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Modified walnut shell for enhanced adsorption for methylene blue from aqueous solution: Preparation, characterisation, isotherm, kinetics and mechanism study

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Human and aquatic health is frequently at risk due to methylene blue (MB) dye pollution in aquatic environments. In order to remediate water contaminated with MB dye, a chemically modified walnut shell (CMWS) adsorbent is developed in the present study. The physico-chemical characteristics of modified walnut shell have been investigated using a variety of characterisation techniques, including pH_{pzc}, FTIR, BET, FE-SEM, and EDS. After optimising the impact of the most important parameters, a maximum removal of 85.6% is noted at pH 6. The MB uptake by chemically modified walnut shell is explained by the multilayer layer adsorption onto energetically equivalent sorption sites. The linear Freundlich model yielded a maximal adsorptive capacity of 66.6 mg MB per g CMWS. The kinetic models also showed that the rate depends on the adsorbent's adsorptive capacity. The pseudo-second order model works well for MB adsorption and R^2 >0.999. Thermodynamic studies indicated that adsorption is feasible, spontaneous and endothermic in nature. This work suggests that CMWS may be investigated further as a possible adsorbent for the removal of MB dye.

Keywords: Adsorption, Isotherm, Kinetics, Methylene blue dye, Walnut shell

Introduction

Colour is added to textiles, leather, paper, and other materials using dyes, which can be synthetic or natural organic colouring substances. In the market, there are over 50,000 trade names and over 9000 synthetic colour options exist[1]. The textile sector alone accounts for two thirds of the world's production of dyestuffs[2-4]. One common example of a cationic dye used extensively in the textile industry is methylene blue (MB). However, since MB dyes have azo groups in their chemical structure, they are difficult to break down. To evaluate the toxicity of MB to *Spirulina platensis* and Chlorella, Moorthy *et al*.[5] exposed unialgal populations of two microalgae to different dye concentrations. They observed that when concentration rose, specific growth rate, pigment, and protein content decreased. Auerbach *et al*.[6] verified that the small intestine tumours observed in male mice are believed to be related to MB utilising a rodent carcinogenicity bioassay. The human body may be harmed by MB. Therefore, before being released into water sources, coloured wastewaters such as water containing MB need to be properly treated[7].

Conventionally employed techniques for eliminating inorganic and organic contaminants from water include chemical precipitation, ion exchange, membrane filtration, coagulation, and adsorption[8]. Adsorption is one of these techniques that offer benefits like adaptability in application and simplicity in design that prevents the creation of hazardous intermediates or final products[9]. Numerous types of forestry and agricultural waste, including lignin, rice husk, pine core, chestnut shell, etc., have reportedly been employed as environmentally beneficial adsorbents[10-12]. Smaller-sized particles are frequently manufactured from these biomass sources to increase their specific surface area. Of these, walnut shell powder (WSP) has drawn the most attention lately because of its outstanding adsorption capability for the removal of colours and its widespread availability[13]. The goal of cultivating walnuts (*Juglans regia* L.) is for culinary purposes. The manufacture of walnuts produces a lot of trash, which is typically burned or dumped in a landfill because of its widespread use as food. Because buried walnut shells are so hard and take so long to breakdown, they create an environmental hazard [14].

Therefore, it can be said that using walnut shells, which are widely available, inexpensive, and simple to deal with in the field of adsorption to treat

wastewater is safe and environmentally acceptable. Here, alkali - oxidative treated chemically-modified walnut shell (CMWS), an appropriate and reasonably priced adsorbent, was created for the adsorption process of MB adsorption from aqueous solutions. As modifying agents, sodium hydroxide and potassium permanganate were utilized to increase the adsorption capacity of walnut shell towards MB adsorption from aqueous solutions. The adsorption mechanism and kinetics of the MB was also investigated in this work, and the many physicochemical parameters influencing the rate of adsorption as well as the adsorption quantity of the adsorbent were identified. Adsorption was investigated in relation to solution pH, initial dye concentration, adsorbent dose, contact time, and temperature.

Experimental Section

Materials and Reagent

The biomass made from walnut shells was bought from the local market, Hisar, Haryana, India. The MB dye removal tests and the walnut shell modifications were carried out using analytical grade chemicals. We purchased sodium chloride, MB dye, sulphuric acid, and sodium hydroxide from Hi-media Laboratory Pvt. Ltd.

Preparation of adsorbent

Water was used to rinse the walnut shell (WS) to get rid of dust and other contaminants. Until the WS was at a consistent mass, it was dried at 333 K for more than 120 h. To obtain the necessary particle size, the dry walnut shells were crushed and sieved through a 40–60 mesh screen. The following procedure was used for modifying the WS. First, 10.0 g of the produced WS was added to a 250 mL conical flask that was filled with 100 mL of 0.1 N NaOH at 298 K. The flask was then shaken continuously for 8 h at 150 rpm. To strengthen its binding site, NaOH solution was used before. The WS was then dried at 333 K for 24 h after being filtered and repeatedly cleaned until the solution's pH was neutral. Following the aqueous NaOH pretreatment, 100 mL of 0.1 M $KMnO_4$ solution was added to the WS. After that, the mixture was placed in an orbital shaker and shaken for 24 h at 303 K at 150 rpm. The adsorbent was then filtered and repeatedly cleaned with distilled water. The obtained adsorbent was then dried for 24 h at 333 K in an oven. For later use, the alkali oxidatively modified WS was stored in an airtight glass bottle and named as CMWS.

