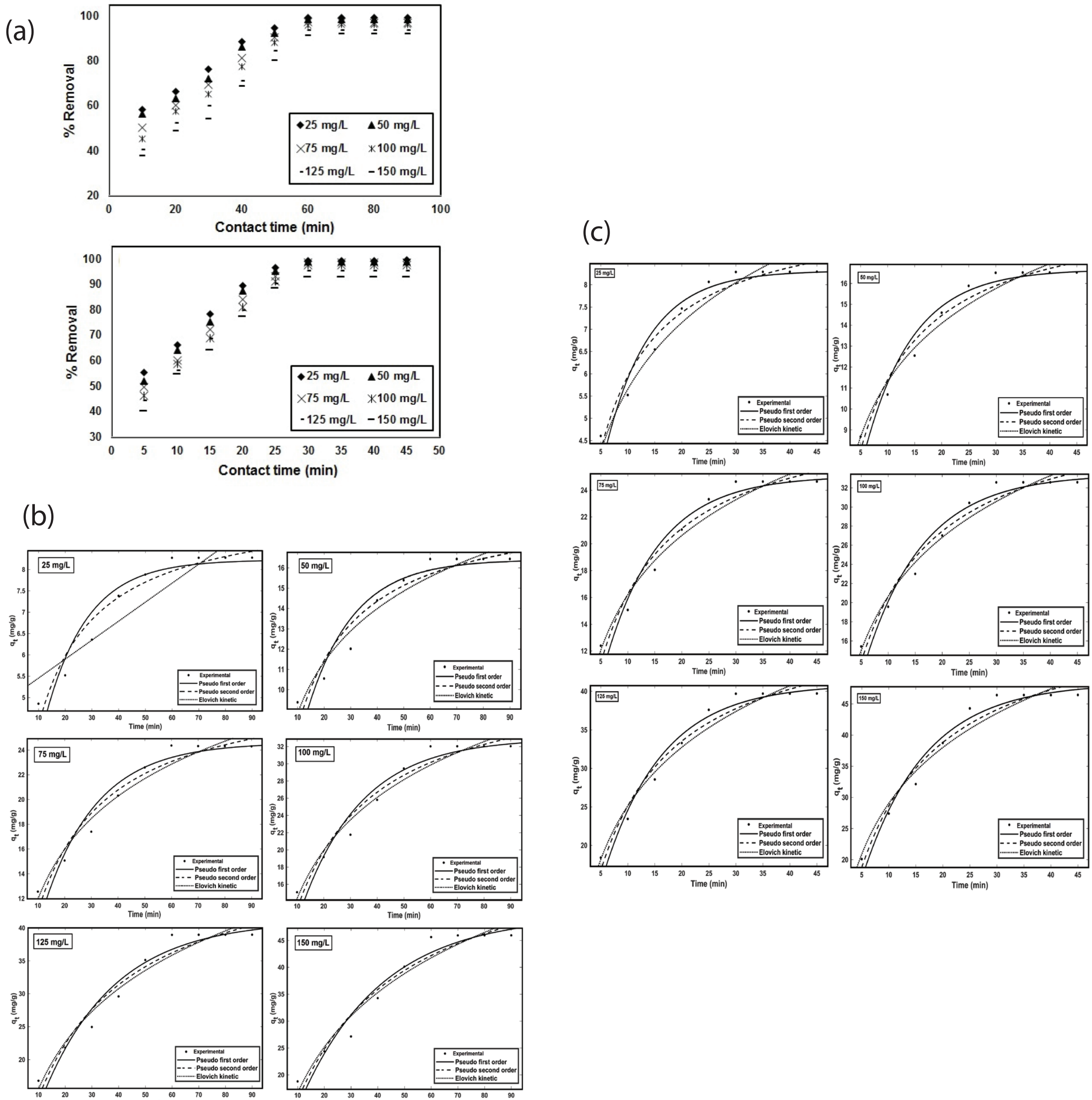

Fig. 6. (a) Effect of contact time on the removal of MB dye onto the RAJ and SMAJ (pH = 7.0, initial MB dye concentration = 25 mg/L, adsorbent dosage = 0.6 and 0.3 g for RAJ and SMAJ, temperature = 30°C and volume = 100 mL), (b) adsorption kinetic study for the removal of MB dye onto RAJ and (c) adsorption kinetic study for the removal of MB dye onto SMAJ.

mechanism. The predicted R^2 values for the present adsorption system by the Elovich kinetic model were found to be low as compared with the other two kinetic models. This indicates that the adsorption of MB dye onto the surface of the biosorbent is not due to chemisorption mechanism.

