



Deep insights into kinetics, optimization and thermodynamic estimates of methylene blue adsorption from aqueous solution onto coffee husk (Coffea arabica) activated carbon

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ABSTRACT

In the current study, an attempt was made to synthesize coffee husk (CH) activated carbon by chemical modification approach (sulphuric acid-activated CH (SACH) activated carbon) and was used as a valuable and economical adsorbent for plant dye remediation of Methylene blue (MB) dye. Batch mode trials were carried out by carefully varying the batch experimental variables: SACH activated carbon (SACH AC) dosage, pH, initial dye concentration, temperature, and contact time. The optimum equilibrium time for adsorption by SACH activated carbon was 60 min, and the maximum adsorption took place at 30 °C. Morphological and elemental composition, crystallinity behaviour, functional groups, and thermal stability were examined using SEM with EDX, XRD, FTIR, BET, TGA, and DTA and these tests showed successful production of activated carbon. The outcomes showed that chemical activation enhanced the number of pores and roughness which possibly maximized the adsorptive potential of coffee husk. The Box-Benken design (BBD) was used to optimize the MB dye adsorption studies and 99.48% MB dye removed at SACH AC dosage of 4.83 g/L at 30 °C for 60 min and pH 8.12, and the maximum adsorption was yielded for sulphuric acid-activated coffee husk carbon carbon with 88.1 mg/g maximum MB adsorption capacity. Langmuir-Freundlich model deliberately provided a better fit to the equilibrium data. The SACH AC-MB dye system kinetics showed a high goodness-of-fit with pseudo second order model, compared to other studied models. Change in Gibbs's free energy (ΔG°) of the system indicated spontaneity whereas low entropy value (ΔS°) suggested that the removal of MB dye on the SACH activated carbon was an enthalpy-driven process. The exothermic nature of the sorption cycle was affirmed by the negative enthalpy value (ΔH°). The adsorptive-desorptive studies reveal that SACH AC could be restored with the maximum adsorption efficiency being conserved after the fifth cycles. Overall, the outcomes revealed that sulphuric acid-activated coffee husk activated carbon (SACH AC) can be used as prompt alternative for low-cost sorbent for treating dye-laden synthetic wastewaters.

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1. Introduction

Dyes are massively exploited to grant color to the substrates in plants, textiles, paint, leather, paper, printing, pharmaceutical, cosmetic, rubber, leather, pulp and paper, and food industries (Cheruiyot et al., 2019). Synthetic dyes requirement of enterprises is expanding each day. Polluted wastewater with dyes affects living organisms directly and is a severe environmental problem (Kopsidas and Politi, 2016). The endurance of dyes in characteristic channel can motive severe threat to the aquatic system by means of growing COD, toxicity, and via hindering photosynthesis process by step downlight infiltration. Additionally, a few dyes contact with Methylene blue (MB) may cause wounds to individuals and fauna through inhalation (quick or troublesome breathing), and also can cause eye burns, sickness, vomiting, intellectual confusion, and others (Rattan et al., 2015).

Crystal violet and methylene blue (MB) are cationic dyes with numerous applications in medical science, biology, chemistry, and dyeing industries, and they are highly poisonous. MB is extensively used as stained paper dyeing, silk material, bamboo, hemp, and wood coloring in addition to usage a chemical agent in dyeing and printing companies. Methylene blue (MB) is also an essential organic dye broadly utilized in pesticide, dyeing fabric, coating for paper stock and printing. Because of its aromatic ring, MB is particularly poisonous and arduous, hence, before discharging, MB must be removed from wastewater (Huang et al., 2018). Different methods are used for dye removal from an aqueous solution like coagulation, membrane separation, chemical oxidation, electrochemical process, and adsorption techniques. However, the adsorption process using activated carbons and biochars was perceived to be both a promising and a financially low adsorbent and eliminate colors from industrial wastewater (Samuel PN et al., 2020). Recently, adsorption has been emphatically suggested as a financially practical feasible innovation for the treatment of wastewater stream (Pietrzyk et al., 2023). Biowastes containing cellulose, lignin, and hemicelluloses have a great structure and physical characteristics for color adsorption, and usually they require low-cost processes to be converted to useful materials.

Some of the normal sorbents have been produced from cork wood bark, rice husk (Chowdhury et al., 2013), castor seed shell (Khan et al., 2017), and coconut husk (Nascimento et al., 2022). Coffee waste coffee husk is classified as an agricultural by-product. Utilizing low-cost adsorbents originated from agricultural waste is enticing since it diminishes the expenses of disposing agricultural waste. In aqueous solutions, coffee residues have been used as an adsorbent to remove natural and inorganic compounds (M et al., 2018). Chemical modifications to the material can enhance its binding sites, improve its ion-exchange properties, and facilitate the adsorption of metals (Abdulhameed et al., 2020; Khan et al., 2018; Jawad et al., 2018a, 2020c, 2021b; Uddin et al., 2023). In the pursuit of raising the efficiency of bio-adsorbents for adsorption of dyes in aquatic conditions, some chemical modifications, for example acid or thermal treatment, have recently been proposed to improve their adsorption capacity (Pietrzyk et al., 2023). For instance, spent coffee grains adsorbent were treated with a citric acid solution to increase the number of carboxylic groups enhance their metal adsorption capacity (Takam et al., 2017). Studies show that the usage of urban waste like coffee husk has recently increased extensively in numerous applications because of their cellulose and lignin composition and significant contents of alcohol, aldehyde, phenolic, carboxylic, and other functional groups, which are favorable in adsorbing dye molecules in solution. Simple traditional pyrolysis technologies can change lignin into hard support which has a greater surface area (Ma et al., 2020).

Coffee Husk (*Coffea arabica*; CH) was exploited as a raw material for producing activated carbon. To the best of our knowledge, this type of husk is a low-cost agricultural waste and its disposal creates a major environmental stress, as there is no profitable use for it. A common method is to incinerate coffee husk, but it creates a major problem, such

as excessive emissions, fouling, and agglomeration. This is due to significant amount of volatile organic matter present in the husks and its low melting point. Sulphuric acid (H_2SO_4) serves as a super oxidizing agent that is used as a low-cost chemical activator for the preparation of carbonaceous adsorbents from various ligno-cellulosic materials such as watermelon (Jawad et al., 2021a). Among the different types of chemical activation precursors, sulphuric acid is commonly used for the synthesis of carbon adsorbents from cellulosic parts of plant materials (Jawad et al., 2016), and it can increase the surface of biomass (Jawad et al., 2019a, 2019b, 2020a). The current study aims to explore the use of sulphuric acid-activated coffee husk carbon (SACH AC) for the adsorption of MB dye. Process variables such as SACH AC dose, pH initial, initial dye concentration, time of contact, and influence of temperature in the batch process were optimized, using response surface methodology (RSM) by Box-Behnken experimental design (BBD) to obtain highest % removal of dye by SACH AC. The MB adsorption for SACH AC was correlated with the sorption capacities, and adsorption mechanism was scrutinized, using thermodynamic studies, sorption isotherms, and kinetic modeling. The reusability of activated carbon usage after the desorption experiments was determined and the results were presented.

2. Materials and methods

2.1. SACH AC preparation

Rice husk powder was treated with concentrated H_2SO_4 (85%) in a proportion by weight, agitating mechanically for 24 h. Then, the mixture was put in a muffle furnace and heated to 450 °C for 60 min (Zhang et al., 2018). To remove the remained acid, twofold distilled water was used to wash the dried-out coffee husk powder till reaching a constant pH in the supernatants. Finally, sulphuric acid-activated coffee husk carbon (SACH AC) was collected, sieved and reduced to a particle size of 0.354 mm at 80 °C for 3 h. The produced SACH AC was used for the effective removal of methylene blue dye from aqueous solutions in batch mode. As a result of this acquisition, a stable adsorbent has been acquired. The adsorbent is stored in a container and used in adsorption studies.

2.2. Methylene blue dye solutions preparation

Methylene blue is a chloride salt of a dye ($C_{16}H_{18}N_3SCL_3 \cdot 3H_2O$; CI 52015; 373.9 kg/kmol, $\lambda_{max} = 664$ nm) and was provided by E. Merck (India). To prepare the stock solution, MB dye powder (500 mg/L) was dissolved in double distilled water. The practical standards of varied desirable concentrations were prepared by dissolving appropriate stock solution into the double distilled water (100–500 mg/L). By using aliquots of NaOH or HCl solutions, the initial pH of each working solution was adjusted to the required value.

2.3. Characterization of coffee-husk

The BET technique was used to calculate the surface area of coffee husk (CH) after N_2 was adsorbed at 77.15 K (Tristar II; M/s Micrometrics, Norcross, USA, GA) and released at 423 K after 1 h in a N_2 environment. SEM technique was used to collect the morphological quality features (Khalesi et al., 2022), for both bare CH and SACH AC using a Zeiss instrument, Jena, Sigma, Germany. To comprehend the fundamental arrangement of the acquired sorbent, an EDX (Zeiss, Germany, Sigma) investigation was conducted. The various functional groups contained in the adsorbent were examined using an FT-IR (PerkinElmer FTIR 100566, UK) spectrophotometer. Using an UV (Shimadzu, Japan) spectrophotometer the solution MB dye concentration was measured, the calibration plot was created by determining the absorbance of varying ranges of MB dyestuff at $\lambda_{max} = 664$ nm; TGA (Wittelsbacherstr 42, 95,100 Selb, Germany, Netzsch, STA449F3A00 Jupiter) was used to study the properties of the activated carbon, like

binding wetness and heat deterioration with respect to temperature. In platinum crucibles, 10 mg of the measured CS adsorbent sample were stored. The material was then heated steadily under a 40 mL/min N₂ flow at 10 °C/min to 600 °C.