Characterization

Infrared (IR) spectra for WS and CMWS were recorded in the range 450-4000 cm^{-1} using a Thermo Scientific spectrometer (Nicolet iS50. The Quantachrome IQ-XR-XR (2Stat.) was used for BET analysis; the sample was degassed for 12 h at 150°C before analysis. The DFT model was used to get the average pore size, the BET equation was used to determine surface areas, and the BJH model was used to determine the total pore volume. Utilising a Quanta 200F microscope (FE-SEM) with an accelerating voltage of 20 kV, the surface morphologies of WS and CMWS were examined.

Dye solution and quantification

A 1000 ppm stock solution of the MB dye was prepared using deionised water. The pH values were changed using 0.1 N solutions of sulphuric acid and sodium hydroxide. The Shimadzu 2600i spectrophotometer was used to detect the amounts of residual MB dye at 664 nm.

Adsorption experiments

The reaction parameters pH, dye solution concentration, amount of adsorbent, contact time, and temperature were optimised by conducting batch studies. As recommended by Kayan and Kayan (2007)[15], the removal efficiency (%) and adsorptive capacity (q_t) were determined using Eqs (1) and (2), respectively.

$$Efficiency = \left(\frac{Initial\ conc. - Final\ conc.}{Initial\ conc.}\right) \times 100 \quad \ldots (1)$$

$$Adsorptive\ capacity = \left(\frac{Initial\ conc. - Final\ conc.}{Mass\ of\ adsorbent}\right) \times Volume \quad \ldots (2)$$

Using MB solution at different concentrations (10, 20, 30, 40, 50, and 60 mg/L), a calibration curve was calculated. The absorbance was then measured at 664 nm using a Shimadzu 2600i spectrophotometer.

Adsorption isotherms and kinetics modeling study

The experimental data was fitted into the Freundlich and Langmuir adsorption isotherms (Eqs (3) and (4)) to ascertain whether the adsorption is physical or chemical. Kinetic modelling was performed by fitting the experimental data into the pseudo-first order and pseudo-second order kinetic equations using Eqs (5) and (6) for non-linear plots.

Langmuir adsorption isotherm

$$q_e = \frac{(q_{max} \times K_L \times C_e}{(1+K_L \times C_e)} \quad \ldots (3)$$

Freundlich adsorption isotherm

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

Pseudo-first order model

$$q_t = q_e(1 - e^{-K_1 t}) \quad \ldots (5)$$

Pseudo-second order model

$$q_t = \frac{{q_e}^2 K_2 t}{1+K_2 t q_e} \quad \ldots (6)$$

Thermodynamic Study

Thermodynamic parameters like Gibbs-free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) can be used to better understand the impact of temperature and investigate the adsorption mechanism of MB onto CMWS (Eqs 7a-c), [16].

$$K_C = \frac{q_e}{C_e} \quad \ldots (7a)$$

$$lnK_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \ldots (7b)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \ldots (7c)$$

Point of zero charge (pH_{pzc})

The salt addition method was used to determine the pH_{pzc} of CMWS. After 50 mL (0.01 M) of sodium chloride solution was mixed with 1.0 g of CMWS, the initial pH (pH_i) varied between 1 and 11. To determine the pH final (pH_f), the biomass solution with different pH values was kept in a shaker at 25±1°C for 48 h. The pH_{pzc} was investigated using the ΔpH (pH_f - pH_i) vs. pH_i plot for CMWS.

Results and Discussion

Adsorbent characterization

FTIR analysis

The FTIR spectra of WS and CMWS before and after dye adsorption are shown in Fig. 1. The prominent hydroxyl group in WS, CMWS, and MB-loaded CMWS has been ascribed to O–H and N–H stretching vibrations and is located between 3400 and 3444 cm^{-1}. Furthermore, peaks located between 2916 and 2925 cm^{-1} show that methyl and methylene groups exhibit C–H stretching vibrations [17] but when compared to WS, the peak intensity was lower in CMWS, and MB-loaded CMWS, respectively. Our results are in accordance with previous cited literature [18-19].

BET analysis

The surface area, pore volume, and pore size values for the WS are found to be 16.7 m^2 g^{-1}, 0.055 cm^3 g^{-1}, and 3.0 nm. Alkaline-oxidative modification of the WS resulted in a slight increase in surface area and affected the surface structure, which established the mechanisms of adsorption[20-21]. In the present study also the surface modification resulted in the surface properties as the surface area, pore volume, and pore size values are found to be 32.6 m^2 g^{-1}, 0.0065 cm^3 g^{-1}, and 3.8 nm for the CMWS.

FESEM and EDS analysis

Using a FESEM, the surface properties of WS, CMWS, and MB dye-loaded CMWS were studied (Fig. 2a-c). The holes and irregularities of the CMWS surface may have served as binding sites for the MB dye during its adsorption[22]. The adsorbent-adsorbate interaction is confirmed by the surface alteration following modification (pretreatment) and dye adsorption process. After MB dye loading, CMWS's surface morphology significantly changes, with holes filled and covered as well as the shiny and appearance of a smooth surface becoming rough[23] as in Fig. 2c. EDS provides evidence of the chemical change happened on adsorbent surface both before and after dye adsorption.

