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Modified rice husk polymeric hydrogel as biodegradable adsorbent for the effective removal of organic pollutant methylene blue dye

Aakriti Verma[1], Malvika Chaudhary[2], Parul Verma[3], Sajid Ali[4], Kushagra Rajendra[1] & Kalpana Singh[5]*

[1]Amity School of Earth and Environmental Sciences, Amity University Manesar, Panchgaon, Gurugram-122412, India

[2]Department of Applied Science and Humanities, Delhi Technical Campus, Greater Noida

[3]Department of Applied Science and Humanities, Ajay Kumar Garg Engineering College, Ghaziabad-201009, India

[4]Department of Chemistry, Maulana Azad National Urdu University Polytechnic, Bangalore-560072, India

[5]Lloyd Institute of Management and Technology, Plot No.11, Knowledge Park-II, Greater Noida-201306, India

*E-mail: kalp.sing23@gmail.com

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Rice husk, sourced from a local processing mill, has been utilized in crafting biodegradable adsorbents: plain rice husk (PRH) and modified rice husk (MRH) polymeric hydrogels. To delve into their structure and morphology, FT-IR and SEM analyses have been conducted. These analyses shed light on the functional groups and structural arrangements, crucial for understanding the adsorption process, particularly for cationic methylene blue (MB) dye removal from water. Batch experiments explored varying parameters such as pH (ranging from 2 to 9), time (up to 300 min), adsorbent dose (0.12 to 0.5 g), and dye concentration (60-120 mg/L). Both PRH and MRH hydrogels demonstrated efficacy in removing methylene blue dye, especially within a time frame of 300 min at 100 mg/L concentration. The efficiency of PRH and MRH hydrogels for MB adsorption was notably high, reaching 85% (315 mg/g) and 90% (333 mg/g), respectively, at 0.37 g of polymeric hydrogel. Results indicated that MB adsorption increased with rising initial concentrations and extended time durations, plateauing at 300 min. Additionally, higher doses of adsorbent enhanced MB removal. The Freundlich isotherm model fitting the equilibrium adsorption data suggested a pseudo-second-order model, indicating monolayer adsorption without an upper coverage limit. This model elucidated surface heterogeneity and the exponential distribution of active site energy. Overall, the study demonstrates the potential of utilizing rice husk-derived hydrogels as effective adsorbents for water purification, with insights into their structural characteristics and adsorption mechanisms, critical for further applications in environmental remediation.

Keyword: Adsorption, Biodegradable adsorbent, Hydrogel, Methylene Blue Dye, Rice husk

Introduction

Over several decades, environmentalists have been extremely worried about the percolation of textile effluents into streams and groundwater systems. Textile, paper, leather, culinary, printing, and plastics industries widely release dyes into the environment[1,2], causing serious soil and water pollution due to biological degradation. Despite their negative impacts, dyes remain an important and major class of chemicals. Methylene blue (MB), one of the many dyes, is known to show resilience to light and oxidation reactions. MB is a cationic dye that is used for different purposes for example as an indicator, biology laboratories for stain, medical science, and dyeing industries. Long-term exposure to MB can lead to cause numerous health issues like vomiting, anemia, and hypertension[3]. According to Ghorai *et al*.[2], Cai *et al*.[4] and Yang & Luan[5], MB is used in the textile industry and is poisonous, carcinogenic and non-biodegradable. It is an environmentally hazardous material that must be removed from the water.

The conventional methods for removing methylene blue from water are expensive and often leave residuals that can poserisks to human and aquatic life. To address this challenge, researchers have been exploring new materials and techniques to remediate contaminated water. Rice husk, an agricultural waste material, has emerged as a promising source for the production of environmentally friendly hydrogels with excellent water absorption and retention properties. Various chemical, physical and biological methods, like biosorption, coagulation/ flocculation, adsorption, ozonation, liquid–liquid extraction, advanced oxidation, and membrane filtration, etc. have been engaged to remove methylene blue from

aqueous solutions. All these techniques have a few advantages and disadvantages associated with them[6]. A lot of study has been has been going on to develop economical and abundantly available adsorbents. Agricultural wastes are a suitable adsorbent for the removal of dyes from wastewater due to their properties (physical and chemical) and cost-effectiveness[7]. Since agricultural wastes are the non-product outputs, available in huge quantities and mostly rejected as waste, they can be used to develop a potent bio-adsorbents. These bio-materials comprise a range of polysaccharides mainly containing lignin, hemicelluloses, and cellulose having a high molecular weight and thereby providing mass to the adsorbent.