2.4. Batch adsorption

The various factors of batch adsorption tests were examined, including adsorbent dose, solution pH, starting MB dye concentration, temperature, and time. Each test involved adding precisely weighed SACH AC to 100 mL of methylene blue, mixing for 10–90 min at 80 rpm constant agitation, then centrifuging the adsorption mixture. The MB concentrations were determined from the absorbance at its specific wavelengths of 664 nm utilizing a UV visible spectrophotometer, the samples were analyzed, and (Shimadzu, Japan). Three directions were given to the experiments, and the values' average was taken. The underlying mass balance relationship was applied to the experimental measurements to determine the amount of MB dye evacuation. (Eq. (1)):

Removal percentage:

$$\% \text{ Removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

In which C_o and C_e are the initial (mg/L) and equilibrium (mg/L) MB dye concentration.

2.5. Batch equilibrium experiments

Batch equilibrium investigations were performed by mixing 0.5 g of SACH AC to every conical flask containing a 100 mL solution of Methylene blue dye with a range of concentrations (100–500 mg/L) and in a constant agitation at 80 rpm for 60 min. The results of experiments were averaged after being directed three times. Using the following formula, the MB dye removed by SACH AC (q_e) was computed using (Eq. (2)).

Sorption capacity:

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

Where m indicates the weight of SACH AC (g), and V is the solution volume (L).

2.6. Equilibrium experiments

The four fundamental methods that are used for describing the adsorption characteristics of SACH AC are: testing the adsorption equilibrium for MB dye are: Langmuir (2002), Freundlich (1907), Langmuir-Freundlich, and the Sips model (Sips, 1948). With MATLAB R2009a software, non-linear regression method was conducted to compute various parameters, and error data. Analysing the equilibrium curves, the best isotherm fit was found.

The Langmuir model is given as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

The maximal monolayer adsorption capacity is denoted by q_m, while K_L denotes Langmuir constant, which is associated with the affinities of MB dye (L/mg). Eq. (4) represents the Freundlich model.

$$q_e = K_F C_e^{1/n} \quad (4)$$

The Value of n is utilized to evaluate adsorption nature, while K_F signifies the Freundlich constant ((mg/g) (L/mg)^{1/n}). Three outcomes for n are demonstrated: n > 1 (chemical); n = 1 (linear operation; and n < 1 (physical). Langmuir- Freundlich model is given below:

$$q_e = \frac{q_{mLF} (K_{LF} C_e)^{m_{LF}}}{1 + (K_{LF} C_e)^{m_{LF}}} \quad (5)$$

where q_e stands for at equilibrium the amount of adsorbed material (mgg⁻¹), C_e for the concentration of the dye at the equilibrium point (mgL⁻¹), q_{mLF} represents the Langmuir-Freundlich adsorption capacity (mgg⁻¹), m_{LF} for the heterogeneity parameter, which ranges from 0 to 1 and K_{LF} for the equilibrium constant ascribed to the heterogeneous sorbent. Sips model is given as:

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + \alpha_S C_e^{1/\beta_S}} \quad (6)$$

Where β_S for the Sips model exponent and α_S for the Sips model constant, and α_S for the Sips isotherm constant. The result is 1 in the case of homogeneous binding sites; the result >1 as in the case of heterogeneous adsorption systems.

2.7. Kinetic studies

Adsorption experiments related to kinetics were performed at 30 °C using mixtures of dye solution with varying starting doses (100–500 mg/L) as well as SACH AC dosage (0.5 g) in 250 mL conical flasks. At predefined intervals, samples were instantly taken & filtered from mixture while the mixture was continuously shaken. The filtrate solution's remaining MB dye percentage was examined. The average of outcomes from three studies was calculated. The following equation was used to compute Lagergren, About the theory of so-called adsorption of soluble substances, Kungl. Svens. Vetensk. Handl., 24 (1898) 1–3, the MB dye removal during time t:

$$\ln \left(\frac{C_o}{C_t} - \frac{V}{m} \right) = -K_1 t \quad (7)$$

where C_t is the MB dye concentration in the solution at time period t (mg/L) and q_t is desorption capacity of SACH AC at any time t (mg/g).

The adsorption process was explained using the kinetic data collected using the pseudo-first order, pseudo-second order, and Elovich models. Following is a list of the kinetic models:

Pseudo-first order model:

$$q_t = q_e [1 - \exp(-K_1 t)] \quad (8)$$

Pseudo-second-order model is given as

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (9)$$

Elovich model is given by:

$$q_t = (1 + \beta_E) \ln(1 + \alpha_E \beta_E t) \quad (10)$$

Where k₁ is the pseudo-first-order kinetic rate constant (1/min), α_E is the initial rate of adsorption (mg/(g min)), β_E (g/mg) is the desorption constant and k₂ is the pseudo-second-order rate constant (g/mg min).

2.8. Thermodynamics approach

Using thermodynamic variables like enthalpy (ΔH⁰), Gibbs free energy (ΔG⁰), and entropy (ΔS⁰), the sorption mechanism was further elucidated. The following equations can be used for thermodynamic calculations (Lima et al., 2019; Peiravi-Rivash et al., 2023; Rahmani-Sani et al., 2020).

$$K_{eq} = \frac{a_{\text{Adsorbate}} a_{\text{Adsorbent},e}}{a_{\text{Adsorbent},e} \times a_{\text{Adsorbate},e}} \quad (11)$$

$$\Delta G^\circ = -RT \ln K_{eq} \quad (12)$$

Table 1

Level selected for RSM-BBD design.

Factor	Name	-1	0	+1
X ₁	SACH AC dosage (g/L)	4	5	6
X ₂	Temperature (°C)	25	30	35
X ₃	Time (min)	50	60	70
X ₄	pH	7	8	9

$$\ln K_{eq} = -\frac{\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (13)$$

where the thermodynamic equilibrium constant (K_{eq}) can be computed from the isothermal studies (Naseri et al., 2023; Peiravi-Rivash et al., 2023), ΔG° (kJ/mol) is the change in Gibbs energy of the processes, R (8.314 J/mol.K) is the universal gas constant, T (in Kelvin) is the temperature of aqueous phase, ΔH° (kJ/mol) is the enthalpy change, and ΔS° (J/mol.K) is the entropy change. The K_{eq} values in various temperatures can be calculated from isothermal results (Hu et al., 2023).

2.9. Optimization study

In order to establish the optimum parameters for the dye removal by SACH AC, Box-Behnken designs (BBD) were used to build a statistical experiment for response surface methodology (RSM). There were three level and four variables in the experiment. From the best adsorption results obtained in one-variable-at-a-time experiments the limits of the variables were fixed for the RSM-BBD design (Table 1). The RSM-BBD design was used to make the most of how different variables like time, temperature, adsorbent dosage and pH affected the dye removal % with the help of RSM-BBD, a set of 29 experiments with 5 main points were designed.

3. Results and discussion

3.1. Characterization of coffee-husk

The Surface morphology and characteristics of prepared samples are primarily studied using SEM. In the present study, the surface

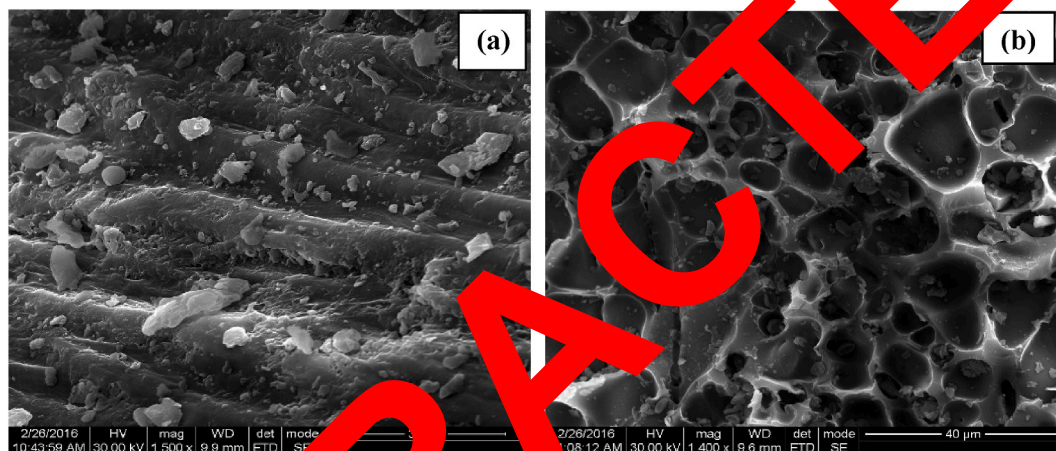


Fig. 1. Field emission scanning electron microscopy (SEM) images of (a) Raw coffee husk (CH) and (b) Sulphuric acid activated coffee husk (SACH AC).