Adsorption studies

The effectiveness of CMWS's adsorption of MB dye was investigated using batch studies. To optimize the pH, MB solutions (20 ppm, 20 mL) with varying pH values from 2 to 10 were prepared. MB solutions with several concentrations (20, 30, 40, 50, and 60 ppm) were prepared in order to optimize the initial concentration. Different amounts of adsorbent doses were taken, i.e., 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 g; and added to MB solution in order to optimize the

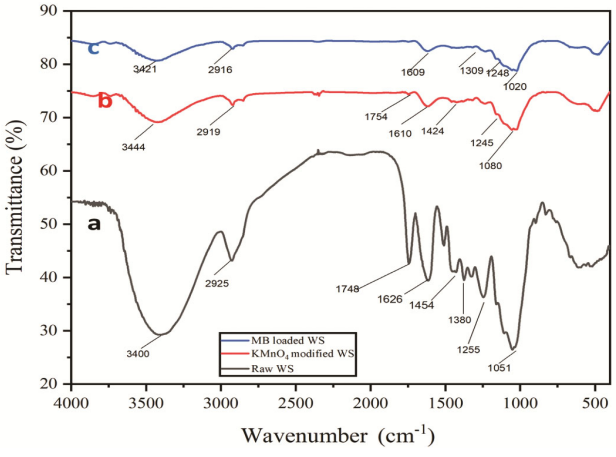

Fig. 1 — FTIR spectra of (a) RWS, (b) CWNS before and (c) after dye adsorption

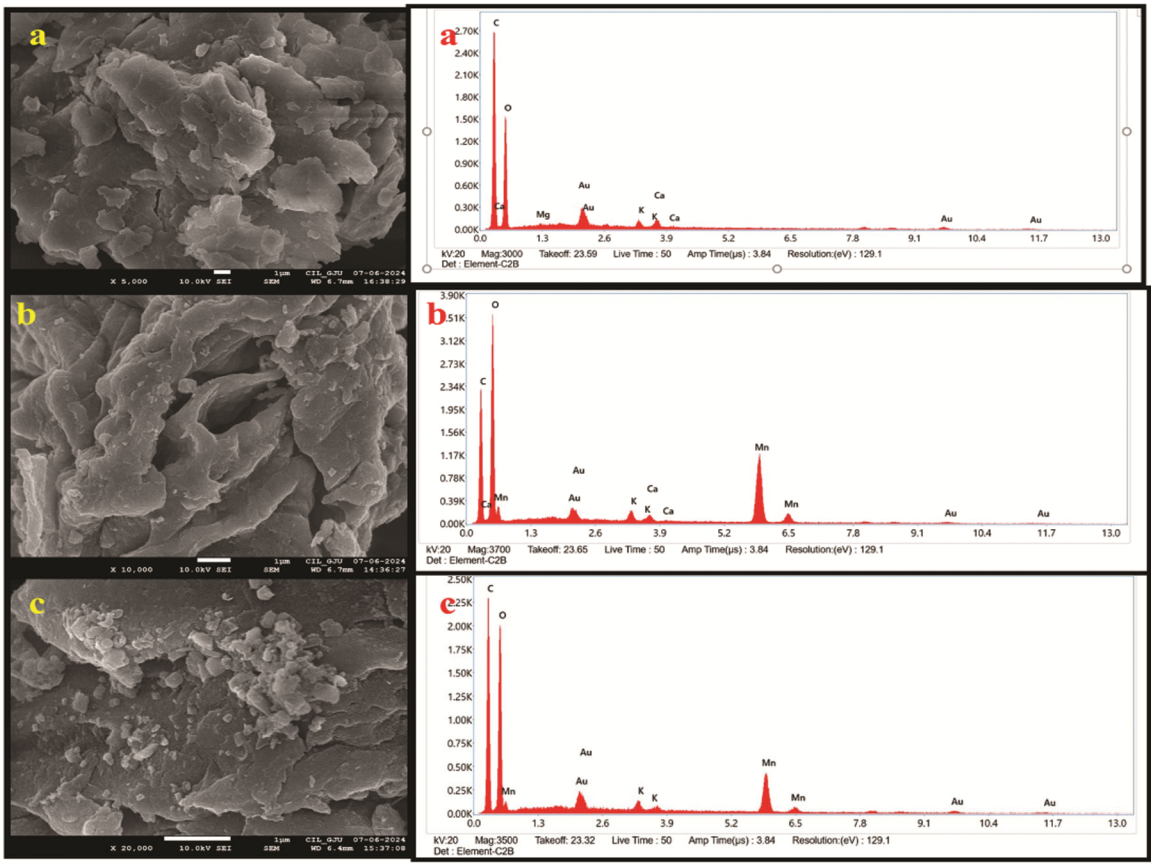

Fig. 2 — FESEM micrographs and corresponding EDX plots for (a) Walnut shell, (b) CMWS before and (c) CMWS after MB dye adsorption

amount of adsorbent. For the optimization of contact time and temperature, adsorption studies were carried out at different temperatures (20°C, 25°C, 30°C, 35°C, 40°C, 45 °C and 50 °C) for different contact time (30, 60, 90, 120, 150, 180 and 210 min).