3.2.7. Influence of temperature

The influence of the process variable temperature for the abstraction of MB dye onto RAJ and SMAJ was carried out at different temperature in the limit of 30°C–60°C and the outcomes are presented in Fig. 7(a). The experimental analysis reveals that the removal percentage of MB dye onto RAJ and SMAJ was diminished with a rise in temperature to 60°C from 30°C. Temperature is specifically identified with the dynamic vitality of the dye molecules in the fluid arrangement. Temperature raise physically reduces the adsorption capacity of the biosorbent; this may be perhaps because of the debilitating of the forces of adsorption linking the dye molecules and the biosorbent material. From the experimental trials, it can be concluded that the dye mass transfer was exothermic, and the optimum temperature for

Table 3
Adsorption kinetic study for the removal of MB dye onto RAJ

Kinetic model	Parameters	MB dye concentration (mg/L)					
		25	50	75	100	125	150
Pseudo-first order	k_1 (min^{-1})	0.0635	0.057	0.0503	0.044	0.037	0.0328
	q_e, cal (mg/g)	8.222	16.4	24.59	32.94	41.1	49.65
	R^2	0.8812	0.8717	0.98	0.9361	0.9413	0.9397
	SSE	1.68	8.053	4.49	21.63	34.82	55.27
	RMSE	0.4899	1.073	2.53	1.758	2.23	2.81
Pseudo-second order	k_2 (g/mg/min)	0.0084	0.0037	0.0019	0.0011	0.0007	0.0004
	q_e, cal (mg/g)	9.543	19.27	29.6	40.69	52.46	65.06
	q_e, exp (mg/g)	9.023	18.569	28.56	38.256	49.52	60.024
	R^2	0.96	0.9261	0.9489	0.9543	0.951	0.9459
	SSE	1.25	2.635	4.42	10.46	20.04	39.62
	RMSE	1.34	0.137	1.097	1.086	1.037	2.062
Elovich kinetic	α_E mg/(g.min)	0.09	1.148	0.2675	0.099	0.0417	0.022
	β_E (g/mg)	3.49	0.7208	1.883	3.279	4.983	6.844
	R^2	0.93	0.9031	0.9264	0.9381	0.9439	0.9389
	SSE	2.83	3.573	7.195	14.18	27.32	46.81
	RMSE	2.01	0.7145	2.014	1.423	1.976	2.586

Table 4
Adsorption kinetic study for the removal of MB dye onto SMAJ

Kinetic model	Parameters	MB dye concentration (mg/L)					
		25	50	75	100	125	150
Pseudo-first order	k_1 (min^{-1})	0.125	0.1122	0.1006	0.0922	0.0917	0.08633
	q_e, cal (mg/g)	8.311	16.66	25.05	33.4	40.88	48.32
	R^2	0.9335	0.9428	0.9416	0.9495	0.9602	0.9665
	SSE	1.031	4.001	10.3	17.18	20.86	26.39
	RMSE	0.3839	0.756	1.213	1.566	1.726	1.942
Pseudo-second order	k_2 (g/mg/min)	0.016	0.0068	0.0036	0.0024	0.0019	0.00148
	q_e, cal (mg/g)	9.72	19.79	30.28	41.02	50.4	60.42
	q_e, exp (mg/g)	9.02	18.52	28.23	39.63	48.26	58.62
	R^2	0.9611	0.9638	0.9596	0.9632	0.9664	0.972
	SSE	0.6026	2.531	6.125	12.52	17.59	26.48
	RMSE	0.2934	0.513	1.009	1.037	1.585	1.745
Elovich kinetic	α_E mg/(g.min)	3.201	1.622	0.4841	0.2246	0.1628	0.15
	β_E (g/mg)	0.0003	0.8341	1.979	3.241	4.263	5.236
	R^2	0.9291	0.955	0.9465	0.9508	0.9583	0.9541
	SSE	1.099	3.147	7.672	13.33	21.83	36.15
	RMSE	0.3962	0.6705	2.047	1.38	1.766	2.126

the highest elimination of MB dye onto RAJ and SMAJ was observed to be 30°C.