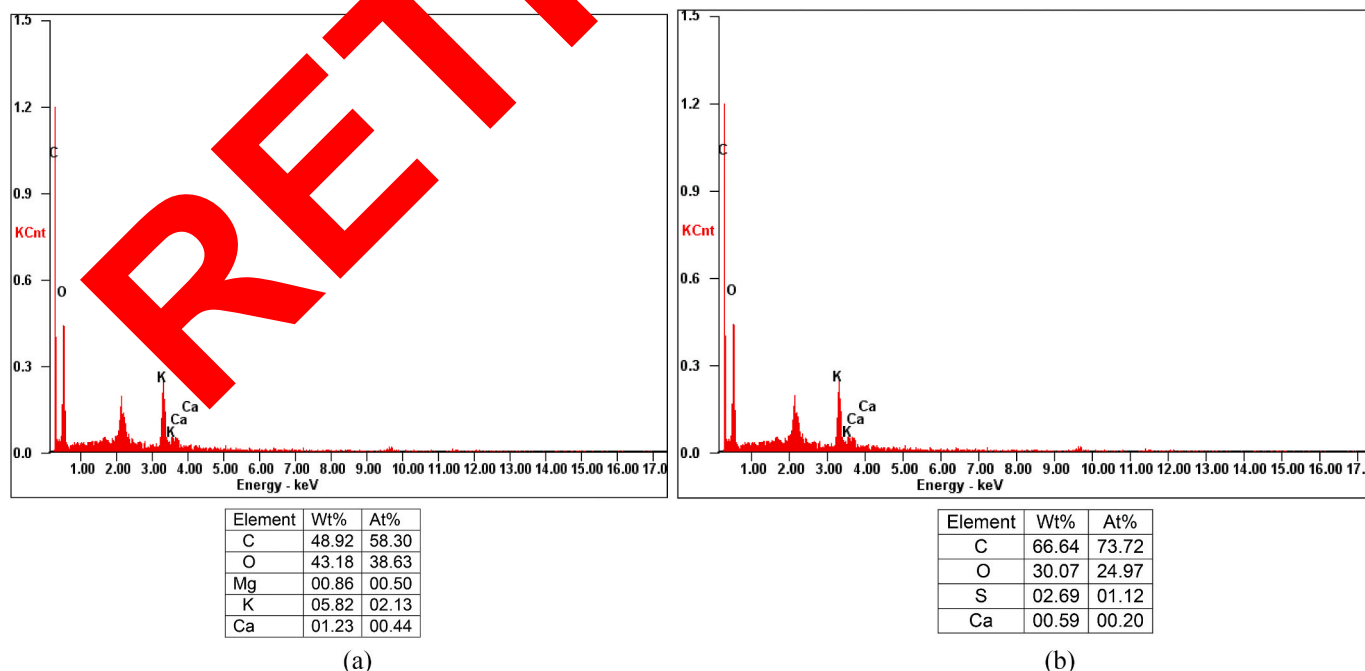


Fig. 2. Energy dispersive x-ray spectroscopy (EDX) spectrum with weight % of (a) Raw coffee husk (CH) and (b) Sulphuric acid activated coffee husk (SACH AC).

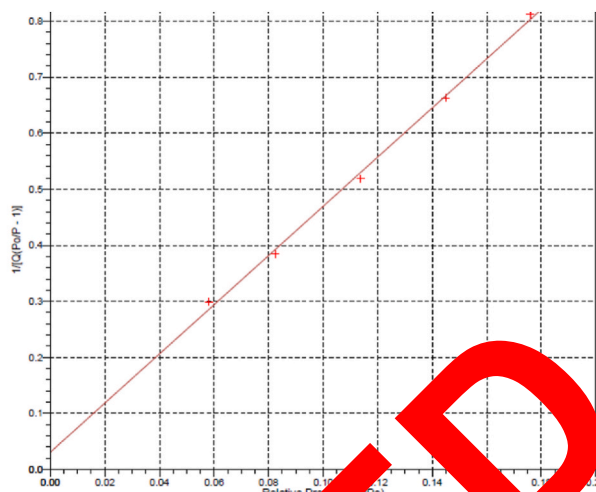
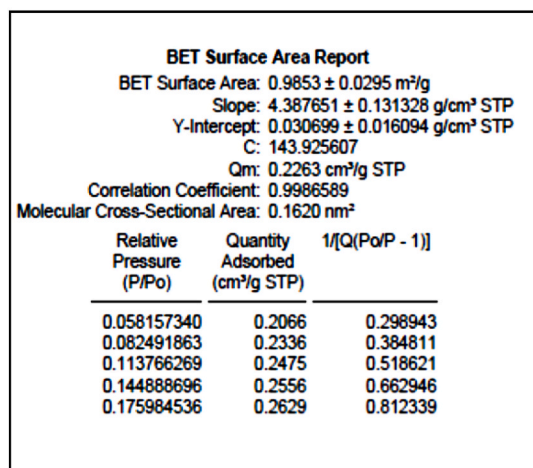


Fig. 3a–b. BET surface area report and plot of Sulphuric acid activated coffee husk (SACH AC).

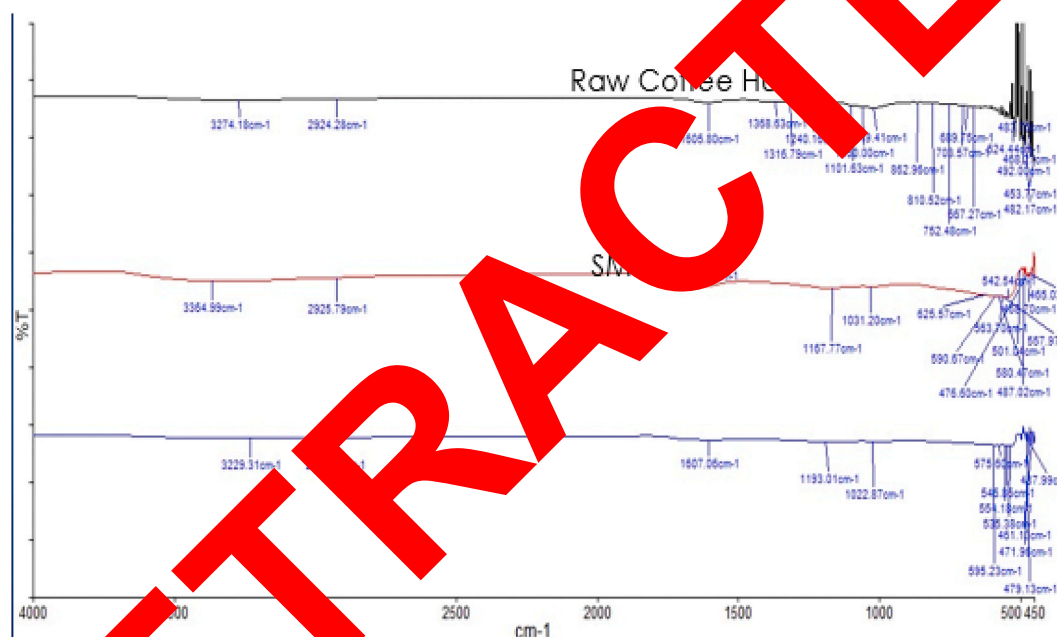


Fig. 4. Fourier transform infrared spectroscopy (FTIR) spectrum of coffee husk.

morphology of raw coffee husk (CH) and sulphuric acid activated coffee husk (SACH AC) were probed by SEM analysis and the recordings are depicted in Fig. 1 (a and b). The smooth morphology and porous structure of SACH AC as compared to CH make it as a suitable and potential bio sorbent and increases the adsorption capacity (Hien et al., 2017). From the SEM image of SACH AC, it is evident that the occurrence of numerous pores on the bio sorbent surfaces and uneven structure onto surface with a large surface area which leads to an excellent biosorption capacity towards the removal of cationic MB dye. These results are in consistent with the previous reports.

Energy Dispersive X-ray Analysis (EDAX) was employed to record the basic elemental mixture of the prepared samples. Fig. 2 (a and b) shows the EDAX pattern with elemental composition in terms of atomic and weight percentage of raw coffee husk (CH) and sulphuric acid activated coffee husk (SACH AC) respectively.

BET report provides a precise analysis of the specific surface area of materials. To measure the total specific surface area available in m^2/g , an approach that includes outer and pore area calculations is employed, which is beneficial in researching the impacts of porosity and particle

size in case of activated carbon. The BET report and plot of SACH AC is shown further. In the current work, Fig. 3a and b shows average monolayer capacity for MB dye removal by SACH AC is 88.31 mg/g and cross-sectional area of the dye is 0.1620 nm^2 , and the specific surface area of the SACH AC was calculated to be around $0.9853 \text{ m}^2/\text{g}$. The modification of raw CH using sulphuric acid results into SACH AC to create porous surface, this in turn increases the sorption capacity. This result is in good fit with the SEM analysis.