Influence of pH

Point zero charge (pH_{PZC}) plots between ΔpH vs pH_i for CMWS is shown in Fig. 3 and the point of zero charge is found to be 2.5. Fig. 4(a) displays the MB adsorption efficiency of CMWS at *p*H values ranged from 2-10. As the pH was raised up to 6-7, the adsorption efficiency of CWNS was also increasing. After that, the removal efficiency remained constant due to a decrease in the number of accessible adsorbent sites for adsorption. The pH increased, but no notable alterations occurred. With an adsorptive capacity of 66.6 mg/g, pH 7 was determined to have the greatest adsorption for the MB removal (85.6%). Zhang et al. [24], also observed the maximum adsorption capacity of 92.17 mg/g for sodium alginate gel beads for adsorption of methylene blue at pH 7. On the

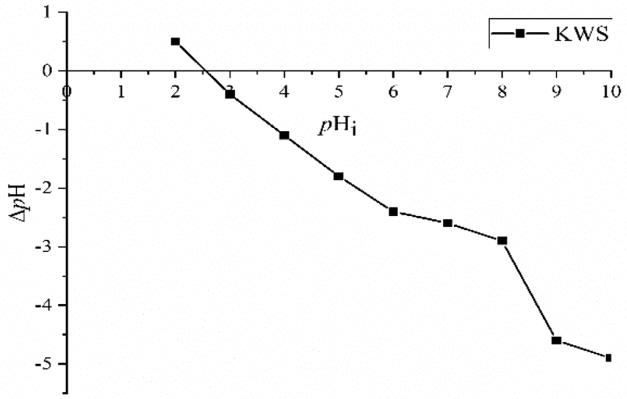

Fig. 3 — Point zero charge (pH_{PZC}) plots between ΔpH vs pH_i for CMWS

surface of adsorbent materials, polar groups such carboxyl groups, alcohols, esters, and phenols are the active sites that interact with MB by hydrogen bonding; also, the π-π interaction enhances the adsorption of MB at low pH levels. Based on the adsorbent's point of zero charge (pH_{pzc}), which was 2.5, there was a negative charge present on the

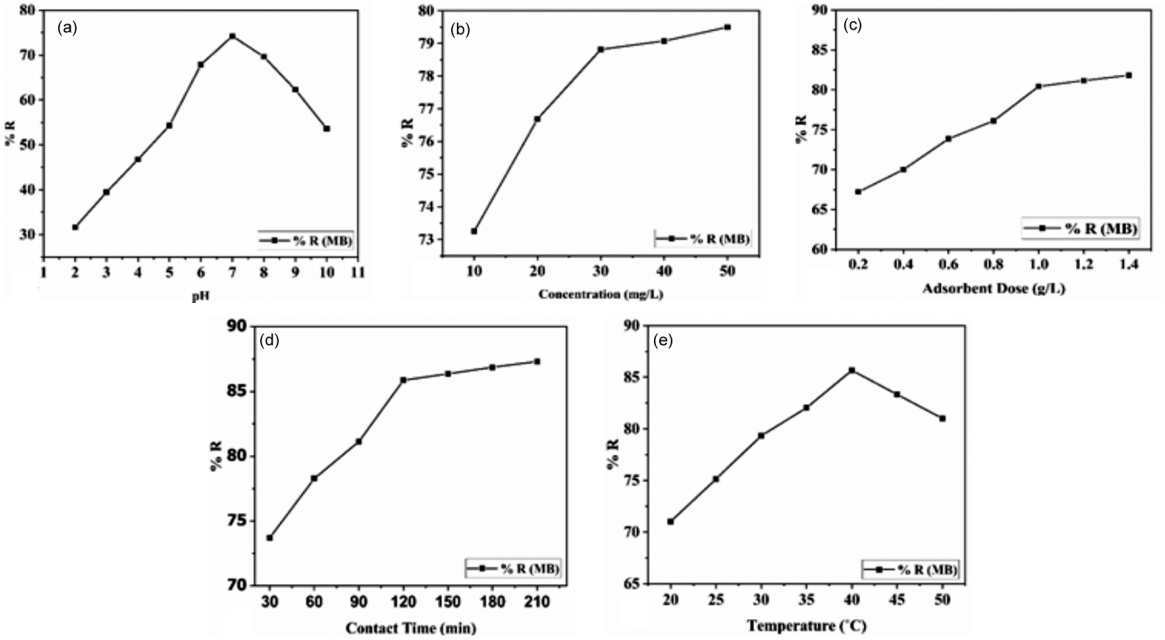

Fig. 4 — Effect of (a) pH, (b) dye concentration, (c) adsorbent dose, (d) contact time (e) temperature on MB adsorption

adsorbent's surface as the pH increased over the pH_{pzc}, which increased the removal effectiveness of MB.

Effect of initial concentration of MB dye

The removal efficacy of CMWS was shown to steadily decline with an increase in MB dye concentration from 10 mg/L to 50 mg/L, with a maximum adsorption of 78.82% reported at 30 mg/L (Fig 4b). Because there are only a fixed number of adsorbent active sites for every concentration of MB dye solution, the removal effectiveness dropped as the concentration of MB dye solution increased [25].