Various adsorbents which can remove dyes from wastewater have been developed from plant produce namely, pomelo peel, Guava leaves, broad bean peels, Gulmohar plant leaf powder, papaya seeds, rubber seed shell, pumpkin seed hull, pine apple stem, castor seed shell, coffee husks, garlic peel, coconut husk, peanut hull, jute waste wheat straw, Neem leaf powder, *etc*.[8]. These locally found produce waste, is converted to activated charcoal which is further modified to be used as an adsorbent with higher efficacy. Although a lot of literature is available on various applications of such low-cost agricultural adsorbents.For further work, a comparative analysis of various adsorbents' efficiency is always interesting[9]. MB dye is an acidic dye finding extensive applications in the aqueous medium. Recent years have reported, rice husk as an economical agricultural waste to be synthesized as a bio-adsorbent for the removal of methylene blue[10] from the effluents. Rice husk is a producewaste of rice that has an annual production of approximately 500 million metric tons worldwide, of which 10–20% is rice husk. Dry rice husk consists of lignin, cellulose, sugars, *etc*. which comprise70–85% of their organic matterand the rest of the matter consists of silica, finding presence in the cellular membrane[11]. Modified and unmodified rice husk have been used as an adsorbent for the removal of pollutants from wastewater[12]. This study aims to investigate the potential of rice husk-derived hydrogel as a potent polymeric modification for the selective reversal of methylene blue from contaminated sources. In this research, rice husk has been used to develop a novel bio adsorbent named plain rice husk (PRH) and modified rice husk (MRH) by carrying out carboxymethylation. Batch studies were performed using rice husk hydrogel for the adsorption of methylene blue along with the investigative study of the effects of varying different parameters such as initial dye concentration, time, and adsorbent dosage on theamount of dye adsorbed.

Experimental Section

Materials

The rice husk was obtained from a local rice mill. It was washed 6 to 7 times with distilled water and dried for over a night in an oven at 35-40°C. It was then grinded and sieved to obtain a fine powder which was stored in a jar in anhydrous condition for further use. All the reagents used were of analytical grade and used without further purification. MB dye (λ_{max} = 668 nm), chloroacetic acid, hydrochloric acid (35%), sodium hydroxide (97%), acetic acid (35%), methanol, ammonium persulfate (1%), N,N-bisacrylamide, acrylic acid and acetone were purchased from Merck Ltd., India. Double distilled water was used to prepare standard dye solutions. 0.5 M HCl and 0.5 M NaOH solution were used to prepare the solutions of different pH. The studies were carried out using exclusively distilled water.

Synthesis of Rice Husk Hydrogel

A mixture of rice husk (10 g) and sodium hydroxide (50 mL) stirred for one hour at 120 rpm. Chloroacetic acid (14 g) was added slowly over a period of 30 min. The reaction mixture was continuously refluxed and the temperature was maintained at 70°C by keeping it in an oil bath. After this, the temperature gradually decreased to room temperature and acetic acid (5 mL) and methanol (4 mL) were added to neutralize the reaction mixture. This reaction is a process of carboxymethylation and product obtained is known as a carboxymethylated mixture. This mixture was grafted with the initiator (ammonium persulfate (1%)), cross-linker (N,N-bisacrylamide (5%)), and water for 3 h[13].The reaction mixture was thoroughly rinsed with double-distilled water and acetone (5 mL) and rested for one hour to eliminate surplus water. It was further dried in a vacuum oven.