Fig. 4, records the FTIR spectra of (a) Raw coffee husk (CH) and (b) Sulphuric acid activated coffee husk AC (SACH AC). From the FTIR spectrum of CH, the peaks at 3274 , 2924 , 1607 and 1101 cm^{-1} were assigned to O–H band (Lignin), C–H band (Lignin), C=C stretching band (Cellulose, Hemicellulose) and C–O along with C–N stretching bands (Cellulose, Hemicelluloses and Lignin). The FTIR spectrum of SACH AC shows the peaks at 3364 , 2926 , 1610 and 1108 cm^{-1} respectively. On comparing the FTIR spectrum of CH and SACH AC, there is shift in wavenumber to higher value which may be due to the surface modification of raw coffee husk (CH) by sulphuric acid. This result confirms that CH and SACH AC consists of various characteristics vibration peaks

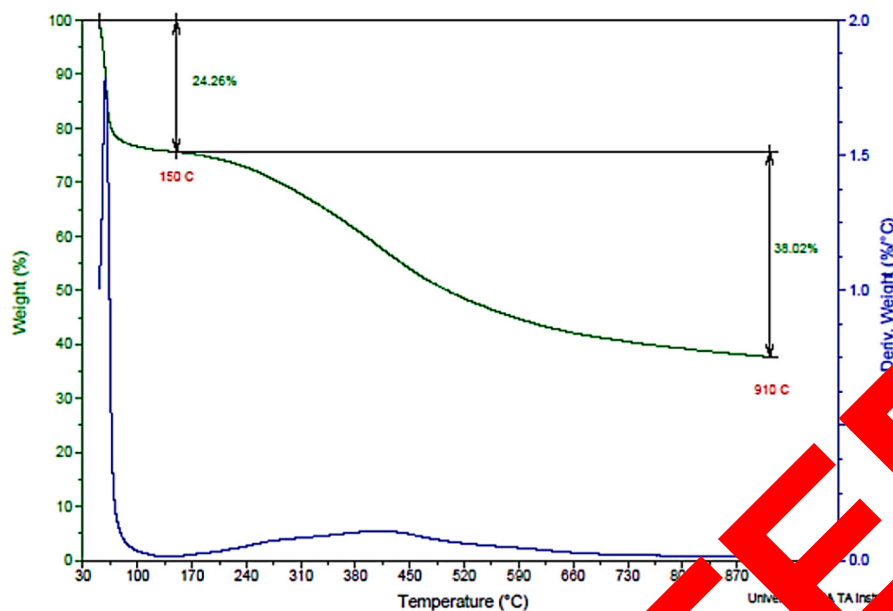


Fig. 5. Thermogravimetric Analysis-Differential thermal analysis TG-DTA curve of Sulphuric acid activated coffee husk (SACH AC).

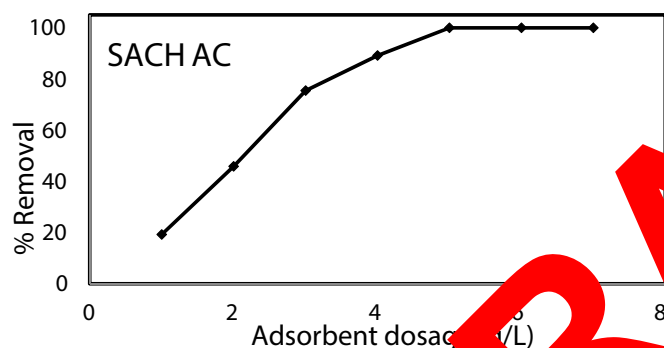


Fig. 6. Influence of activated carbon dosage on the adsorption of MB dye onto SACH AC (MB dye concentration = 100 mg/L, pH = 8.0, volume of the sample = 100 mL, equilibrium time = 60 min, and temperature = 30 °C).

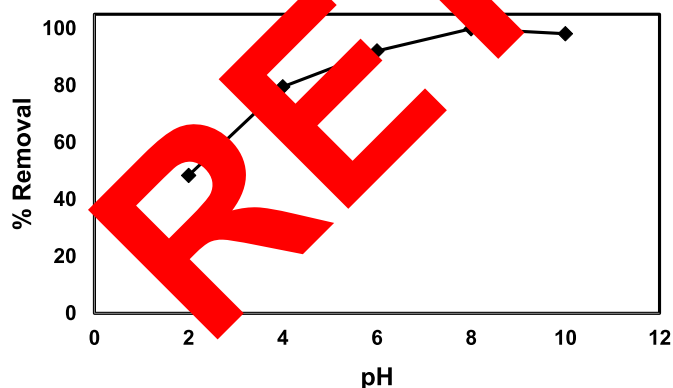


Fig. 7. Influence of pH on expulsion of MB dye onto SACH AC (MB dye concentration = 100 mg/L, adsorbent dose = 5 g/L, volume of the sample = 100 mL, equilibrium time = 60 min, and temperature = 30 °C).

of Lignocellulose. These findings are consistent with prior reports (Hien et al., 2017; Mebrahtom et al., 2017).

The thermal properties of the prepared sample are studied using Thermogravimetric analysis- Differential thermal analysis (TG-DTA).

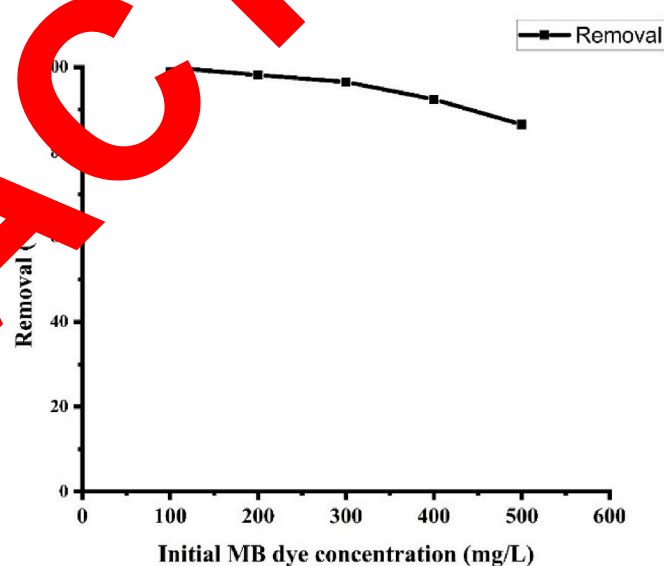


Fig. 8. Influence of initial concentration on expulsion of MB dye onto SACH AC (MB dye concentrations = 100–500 mg/L, solution pH = 8.0, adsorbent dose = 5 g/L, volume of the sample = 100 mL, equilibrium time = 60 min, and temperature = 30 °C).

Fig. 5 records the TG-DTA curve of Sulphuric acid activated coffee husk (SACH AC). From the DTA curve, the two exothermic peaks were observed at around 75 °C and 410 °C respectively which is due to release of free water and degradation of organic constituents available in SACH AC. From the TG curve, the weight loss of around 24.26% and 38.02% occurs at around 150 °C and 910 °C respectively which is corresponds to the elimination of adsorbed moisture and the decomposition of residual carbon skeleton in the prepared sample (Takam et al., 2017).

3.2. Adsorption studies

Process variables such as SACH AC dosage, contact time, initial MB dye concentration, and pH must be optimized to ensure maximal MB dye removal. These variables affect the rate of solute MB dye adsorption

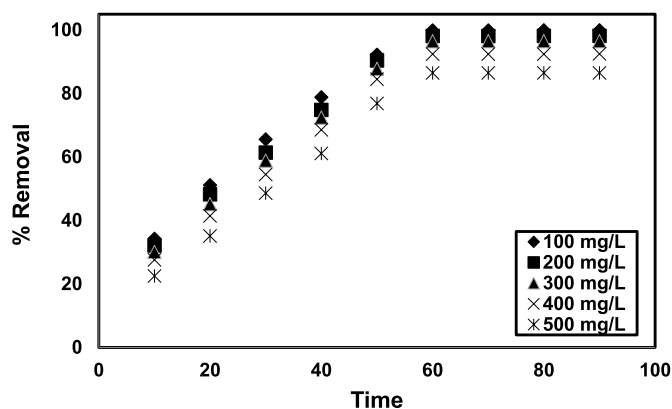


Fig. 9. Influence of time on expulsion of MB dye onto SACH AC (MB dye concentration = 100 mg/L, adsorbent dose = 5 g/L, solution pH = 8.0, volume of the sample = 100 mL and temperature = 30 °C).

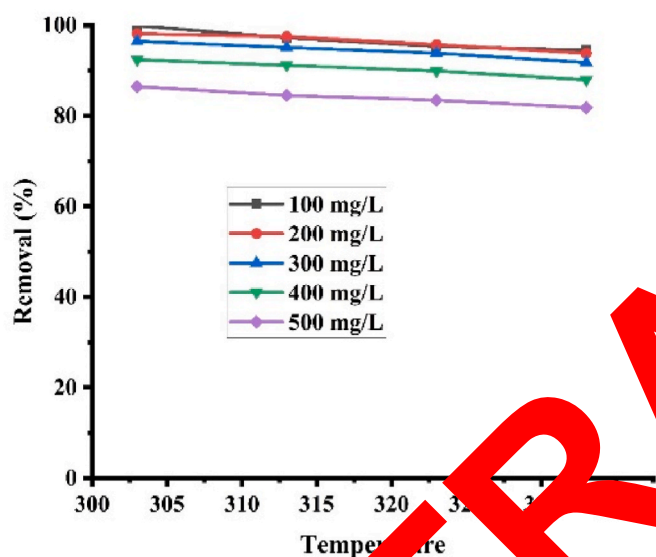


Fig. 10. Influence of temperature on expulsion of MB dye onto SACH AC (MB dye concentration = 100–500 mg/L, adsorbent dose = 5 g/L, solution pH = 8.0, volume of the sample = 100 mL, equilibrium time = 60 min).

onto SACH AC.