Effect of amount of adsorbents

Fig. 4(c) shows a noticeable increase when the quantity of CMWS was increased from 0.1 g to 1.4 g. At 1.0 g, CMWS showed 80.43% removal. The removal effectiveness decreases as the amount of adsorbent is increased further. The reason behind the decline in removal effectiveness as the concentration of adsorbent is increased, there is the agglomeration of adsorbent particles, which leads to a reduction in the active sites that are accessible for adsorption[26-27]. The removal efficiency was constant as the adsorbent concentration increased. This could be due to a decrease in the gradient of adsorbent species concentration. The saturation of adsorption with increasing adsorbent dosages is caused by the competition of dye molecules for available adsorption sites[24].

Effect of contact time

After increasing the reaction time from 10 to 210 min, CMWS achieved its maximum adsorption of 85.67% in 120 min (Fig. 4(d)). Removal efficiency has been steadily increasing until it reaches a constant value at equilibrium contact time suggesting that the adsorbed MB molecules have virtually saturated the adsorption sites of CMWS. When the adsorbent surface area started to become saturated, the removal rate decreased until equilibrium was established [26]. Similar outcomes were also noted by Parlayici and Aras[27] when MB was removed from aquatic medium using composite beads based on biopolymers. Krishni et al.[28] reported a contact time of 120 min for removal of MB for composites based on banana leaf.

Effect of temperature

The effect of solution temperature on removal of MB dye was determined in temperature range from 10-60℃ by keeping others parameters constant. The maximum efficiency of removal for MB on CMWS was noted to be 85.67 % at 40℃ (Fig. 4e). Increasing the temperature led to an increase in removal efficiency because more molecules had the threshold energy for an effective collision, hence increase the adsorption. At 40°C, MB dye's maximum adsorption capacity (q_m) was 305.3 mg/g [29]. Additionally, the maximum removal of methyl orange from water using anchote peel adsorbent was attained at 40°C [30].

Adsorption isotherms and kinetics

To investigate the kind of cationic dye adsorption on the adsorbent surface, the experimental data was fitted into Langmuir and Freundlich isotherms. The data in Table 1 was better suited to Freundlich isotherms since the R^2 value was nearer 1 as in Fig. 5. It revealed the multilayer adsorption of MB dye on the surface of adsorbent. Using the regression equation y=0.744x+0.567, the linear curve of the Freundlich adsorption isotherm of CMWS showed an R^2 value of 0.9965. The value of calculated maximum adsorptive capacity for CWNS was 66.6 mg/g. The Freundlich isotherm model provided an excellent description of the MB dye adsorption mechanism onto the activated carbon surface of the bamboo chips [29]. Using the pseudo-second-order kinetic model, anchote peel adsorbent was used to remove methyl-orange from water with a removal efficiency of 94.47%. [30].

Table 2 shows the kinetics model parameters description of MB dye adsorption. Both linear and non-linear curves were plotted for pseudo-first and pseudo-second order models in order to model the data kinetically (Fig. 6). The findings showed that the rate was dependent on the adsorbent's adsorptive capacity, which is consistent with pseudo-second order kinetic models. At various doses of 10, 20, 30, 40, and 50 mg/L, the pseudo-second order (Fig. 6-c) linear curve of the adsorbent has R2=0.9992, 0.9993, 0.9995, 0.9995, and 0.9996, respectively. There is also a correlation between pseudo-second order and the literature available for MB adsorption onto different agricultural wastes[31]. The adsorption process for the removal of MB from porous poly(lactic acid)/alkali-treated walnut shell powder composites was in accordance with pseudo-second-order kinetics [32].

Table 1 — Adsorption Isotherm parameters description of MB dye adsorption

Adsorption Isotherm Model	Parameter	MB
Freundlich (non-linear)	1/n	1.1964
	K_F(mg/g)(L/mg)$^{1/n}$	2.4797
	R^2	0.9964
Freundlich (linear)	1/n	1.2659
	K_F(mg/g)(L/mg)$^{1/n}$	2.1599
	R^2	0.9965
Langmuir (non-linear)	q_m(mg/g)	66.3160
	K_L(L/mg)	0.0563
	R^2	0.9721
Langmuir (linear)	q_m(mg/g)	54.0540
	K_L(L/mg)	0.0453
	R^2	0.9920