3.2.8. Thermodynamic studies

Using Eqs. (11) and (12), thermodynamic parameter, Gibbs free energy change ($\Delta G°$) can be evaluated. As shown in Fig. 7(b), the graph was plotted between log K_c vs. $1/T$, from the slope and intercept enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were ascertained. The calculated thermodynamic parameters for the phase transfer of MB dye on the RAJ and SMAJ are tabulated in Table 4. Experimental trails show that the Gibbs free energy ($\Delta G°$) was raised with increase in temperature, showing the achievability of the adsorption of MB dye onto the biosorbent. The diminishing in $\Delta G°$ esteems by expanding the temperature to 333 K from 303 substantiates the physical idea of adsorption. The estimation of change in enthalpy ($\Delta H°$) demonstrated that the adsorption of MB dye onto

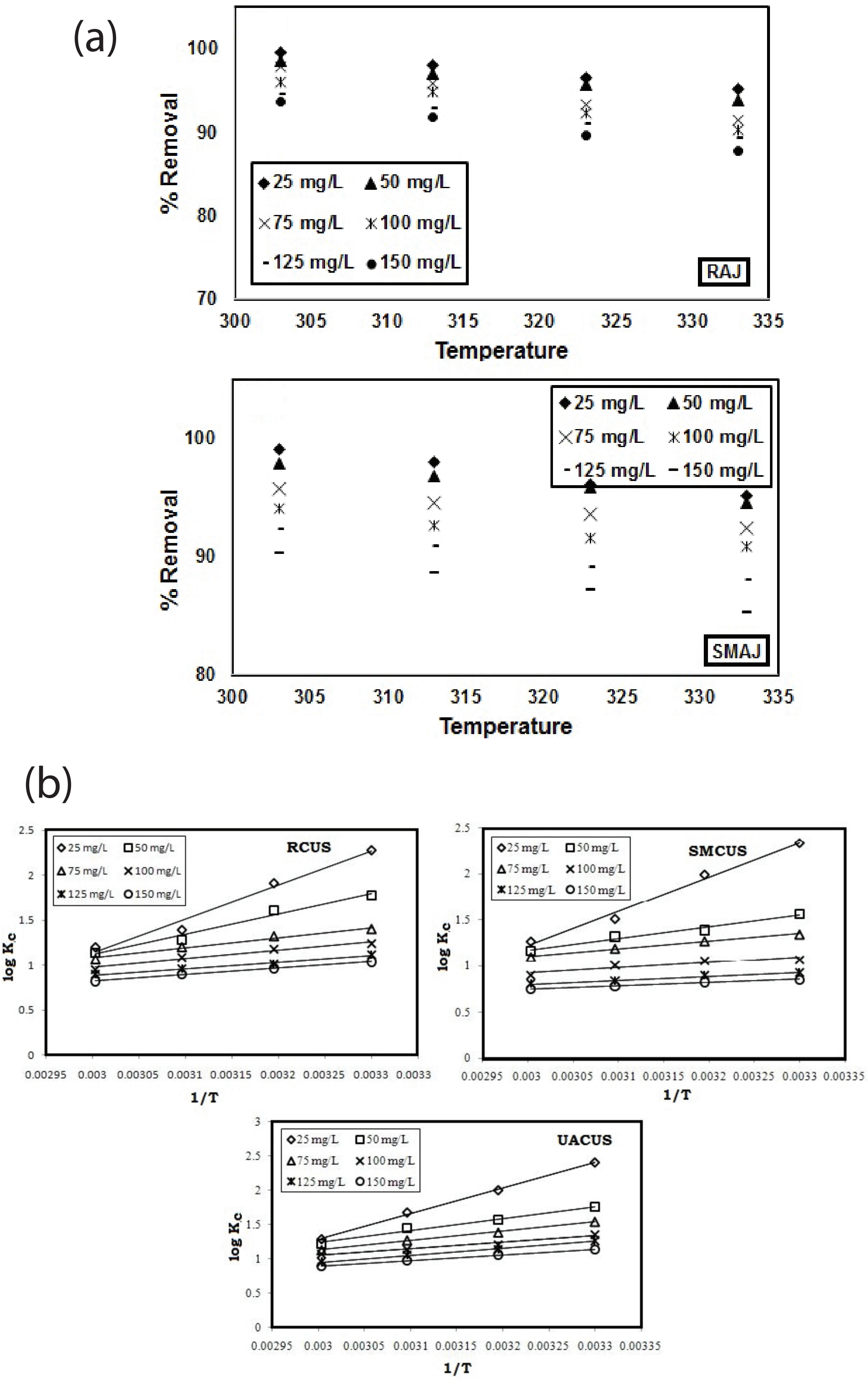

Fig. 7. (a) Effect of temperature on the removal of MB dye onto the RAJ and SMAJ (pH = 7.0, initial MB dye concentration = 25 mg/L, contact time = 60 min for RAJ and 30 min for SMAJ, adsorbent dosage = 0.6 g for RAJ and 0.3 g for SMAJ and volume = 100 mL) and (b) thermodynamic studies.