3.2.1. Influence of SACH AC dosage

The impact of SACH AC dosage on the removal of MB dye was tested by altering the dosage, as shown in Fig. 6. Due to the fact that when the adsorbent dose increases, the number of sites available for sorption also increases, it was found that the sorption initially rose significantly upon the addition of SACH AC. The removal of MB dye varies from 89.124% to 99.917% when the adsorbent concentration changed from 4 g/L to 5 g/L. According to the obtained results (Fig. 6), it is obvious that at 5.0 g/L SACH AC has adequate interchangeable active areas for the sorption of MB dye and reaches equilibrium at 5.0 g/L SACH AC. With increasing dosages, adsorption rates attain saturation as a result of decreased accessible surface area or buildup of sorption zones (Malkoc and Nuhoglu, 2007).

3.2.2. Influence of initial pH

The pH has the prominent effect in the dye removal techniques. In comparison to other ions in the solution, the ions hydronium and hydroxyl are easier to adsorb. This illustrates that the pH of the solution influences how other ions in the solution adsorb. It is critical to

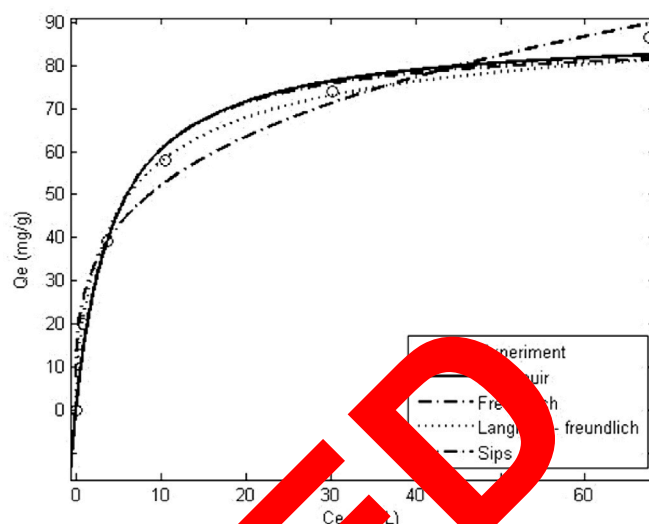


Fig. 11. Fitness of various isotherm models to the adsorption of MB dye.

Table 2
MB dye adsorption on to SACH AC -Isotherm Parameter.

Adsorbent	Isotherm model	Parameters	Values	R ²
Langmuir		q_m	88.1 mg/g	0.9857
		K_L	0.2175 L/mg	
		SSE	3.95	
		RMSE	0.486	
		K_F	26.07 g/L	0.9863
Freundlich		n	3.504 (mg/g) (L/mg) ^(1/n)	
		SSE	4.27	
		RMSE	0.48	
		K_{LF}	0.1831	0.9937
Langmuir-Freundlich		q_{LF}	0.689	
		SSE	95.63	
		RMSE	3.76	
		α_S	0.42	0.9914
Sips		K_S	21.47	
		β_S	0.315(L/g) ^{β_S}	
		SSE	4.38	
		RMSE	0.46	

Table 3

Comparison of adsorption capacities for MB onto different activated carbons prepared by H₂SO₄ activation.

H ₂ SO ₄ -treated sorbents	Adsorption Capacity (mg/g)	Reference
Coconut leaves	127–149	(Jawad et al., 2016)
Ficus carica	47.62	(Pathania et al., 2017)
Parthenium	39.7	(Lata et al., 2007)
<i>hysterophorus</i>		
Coconut shell	50.6	(Jawad et al., 2020a)
Sunflower oil cake	16.43	(Karagoz et al., 2008)
Wild carrot	21	(Swamy et al., 2017)
Watermelon peel	200	(Jawad et al., 2019b)
Bagasse	49.8–56.5	(Low et al., 2010)
Rubber leaf	263.2	(Jawad et al., 2018b)
SMCS Biochar	163.5	(Prabu et al., 2020)
Mango peels	277.8	(Jawad et al., 2017)
SACH AC	88.1	(Current study)

understand how pH (2.0–10.0) affects the removal of MB dye by SACH AC. Fig. 7 depicts the experimental results. As seen in Fig. 7, when the pH rises, the removal of MB dye shows the consistent value, eventually reaching a value close to 8.0. The most MB dye is removed when the pH is set to 8.0. The floor of the adsorbent at acidic pH acquires wonderful

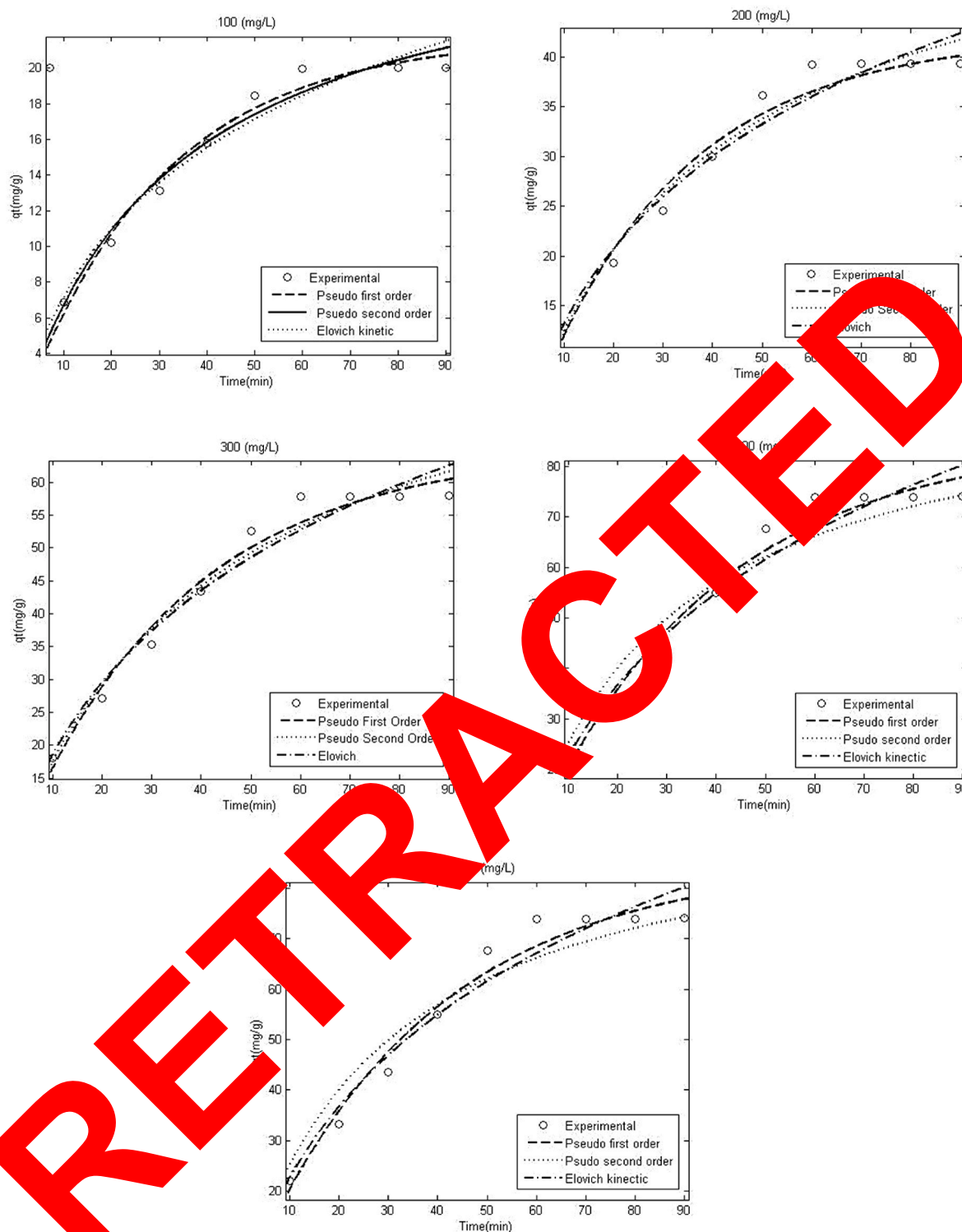


Fig. 12. Adsorption kinetics of MB dye onto SACH AC adsorbent for various concentrations.

expenditures by accumulating the hydronium ions, which limits the sorption of MB dyes onto the SACH AC area due to the electrostatic attraction between the molecules of MB dye and the spectacular costs of the SACH AC surface. Furthermore, increased. When the pH of the solution is raised, the removal of MB dye molecules due to electrostatic attraction accelerates (G et al., 2018). This is due to the great diversity of negatively charged sorbent being accelerated when the pH of the solution is raised. However, when the pH ranged from 2.0 to 10.0, the SACH AC-MB dye system only experienced minor changes in the percentage of

MB dye elimination, indicating that the electrostatic attraction/repulsion mechanism used by the hydronium ions and MB dye to compete with one another was now also the mechanism used to remove MB dye in the current apparatus. The chemical interaction between the SACH AC and the MB dye reduced the proportion of MB dye molecules removed even further. Because the MB dye solution's true pH was closer to 8.0, there was no need to change the pH of the solution for future experiments.