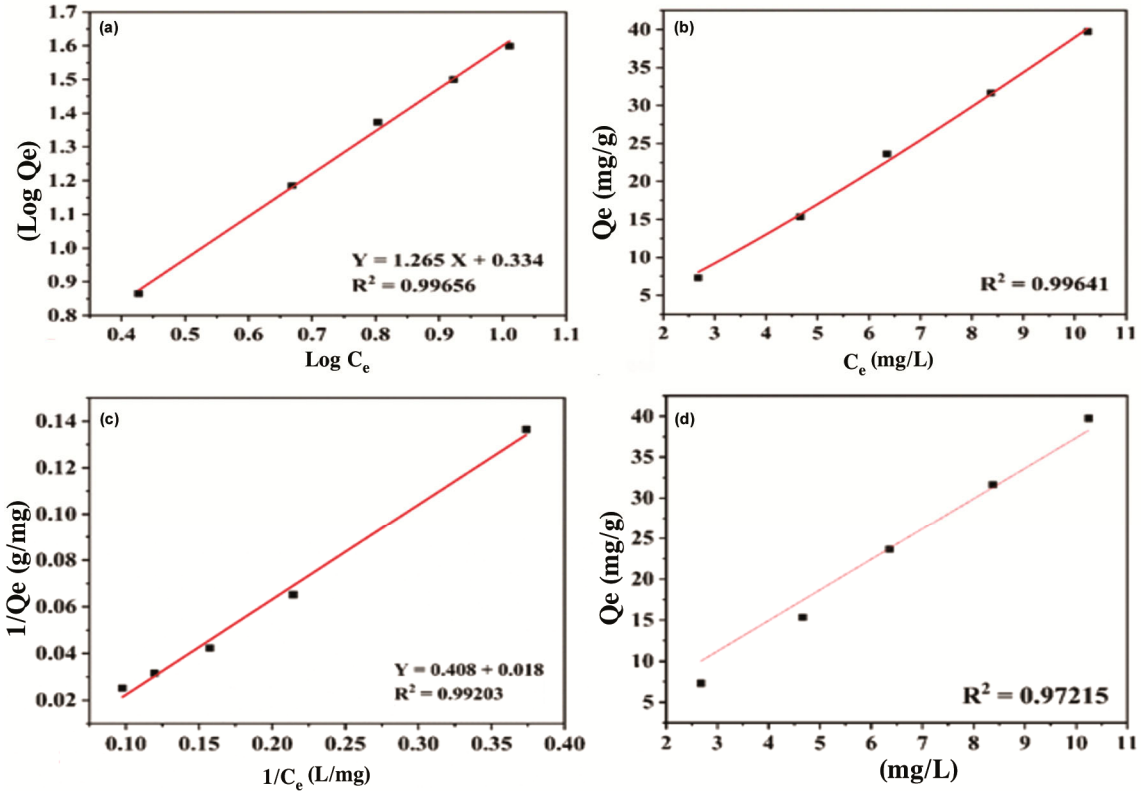

Fig. 5 — Freundlich (a) linear & (b) nonlinear; Langmuir (c) linear & (d) nonlinear plot for CMWS

Table 2 — Kinetics model parameters description of MB dye adsorption

Kinetic models	Parameter	10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L
PFO(non-linear)	$q_{e,cal}$ (mg/g)	8.442	17.0610	25.7292	34.6437	43.6704
	K_1 (min^{-1})	0.3893	0.0409	0.0434	0.0468	0.0495
	R^2	0.8322	0.8085	0.8101	0.7850	0.8187
PFO(linear)	$q_{e,cal}$(mg/g)	24.100	116.95	348.56	1675.8	1283.2
	K_1 (min^{-1})	0.0327	0.0345	0.0391	0.0565	0.0439
	R^2	0.9817	0.9898	0.9958	0.9362	0.9673
PSO(non-linear)	$q_{e,cal}$ (mg/g)	9.4311	18.8250	28.2224	37.7146	47.2242
	K_2(g/mg min^{-1})	0.0065	0.0035	0.0025	0.0021	0.0019
	R^2	0.9690	0.9622	0.9736	0.9713	0.9847
PSO(linear)	$q_{e,cal}$ (mg/g)	9.5192	1.1729	1.5748	38.2995	47.8011
	K_2 (g/mg min^{-1})	0.0060	0.8467	0.7545	0.0018	0.0016
	R^2	0.9992	0.9993	0.9995	0.9995	0.9996