Synthesis of Modified Rice Husk Hydrogel

As shown in Fig. 1, carboxymethylation process was carried out. The carboxymethylated mixture was grafted with acrylic acid (10 g), ammonium persulphate (1%) as initiator and N,N,-bisacrylamide (5%) as a cross-linker by stirring in water (20 mL) at 50°C for 3 h. Finally, the yellow colour hydrogel

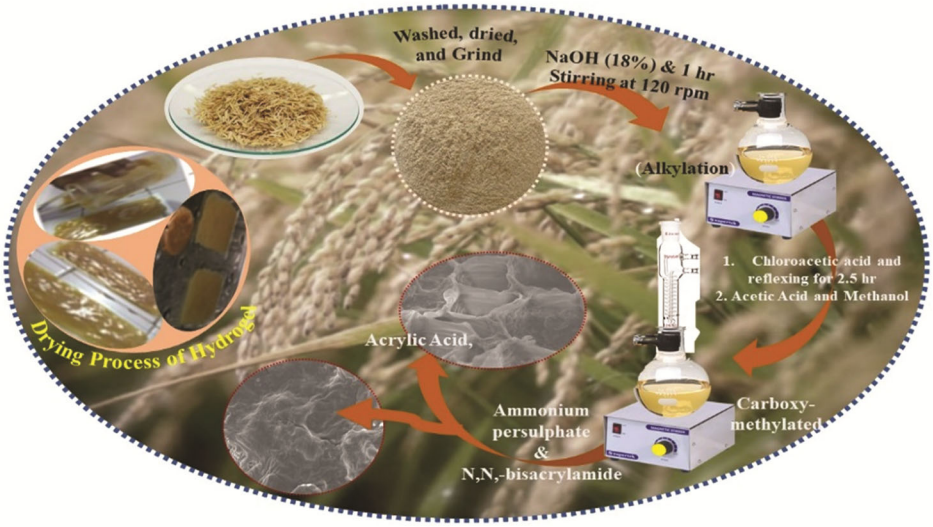

Fig. 1 — Carboxymethylation process of rice husk hydrogel (RH) and modified rice husk (MRH) with acrylic acid

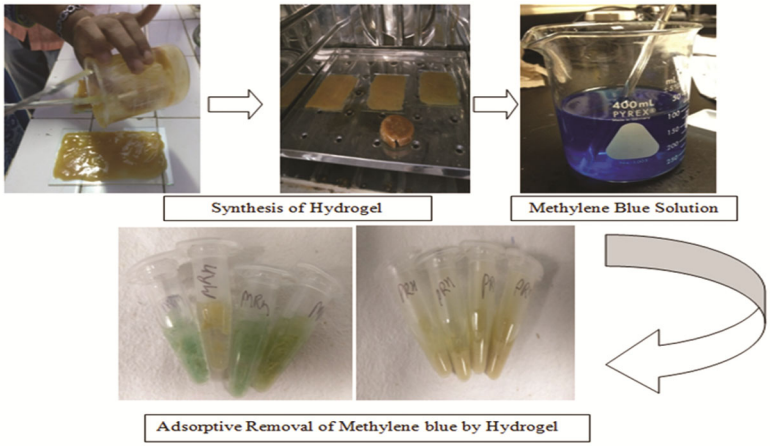

Fig. 2 —Batch Experiment for adsorption of methylene blue

material was obtained which was thoroughly washed with double-distilled water and acetone (5 mL) to eliminate surplus water.It was further dried in a vacuum oven.

Characterization

Fourier transforms infrared (FTIR) spectra of the samples were captured by a Thermo-Fisher NICOLET IS50 FTIR spectrometer using KBr pellets in the 400–4000 cm^{-1} range. Diffraction spectra and pictures were recorded using scanning electron microscopy (Bruker D8 Discover) with Cu as the X-ray source. Perkin Elmer UV-visible spectrometer was used to record the absorption spectra.