Table 4
Computed Kinetic parameters for MB dye removal onto SACH AC.

Kinetic model	Parameters	Concentration of MB dye Solution (mg/L)				
		100 mg/L	200 mg/L	300 mg/L	400 mg/L	500 mg/L
Pseudo-first-order equation	q_e , exp (mg/g)	19.9884	39.225	59.9	73.988	93.990
	k_1 (min^{-1})	0.03382	0.036	0.02924	0.0272	0.04103
	q_e , cal (mg/g)	21.75	42.12	65.12	85.16	98.01
	R^2	0.9811	0.9732	0.975	0.9707	0.949
Pseudo-second-order equation	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.001052	0.000452	0.000266	0.0003471	0.002344
	$q_{e,cal}$ (mg/g)	28.86	59.01	90.14	98.46	123.1
	R^2	0.972	0.9672	0.9663	0.9343	0.9567
Elovich kinetic model	α (mg/g.min)	0.0501	0.01687	0.008559	0.005302	0.02084
	β (g/mg)	2.599	6.644	11.06	15.41	12.51
	R^2	0.9596	0.9506	0.9565	0.941	0.9551

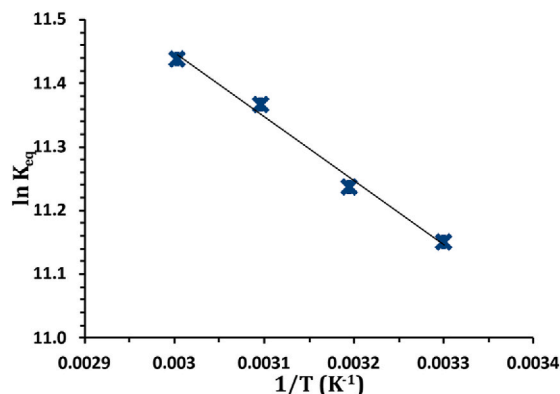


Fig. 13. Thermodynamic studies of adsorption of MB dye onto SACH AC.

Table 5
Computed thermodynamic parameters for MB dye on to SACH AC.

Temperature (K)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (J/mol)
303	-8.77	121.35	-21.98
313			-23.52
323			-30.52
333			-31.67

3.2.3. Influence of initial concentration

The removal of MB dye from aqueous medium by SACH AC was studied at pH 8 and 30 °C for 100 to 500 mg/L dye concentration (Fig. 8). The clearance efficiency increases as the dye concentration increases. At low concentrations, most all dye molecules surround the active regions, while some vacant patches on the adsorbent surface exist.

Each site is covered by multiple dye molecules at increasing concentrations, resulting in virtually constant adsorption capacity due to saturated adsorption sites. The available number of sites remained constant for a given adsorbent dosage and adsorbate. The same quantity of adsorbate, resulting in a drop in removal efficiency (Kharissova et al., 2015). Unpleasant absorption of water concentrations caused by a rise in the ratio of beginning moles to accessible empty sites.

3.2.4. Influence of time

The removal profile increased from 89.124% to 99.917% in the first 50 min and remained consistent in the following 60 min (Fig. 9). Following this time, there was no significant change in adsorption rates. As a result, the best time for all subsequent studies was 60 min. This is because the number of unoccupied sites will decrease with time. Furthermore, the rapid adsorption rate occurs mostly on the large pores of SACH AC. Removal of MB dye will attach on the surfaces of the interior tiny pores as time passes. In the meanwhile, a stable complex will form. As a result, it will cause a moderate adsorption rate that will reach an asymptote when time is sufficient (Barakat, 2011).

3.2.5. Influence of temperature

The effects of SACH AC on the elimination of MB dye were examined at temperatures in the 300–325 K range under ideal circumstances. Fig. 10 displays the conclusions. The clearance rate was seen to decrease with rising temperature (Pham et al., 2016). The decline in the percentage removal can be explained by a weakening of the adsorbents forces between the SACH AC and MB dye molecules. In addition, the MB dye molecules close on the sorbent surface are subject to forces (Ahmad et al., 2012). At 30 °C, the highest strong adsorption was seen for the innovative approach.

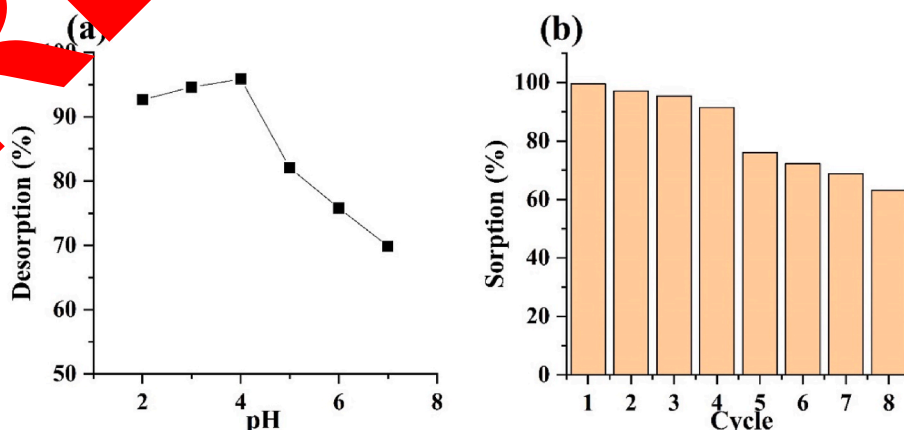


Fig. 14. (a) Desorption study (b) Reuse study.

Table 6

Response surface methodology– Box–Behnken design.

Standard Run	SACH AC dosage (g/L)	Temperature (°C)	Time (min)	pH	Dye Removal (%)	
					Actual	Predicted
1	4	25	60	8	95.1	95.5
2	6	25	60	8	97.2	97.3
3	4	35	60	8	97.8	97.9
4	6	35	60	8	94.8	94.6
5	5	30	50	7	95.8	95.8
6	5	30	70	7	95.5	95.5
7	5	30	50	9	96.3	96.4
8	5	30	70	9	95.9	96.0
9	4	30	60	7	96.2	96.1
10	6	30	60	7	95.7	95.8
11	4	30	60	9	97.1	97.0
12	6	30	60	9	95.9	95.9
13	5	25	50	8	96.3	96.2
14	5	35	50	8	96.1	96.2
15	5	25	70	8	96.1	96.0
16	5	35	70	8	95.7	95.7
17	4	30	50	8	96.6	96.5
18	6	30	50	8	95.7	95.7
19	4	30	70	8	96.2	96.1
20	6	30	70	8	95.3	95.4
21	5	25	60	7	96.9	96.8
22	5	35	60	7	95.3	95.3
23	5	25	60	9	96.1	96.0
24	5	35	60	9	97.1	97.1
25	5	30	60	8	99.2	99.2
26	5	30	60	8	99.2	99.2
27	5	30	60	8	99.2	99.2
28	5	30	60	8	99.2	99.2
29	5	30	60	8	99.2	99.2

3.3. Equilibrium analysis

The prerequisite for building an adsorption system is the existence of adsorption isotherms. The MB dye concentration plays a vital role in the removal process of MB dye onto the adsorbents (SACH AC) and provides a crucial riding pressure to get past the mass transfer barrier of MB dye between the liquid phase and strong segment. 100–200 mg/L MB dye concentration were used for studying equilibrium adsorption. The adsorption equilibrium isotherm may be crucial in examining how the interactions between adsorbents and solutes behave. The equilibrium adsorption quantity increased as MB dye equilibrium concentrations rose, according to the adsorption isotherm. The MB dye's adsorption properties have been assessed, and the practical data have been matched to the four widely used isotherm models, including the Langmuir, Freundlich, Langmuir–Freundlich, and Sips models for SACH AC (Fig. 11). The Freundlich isotherm compared the Langmuir–Freundlich isotherm constants, the Sips model constants, and the Langmuir constants were all estimated from the values of q_{max} and C_e . The parameters for the adsorption isotherm, coefficients of correlation (R^2), and errors value [SSE (sum of squared errors), RMSE (root mean squared error)] have indeed been estimated by fitting the isotherm data to the isotherm models; details are provided in Table 2. To assess the affinities between MB Dye and the SACH AC, one can utilise the Langmuir adsorption isotherm parameters. Table 3 compares the MB adsorption capacity among other sorbents's from previous studies. According to the Freundlich model, the adsorption level is better at higher concentrations but poorer at lower concentrations. This implies that the adsorption surfaces of the adsorbents are heterogeneous (Hemavathy et al., 2020; Naushad et al., 2019). The Langmuir–Freundlich version, as shown in Tables 2 and is unquestionably the best representation of the adsorption equilibrium for SACH AC for the range of starting MB dye concentrations. For SACH AC, the Langmuir–Freundlich version has excessive R^2 (0.9937) and high error levels (SSE = 3.76 and RMSE = 0.42).