Table 5
Adsorption thermodynamic study for the removal of MB dye onto RAJ and SMAJ

			Concentration of MB dye (mg/L)					
			25	50	75	100	125	150
RAJ	ΔH° (KJ/mol)		–7.905	–4.814	–4.653	–3.094	–2.216	–2.245
	ΔS° (J/mol/K)		–20.95	–11.92	–11.6	–6.96	–4.43	–4.66
	ΔG° (KJ/mol)	30°C	–13.66	–10.65	–9.58	–8.04	–7.15	–6.81
		40°C	–10.17	–9.16	–8.20	–7.58	–6.68	–6.28
		50°C	–8.97	–8.32	–7.09	–6.70	–6.22	–5.79
		60°C	–8.23	–7.55	–6.55	–6.19	–5.89	–5.47
SMAJ	ΔH° (KJ/mol)		–5.906	–3.071	–1.906	–1.426	–1.333	–1.315
	ΔS° (J/mol/K)		–14.87	–6.319	–3.157	–2.92	–2.503	–2.246
	ΔG° (KJ/mol)	30°C	–11.915	–9.612	–7.814	–6.942	–6.269	–5.611
		40°C	–10.11	–8.916	–7.428	–6.588	–5.978	–5.335
		50°C	–8.59	–8.441	–7.206	–6.395	–5.648	–5.132
		60°C	–8.22	–7.917	–6.896	–6.365	–5.519	–4.853

Table 6
Comparison of monolayer adsorption capacity of RAJ and SMAJ for the removal of MB dye with other adsorbents

S. No.	Adsorbents	q_m (mg/g)	References
1	Fe_3O_4–TSC nanocomposite	435	[38]
2	Pine nut shell modified	175.43	[39]
3	Brown macroalga	95.45	[40]
4	Raw Algerian kaolin	52.76	[41]
5	SMAJ	48.91	This study
6	Luffa cylindrical fibres	47	[42]
7	RAJ	45.78	This study
8	Activated lignin–chitosan extruded	36.25	[43]
9	Raw mango seed	25.36	[44]
10	Natural clay	22.2	[45]
11	Zeolites from kaolin	11.13	[46]
12	Raw beech sawdust	9.78	[47]
13	Cashew nut shell	5.184	[48]
14	Apricot stones-AC	4.11	[49]
15	Walnut shell-AC	3.53	[50]
16	Fine grinded wheat straw	2.23	[51]

the RAJ and SMAJ was of exothermic in nature. Similarly, the change in entropy (ΔS°) infers that the phase transfer of MB dye on the RAJ and SMAJ was enthalpy driven. Hence physisorption occurs through the electrostatic connection between MB dye and biosorbent. This cooperation is attributed to the utilitarian gatherings on the outward of the RAJ and SMAJ. The decided thermodynamic parameters affirmed that the RAJ and SMAJ have more productivity on the expulsion of MB dye from the watery arrangement.

3.3. Comparison of monolayer adsorption study

Thermodynamic parameters for Langmuir monolayer adsorption of MB dye from wastewater by RAJ and SMAJ for different initial dye concentration are shown in Table 5. The analysis shows that SMAJ has superior adsorption capacity than RAJ due to the presence of macropores and huge inter-connected cavities.

4. Conclusion

The fundamental goal of this work was to contemplate the possibility of enhancing the biosorption of MB dye by dead fungal biomass, *A. japonicus*. The characterization studies, such as FTIR and SEM, infer that RAJ and SMAJ have an exceptional capacity for MB dye evacuation. Batch adsorption studies were carried out using various factors influencing parameters. The optimum conditions for the maximum removal of MB dye for an initial MB dye concentration of 25 mg/L were measured as follows: pH of 7.0, adsorbent dose of 0.6 g/L for RAJ and 0.3 g/L for SMAJ, contact time of 60 min for RAJ and 30 min for SMAJ, and temperature of 30°C. Experimental studies reveal that the adsorption of MB dye on biosorbent fitted well with Freundlich isotherm amid correlation coefficient of 0.9955 for RAJ and 0.9965 for SMAJ. The maximum adsorption capacity (q_m) was calculated 45.78 mg/g using Langmuir equation. The kinetic analysis portrays that adsorption kinetics follows pseudo-second order with higher regression coefficient on contrast with different models, and the calculated adsorption limit ($q_{e,\,\mathrm{cal}}$) was near the experimental adsorption limit ($q_{e,\,\mathrm{exp}}$). The thermodynamic parameters assessment demonstrated that adsorption was possible, unconstrained and exothermic. Accordingly, the non-contagious biomass *A. japonicus* could be used as a non-traditional and savvy adsorbent for the expulsion of MB dye from both the watery arrangements and saline waters.

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