Application of MRH Hydrogel for Dye Adsorption

Adsorption studies by the batch adsorption method were conducted with a variable dose of adsorbent, pH, dye concentration, and time for adsorption in order to evaluate the behaviour of the dye adsorption process on MRH Hydrogel.The batch adsorption experiments were carried out using 250 mL of Erlenmeyer flask containing 0.01 g of adsorbent and 100 mL of MB solution of varying concentrations (Fig. 2). The flasks were agitated on a rotary shaker at 120 rpm at room temperature. After decantation and filtration, the concentrations of MB in the solution were measured at 665 nm using a UV-visible spectrophotometer. The pH of the solution was varied using 0.5 N HCl and 0.5 N NaOH solutions to evaluate the impact of pH on adsorption. The following equations were respectively used to calculate, the amount of dye adsorbed and the percentage of MB dye removed:

$$q_{max} = \frac{(C_o - C_e)V}{m} \quad \ldots(1)$$

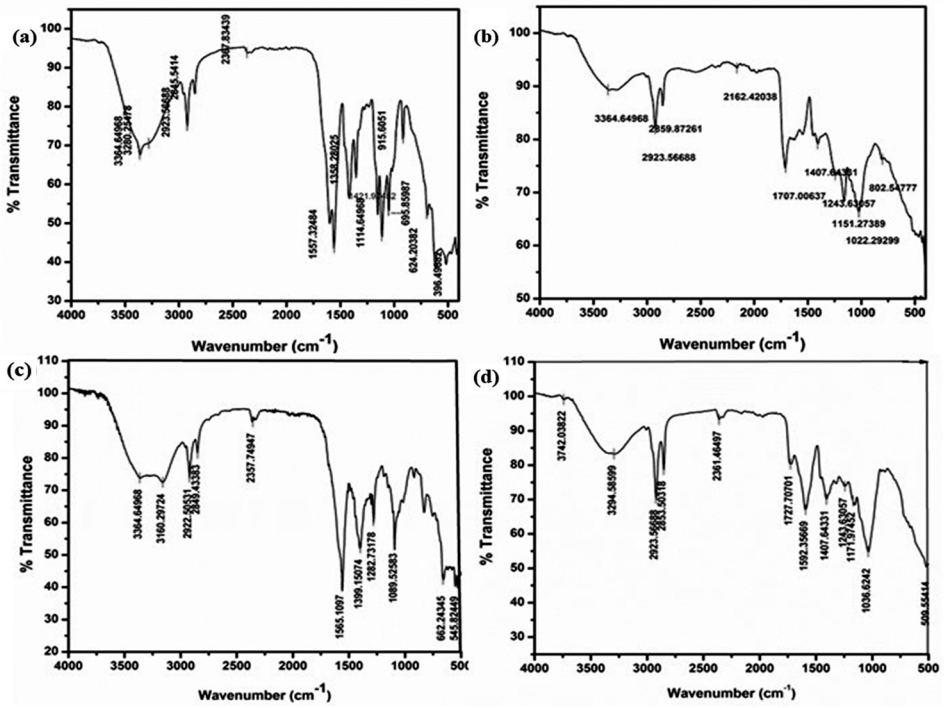

Fig. 3 — FTIR spectra for (a and b) before dye adsorption and (c and d) after dye adsorption in PRH & MRH hydrogels, respectively

$$Adsorption\ \% = (\frac{C_o - C_e}{C_o}) * 100 \quad \ldots(2)$$

The content of the dye adsorbed at equilibrium, q_e (mg/g) defined as equilibrium adsorption capacity, and the adsorption percentage were calculated from the Eqs (1) and (2), respectively, where C_o and C_e are the initial and equilibrium concentrations of MB in solution mg/L, respectively, m is the mass of the adsorbent in g and V is the volume of solution in L.