3.4. Kinetics and removal mechanism

So as to design a commercial – primarily based sorption remedy scheme, the design of the manner and operation in addition to the kinetics of the manner are vital to the success (Shukla and Kisku, 2015). Particularly, the evaluation of adsorption kinetics is important, because it offers important records at the response pathways in addition to mechanisms worried in sorption. To look at the adsorption kinetics of the elimination of the MB dye using the SACH AC the pseudo-first-order, pseudo-2nd-order and Elovich models are used. The results on the adsorption kinetics for SACH AC-MB dye systems had been displayed in Fig. 12. Table 4 shows the anticipated parameters of kinetic fashions, R^2 , RMSE, and SSE values from the kinetic plots (Fig. 12). The mass stabilization equation was used to forecast the equilibrium adsorption capacity based on experimental data, and it is listed in Table 4. The equilibrium adsorption capabilities of SACH AC were listed in Table 4 along with the elimination kinetic statistics that were used in the kinetic models. The pseudo-first order model, when contrasted to the pseudo-second-order model, corroborated the results that were closer to all those two adsorption equilibrium capacity values. This showed that the more desirable version of the SACH AC-MB dye system is the pseudo-first-order variant. This proved to be more proof that the pseudo-first-order version had higher R^2 values and less errors values than other kinetic models.

The chemisorption reaction at the heterogeneous surface is often explained by the Elovich kinetic version (Shukla and Kisku, 2015). Table 4 contains the Elovich parameters and the related correlation coefficients. Based on errors and R^2 values, the Elovich model somehow doesn't match the SACH AC-MB dye systems as well as other models do (Ghosh et al., 2014). Commonly, the kinetic effects show that a pseudo-first-order model followed the removal of MB dye using SACH AC.

3.5. Thermodynamic analysis

The thermodynamic variables together with enthalpy (ΔH^0 , J mol⁻¹), entropy (ΔS^0 , J K⁻¹ mol⁻¹), Gibbs free strength (ΔG^0 , J mol⁻¹) had been calculated the usage of the (Eqs. (11)–(14)). The values of ΔH^0 and ΔS^0 have been evaluated from a plot of $\log K_{\text{eq}}$ v/s $1/T$ (Fig. 13). The values of diverse thermodynamic parameters were tabulated in Table 5. Negative Gibbs energy (ΔG) values show that MB adsorption is possible and spontaneous (Rahmani-Sani et al., 2016), and the ΔH^0 value indicates a physisorption procedure reconfirming previous end result (Kumar et al., 2016; Sunkar et al., 2023). The poor value of entropy changes (ΔS) indicates that physisorption, which occurs through electrostatic interaction, showing that the process was exothermic and enthalpy driven (Prabu et al., 2020; Sundaraman et al., 2020). The calculated thermodynamic parameters showed that the MB adsorption onto SACH AC has greater favorability at higher temperatures (Mohammadzadeh et al., 2023).

3.6. Reuse study

Desorption studies were performed to investigate the reuse of the adsorbent. For industrial use, adsorbent regeneration is required. Desorption increases adsorption efficiency while decreasing adsorption treatment plant maintenance costs. Because the removal process was conducted at a pH of 8, the desorption process was conducted in an acidic to neutral environment (pH 2 to 7). As demonstrated in Fig. 14a, maximal desorption of MB dye on the surface of SACH AC occurs at acidic conditions (pH 2 to 4). As shown in Fig. 14b, the SACH AC may be reused for 5 cycles with considerable MB dye elimination. The steady decline in MB dye removal percentage by SACH AC can be attributed to factors such as adsorbent material deterioration over time due to saline conditions at higher pH or dye molecule saturation of active sites (Soosai et al., 2023).

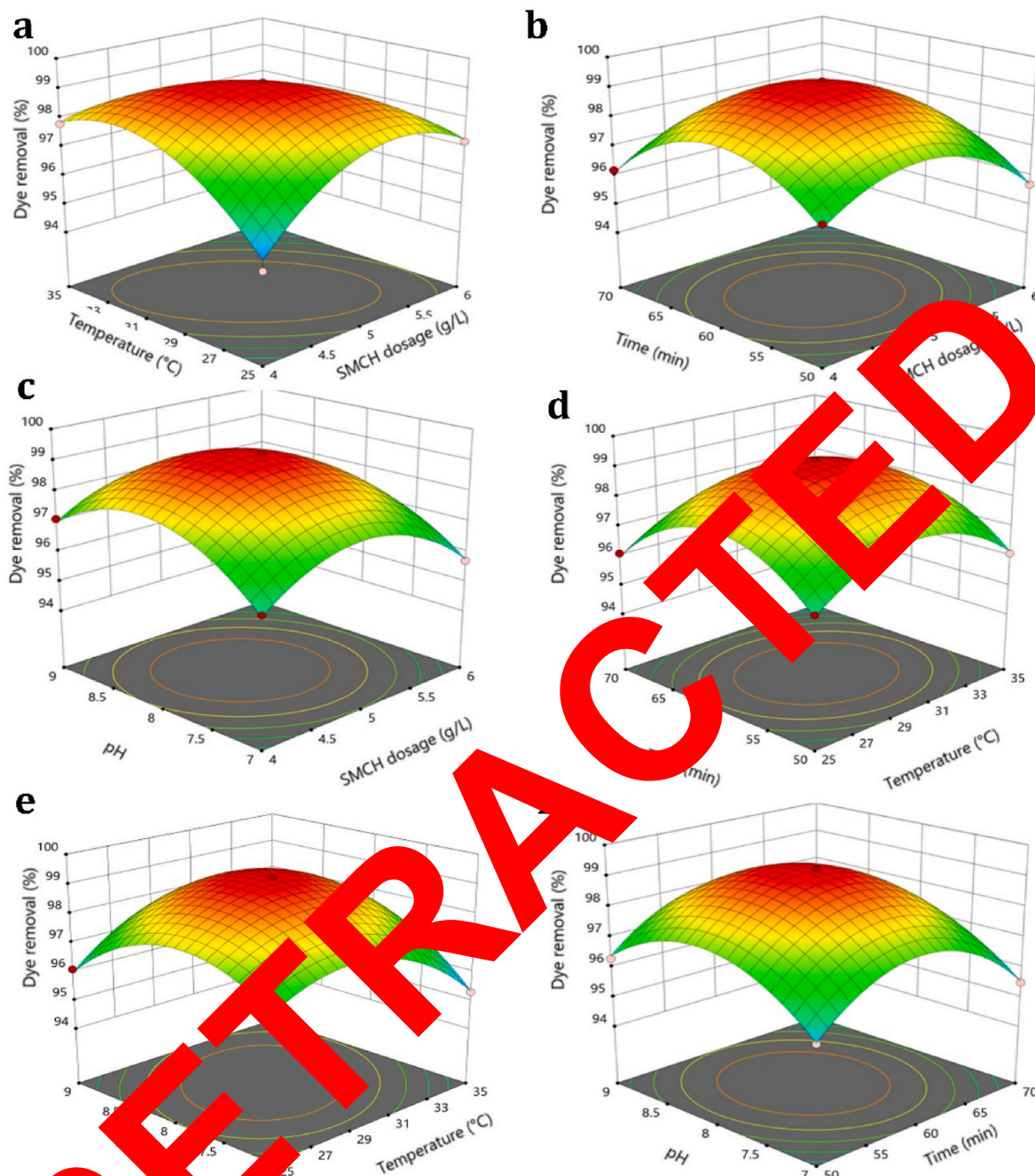


Fig. 15. Relationships between variables on a 3D response surface plot that affect MB dye removal.

3.7. Optimization of process

The one-variable-at-a-time experiments yielded maximum MB adsorption of 88.1 mg capacity at 30 °C, pH 8 for 5 g/L SACH AC dosage in 60 min. Using this variable condition, a four-factor, five-level RSM-BBD was employed to develop the experiments for maximising the MB dye removal %. Table 6 shows the actual and predicted MB dye removal percentage. Relationships between the variables on a 3D response surface plot that affect MB dye removal is shown in Fig. 15.

The analysis of variance (ANOVA) for the RSM-BBD design is shown in Table 7. To determine the significance of individual, interacting, and quadratic terms the F-value and probability p-value were analyzed. The F-value of the model is 162.96, and the p-value is lower than 0.0001 which indicates that the model is statistical significant for the adsorption of MB by SACH AC (Abdulhameed et al., 2021). The significance of the

BBD model term (X_1 , X_2 , X_3 , X_4 , X_1X_2 , X_1X_4 , X_2X_3 , X_2X_4 , X_3X_4 , X_1^2 , X_2^2 , X_3^2 , X_4^2) was established in second-order polynomial expression using the p-value to produce the suitable fitness outcome (Reghioua et al., 2021). As a result, the quadratic model has importance. The lack of fit for the model is not significant, indicating that the expected model is satisfactory. Graphical analysis is one of the ways used to validate the model by examining the characteristics of the residual's distribution as well as the actual and projected response values (Jawad et al., 2020b). The predicted MB dye removal % using the quadratic model is close to the actual value, as shown in Fig. 16 (Jawad et al., 2021b). R^2 for the projected quadratic model is 0.9939 this implies a strong relationship between actual and predicted values (Jawad et al., 2020c). As a consequence, the model can explain 99.39% of total variation. The adjusted R^2 of 0.9878 agrees with each other reasonably well. The From the Derringer's desirability a maximum dye removal of 99.24% is reported at an

Table 7
ANOVA for biodiesel production using RSM-BBD.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	51.20	14	3.66	162.96	<0.0001 ^a
SACH AC dosage	1.61	1	1.61	71.89	<0.0001 ^a
Temperature	0.0675	1	0.0675	3.01	0.1048
Time	0.3675	1	0.3675	16.38	0.0012
pH	0.7500	1	0.7500	33.42	<0.0001 ^a
X ₁ X ₂	6.50	1	6.50	289.77	<0.0001 ^a
X ₁ X ₃	0.0000	1	0.0000	0.0000	1.0000
X ₁ X ₄	0.1225	1	0.1225	5.46	0.0349
X ₂ X ₃	0.0100	1	0.0100	0.4456	0.5153
X ₂ X ₄	1.69	1	1.69	75.31	<0.0001 ^a
X ₃ X ₄	0.0025	1	0.0025	0.1114	0.7435
X ₁ ²	14.84	1	14.84	661.25	<0.0001 ^a
X ₂ ²	12.71	1	12.71	566.54	<0.0001 ^a
X ₃ ²	20.44	1	20.44	910.70	<0.0001 ^a
X ₄ ²	14.35	1	14.35	639.57	<0.0001 ^a
Residual	0.3142	14	0.0224		
Lack of Fit	0.3142	10	0.0314		
Pure Error	0.0000	4	0.0000		
Cor Total	51.51	28			

^a Significant.