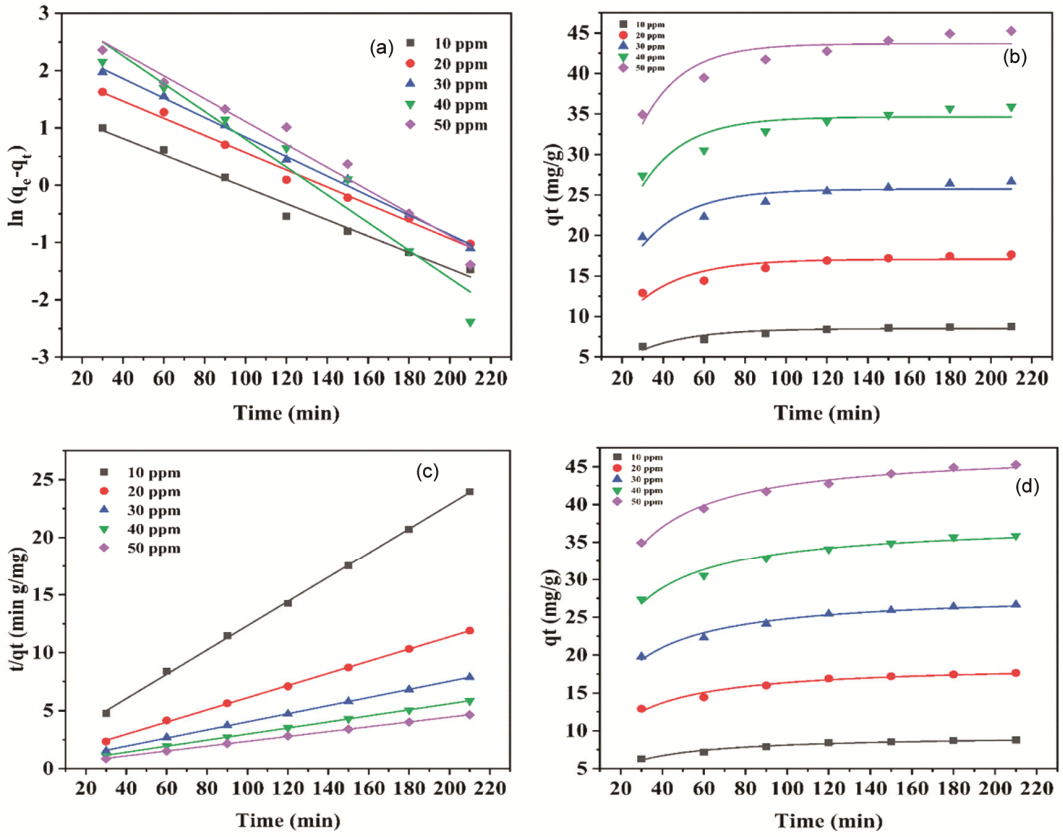

Fig. 6 — Pseudo-first-order (a) linear (b) non linear, pseudo-second-order (c) linear and (d) non linear plots for CMWS

Table 3 — Thermodynamic parameters description of MB dye adsorption

Temperature (K)	1/T	K_L	ln K_L	ΔG° (kJ mol^{-1})	R^2	ΔH° (kJ mol^{-1})	ΔS° (J $K^{-1}mol^{-1}$)
293	0.0034	1.2304	0.2074	-0.5052	0.9944	24.0248	83.5747
303	0.0033	1.6501	0.5008	-1.2617			
313	0.0031	2.2119	0.7938	-2.0659			
323	0.0030	3.0927	1.1290	-3.0320			

Thermodynamic study

Table 3 contains the experimentally determined thermodynamic parameters. The adsorption of dyes by CMWS occurs spontaneously, as indicated by the negative ΔG^o value. A higher temperature indicates a greater favourable environment for adsorption, as indicated by the increase in the negative absolute value ΔG^o. The reaction is endothermic, as indicated by the positive value of $\Delta H°$. However, the solid-liquid interphase exhibits a rise in molecular randomisation as

indicated by the positive ΔS^o [25]. Because most adsorption processes are endothermic, contact with the adsorbent is beneficial because the dye molecules move more actively at higher temperatures [33-35].

The CMWS adsorbent was used for MB at optimized parameters, and after that, it was regenerated by drying at 60°C and washing with 0.1 M NaOH. In order to determine reusability, the dried adsorbent was utilized once again for adsorption. After conducting the study for a maximum of four cycles, it was determined that the CMWS adsorbent could maintain its adsorptive efficiency for a maximum of four cycles (Fig. 7).

Application for real waste water samples

The samples of wastewater were collected from the dye industry in Panipat district in Haryana, India. MB was extracted from actual wastewater samples using the chemically altered walnut shell. It was found that the initial MB content in actual effluent was 30 mg L^{-1}. On real wastewater samples, the produced CMWS adsorbent was able to extract MB at a rate of over 85%, with a final concentration of 0.075 mg L^{-1}.

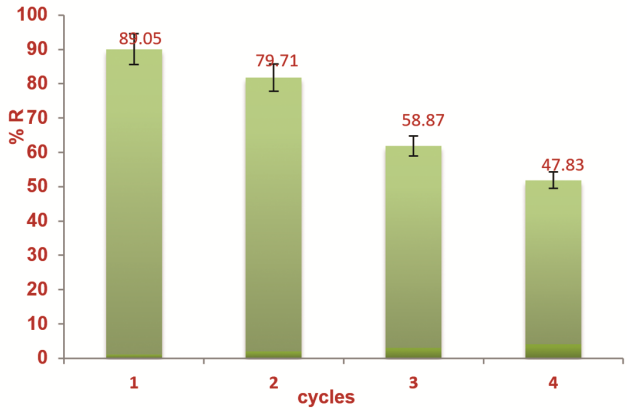

Fig. 7 — Reusability of CMWS adsorbent for MB adsorption

Adsorption mechanism

The process parameters that determine the mechanism of cationic dye adsorption include pH_{pzc}, solution pH, surface functional groups, and adsorbent porosity [35].The negatively charged chemically modified walnut shell attracts the molecules of MB dye *via* electrostatic forces (Fig. 8). The hydroxyl (-OH) and negatively charged carboxyl ($-COO^-$) groups on the adsorbent surface interact with the cationic dye molecules at pH >pH_{pzc}. Hydrogen bonds are also involved between the carboxyl (–COOH) group and water molecules on the adsorbent's surface may be exposed to produce a hydrogen bond with the polar N– atoms of the MB dye when the adsorbent's pH is less than pH_{pzc}. The adsorption of cationic dye molecules onto the adsorbent is also regulated by the π-π interaction. The adsorbent possesses an aromatic structure with a C=C bond π-system and the π-electron of the aromatic ring of MB dye were in contact with it through a π-π interaction. In addition to physical processes, the porous structure of CMWS raises the possibility that cationic dye molecules may also be absorbed by pore filling or diffusion. The FTIR analyses of the adsorbent performed before and after adsorption with cationic dyes revealed that the