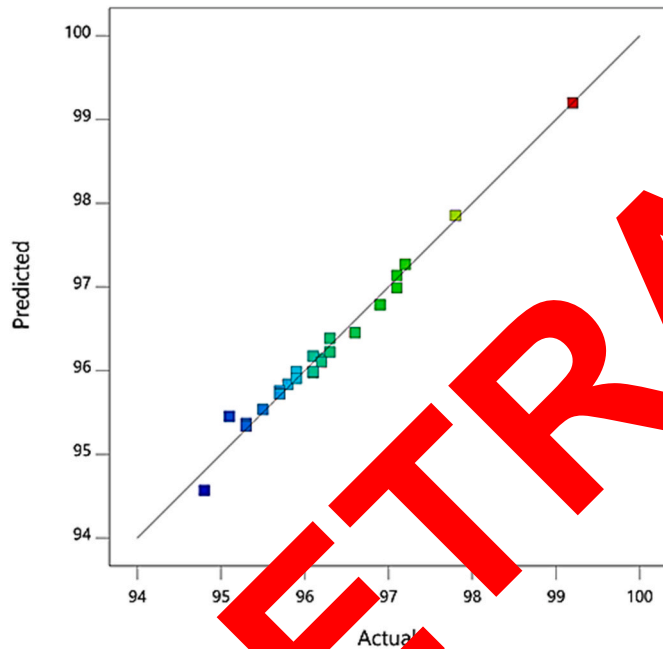


Fig. 16. In a design plot, the predicted vs. actual removal of MB dye.

optimum condition of x_1 (SACH AC dosage) = 4.88 g/L, x_2 (temperature) = 30 °C, x_3 (time) = 60 min and x_4 (pH) = 8.11.

The experiment employing RSM-CCRD produced a quadratic polynomial non-linear equation no. 15 for attaining a better MB dye elimination % by fitting the actual value of independent variables data.

Dye removal %

$$Y = -163.8 + 23.81 X_1 + 3.640 X_2 + 2.162 X_3 + 21.18 X_4 - 0.2550 X_1 X_2 - 0.1750 X_1 X_4 - 0.0010 X_2 X_3 + 0.1300 X_2 X_4 - 0.0025 X_3 X_4 - 1.513 X_1^2 - 0.056 X_2^2 - 0.0178 X_3^2 - 1.488 X_4^2 \quad (15)$$

Stationary points were calculated to check the optimal value of the independent variables in order to get the most effective response. By equating the first derivative of response to zero, the stationary point was calculated to yield the maximum response (MB dye removal %) to be

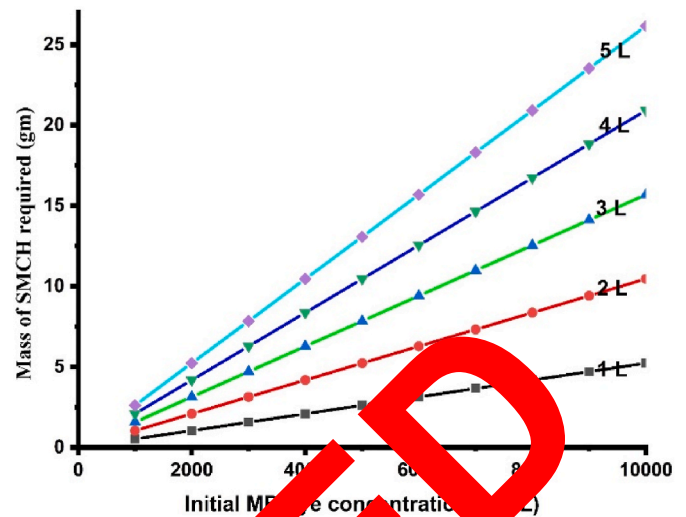


Fig. 17. Design of single stage batch adsorber.

99.84% at the stationary points (Sachin et al., 2023). These findings were verified via lab experiment where 99.48% MB dye removal was observed at x_1 (SACH AC dosage) = 4.83 g/L, x_2 (temperature) = 30 °C, x_3 (time) = 60 min and x_4 (pH) = 8.12

3. Single-stage batch adsorber design

The Langmuir-Freundlich isotherm convergent validity adsorption best-fit equation was used to design a single-stage batch adsorber. The adsorber reduces MB dye molecule concentration from C_0 (mg/L) at $t = 0$ to C_1 (mg/L) at t min. SACH AC adsorb q_0 (mg/g) at $t = 0$ to q_t (mg/g) at t . C_e (mg/L) and q_e (mg/g) reflect the solution's MB dye concentration and SACH AC adsorbent's biosorption capacity at equilibrium. At time t , the material balance throughout the single-stage batch adsorber is:

$$V(C_0 - C_1) = M(q_1 - q_0) \quad (16)$$

where M is the mass of adsorbent (g). Assuming initially no adsorption occurs

$$V(C_0 - C_1) = Mq_1 \quad (17)$$

MB dye concentration and SACH AC adsorbent biosorption capacity at equilibrium is given as

$$V(C_0 - C_e) = Mq_e \quad (18)$$

using the Langmuir-Freundlich equation, the above equation becomes

$$M = \frac{V(C_0 - C_e)}{q_e} = \frac{V(C_0 - C_e)(1 + (K_{LF}C_e)^{m_{LF}})}{q_{m_{LF}}(K_{LF}C_e)^{m_{LF}}} \quad (19)$$

Equation no. 23 was used to construct a single-stage batch adsorber to reduce MB dye concentration by 95% (approximately 99% of dye is removed at lab size experiment, therefore assuming 95% can be removed in large-scale operation). Fig. 17 shows the mass of SACH AC adsorbent needed for 1–5 L of effluent entering the single-stage batch adsorber at dye concentrations from 1000 to 10,000 ppm. Suppose 5000 ppm MB dye enters 1 L adsorber, the above design suggests using 2.6 g of SACH AC adsorbent is required to reduce the initial dye concentration to 250 ppm. The graph shows that only 26.14 g of adsorbent is enough to remove 10,000 ppm of dye from 5 L of effluent.

4. Conclusion

Raw coffee husk is a cheap waste material, which is produced by

chemically activating raw coffee husk with sulphuric acid (SACH AC), to produce an effective adsorbent SACH AC for eradicating MB dye from synthetic wastewater. Common characterizations such as SEM with EDX, XRD, FTIR, BET, TGA, and DTA analysis were performed to investigate the chemical properties of the synthesized activated carbon. Out of the experimentally significant factors investigated, the optimal adsorbent dosage, contact duration, pH, and temperature were found to be 5 g/L, (ii) 60 min, (iii) 8, and (iv) 30 °C respectively, for highest percentage removal of MB dye by the SACH AC. The Langmuir, Freundlich, Langmuir-Freundlich, and Sips versions of the non-linear regression analysis of the MB dye adsorption isotherms onto the adsorbents were used to illustrate the results. On the basis of the high estimation coefficient values and the low errors values, Langmuir-Freundlich was chosen as the suitable adsorption isotherm type for the MB Dye-SACH AC system. With the help of the pseudo-first-order version, kinetic facts have been very effectively evaluated. Langmuir adsorption capacity of the SACH AC for MB dye was found to be 88.1 mg/g. As the temperature rose, the amount of MB dye that was expelled decreased, indicating that the adsorption of the dye onto the SACH AC had converted to an exothermic process. The analysis of BBD model in RSM helps to identify the optimal parameters to obtain the maximum % removal of MB using SACH AC is (99.48%). This was further supported by the fact that the current adsorption machine's negative values of the change in enthalpies were seen. The adsorption-desorption reusability study indicated that SACH AC could be reused for 5 cycles with higher MB dye removal efficiency. As a result, it was determined that the current SACH AC is an excellent and affordable adsorbent that can be used to remove MB dyes from liquid systems.

Credit author statement

Prabu Deivasigamani^{1**} - Corresponding and original draft, Sathish Sundaraman¹ - draft review, Sathish Sundaraman¹ - conceptualization, Michael Rahul Soosai¹ - methodology, Annam Renita¹ - project resources, Karthikeyan M¹ - project execution, A. Nessipriya¹ - revision, Omirserik Baigzenhenov² - revised version language editing, D.Venkatesan¹ - proofreading, Aravind Kumar J^{6*} - revised draft writing and correspondence.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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