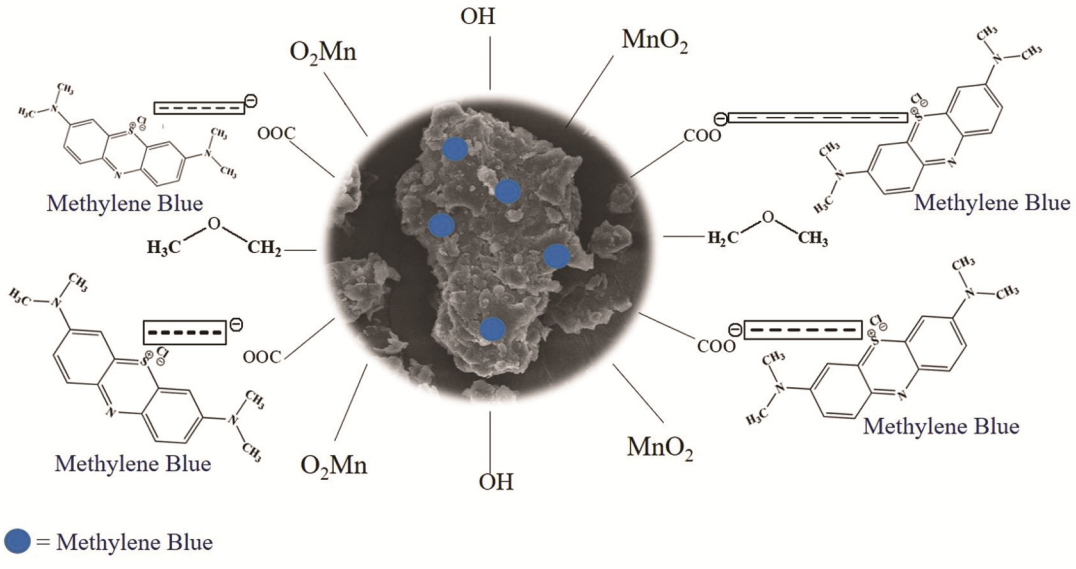

Fig. 8 — Possible Mechanism for the adsorption of MB on CMSW surface

Table 4 — Comparative removal capacity of MB removal using different biosorbents

Adsorbent	pH	Concentration range(mg/L)	Adsorbent dose(g/L)	Isotherms	Uptake capacity (mg/g)	Kinetics	References
Alkali treated walnut shell	11	100	-	Langmuir	56.75	Pseudo second order	39
Walnut tree waste based composite	3-8	10-250	2-10	Langmuir	85.47	Pseudo second order	40
Olive tree waste based composite	3-8	10-250	2-10	Langmuir	53.48	Pseudo second order	40
Walnut shell	8.5	60	60	Langmuir	50.00	Pseudo second order	41
Walnut shell	5	15	0.1	Langmuir	96.76	Pseudo second order	42
Walnut shell	-	60	-	Langmuir	50.47	Pseudo second order	43
Macrolepiota procera mushroom biomass	9	14	20	Langmuir	51.11	Pseudo second order	44
Modified Walnut shell	6	10-50	1-4	Freundlich	66.6	Pseudo second order	Present study

functional groups of the adsorbent bonded with the cationic dye molecules via hydrogen bonding, π-π interaction, and electrostatic contact [36-37].

Comparison with other biosorbents

The comparison of CMWS adsorption effectiveness with that of other adsorbents is summarized in Table 4. The CMWS adsorbent's q_m value for MB was 66.6 mg g^{-1}, indicating that it is one of the efficient adsorbents for removing MB from industrial wastewater. When compared to other adsorbents, CMWS offers the advantages of a comparable adsorption effectiveness of over 90% and a low cost of production. The high adsorbent efficiency may be due to the existence of several functional groups, such as -OH, -COO-, -C=O, etc., which interact chemically with dyes.

Conclusion

From the perspective of sustainability and the environment, dye removal from water bodies is essential. Experimental conditions were optimised for MB dye removal using CMWS. The best fit between the kinetics of MB dye utilising chemically modified walnut shells is believed to be pseudo-second order. The alkaline oxidative modified walnut shell demonstrated multilayer adsorption for MB dye, meaning that Freundlich was the best-fitted isotherm. After MB dye loading, CMWS's glossy, smooth surface becomes rough and the holes are filled and covered, resulting in an important shift in the material's surface morphology. Accordingly, this investigation showed that CMWS was used to adsorber MB dye through hydrogen bonding, pore fills, and electrostatic attraction. This study came to a conclusion with more suggestions for MB dye removal with walnut shells that are worthwhile investigating. However, batch experimentation is a major component of the present literature. In order to examine situations, that more nearly represent real-world circumstances, it is recommended that future research will be conducted using actual wastewater collected from different places, each with varying levels of contaminants. The impact of impurities and interfering ions in an actual aquatic environment that may significantly reduce sorption capacity will therefore be closely examined. Future research should also examine the process's scalability for industrial applications, with an emphasis on resolving issues with regeneration efficiency. To ascertain the process's economic viability, it will also be crucial to assess its cost implications.

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