Desorption experiment

The adsorption of MB dye was done by the addition of 0.01 g of adsorbent PRH and MRH in two batches of experiments to a solution of MB (25 mL, 50 mg L^{-1}) and shaking the mixture for 3 h at 25°C in the orbital shaker. The adsorbents RH and MRH loaded with adsorbed MB were filtered and separated after centrifugation and washed with distilled water. The isolated MB-loaded adsorbent was then treated with the solution of HC1 (25 mL, 0.5 M) for desorption by shaking for 12 h at room temperature. The concentration of desorbed MB in the solution was determined using UV-visible spectroscopy. The adsorbent was filtered, washed with distilled water, and isolated. It was allowed to dry for further use.

Results and Discussion

Characterizations

FTIR study conducted to investigate the formation of hydrogels and the functional groups responsible for the removal of MB dye by adsorbents (PRH & MRH hydrogel) and the spectra are presented in Fig. 3a-d.

In Fig. 3a, the absorption peaks around 3280.25 cm^{-1} and 3364.64 cm^{-1} indicate the presence of bonded and free hydroxyl groups. The peaks around 2923.56 cm^{-1} and 2845.54 cm^{-1}correspond to the C-H stretching mode, and 1421.97 cm^{-1} and 1358.28 cm^{-1}peaks are proof of the presence of carboxyl groups[14]. Fig. 3b, shows a big hump at 3364.64 cm^{-1}indicating the presence of hydroxyl groups in modified rice husk hydrogel which is responsible for interaction with other molecules. Two intense peaks observed at 2859.87 cm^{-1} and 2923.56 cm^{-1} correspond to C-H stretching vibrational mode. Peaks at 1707.01 cm^{-1} indicates the presence of a carboxylic group. It can be concluded that carboxylic group participates in adsorption process as the peak shifts from 1706.01 to 1606.70 cm^{-1} in the spectrum observed after the adsorption of dye. In the spectrum of chemically modified rice husk (MRH) hydrogel Peaks at 1151.27 and 1022.29 cm^{-1} correspond to Si-O-C and Si-O-Si groups, respectively [15].

As shown in Fig. 3c, some bands are showing bathochromic shift i.e., 1421.97 cm^{-1} to 1565.11 cm^{-1} and 1358.28 $cm^{-1}$to 1399.00 cm^{-1} due to the adsorption of methylene blue molecules on the surface of the adsorbent (Plain rice husk hydrogel). The presence of the carboxylic group favours the absorption of the dye[16], which is indicated by the peak at 1507.40 cm^{-1}. The peak at 1089.52 cm^{-1} is due to the presence of silica groups Si-O-Si or silicone groups, and peak at 662.24 cm^{-1} is due to in the plane bending of C-H bond[17].

In MRH hydrogel after the adsorption of MB (Fig. 3d), the peaks are shifted from 3364.64 cm^{-1} to 3742.04 cm^{-1} which corresponds to OH-stretching mode. Peaks at 2923.57 cm^{-1} and 2853.51 cm^{-1} correspond to the bending vibration of the C-H bond in the CH_3 group. Adsorption bands of carboxyl groups are observed at 1727.71 cm^{-1} and 1592.36 cm^{-1}. The peaks at 1407.64 cm^{-1} and 1243.64 cm^{-1} correspond to the stretching vibration mode of C-O from the carboxyl group[18].

SEM was used to examine and contrast the surface morphological changes that took place throughout the adsorption process. It is clear from the micrographs that PRH (Fig. 4a) displayed a wrinkled and fibrous morphology with a porous surface texture prior to MB adsorption. Many crack-like structures were also observed, which may be responsible for MB penetration and ultimately caused the hydrogel to swell and enlarge. Its creased surface composition can increase the PRH's spatial arrangements of surface area, which in turn leads to an increase in the capacity for MB and water absorption.The porosity in the network structure is increased in the modified rice husk hydrogel with acrylic acid (Fig 4c), making the surface morphology more favourable towards increased adsorption. This allows for enhanced MB diffusion across the hydrogel in the polymeric network, boosting MB adsorption[19].

The SEM images of the rice husk hydrogel and the acrylic acid modified hydrogel after adsorption of MB showed that the surface morphology of the two materials was significantly different. The images revealed that the surface of the modified rice husk hydrogel (Fig 4c) was smoother and more uniform compared to the surface of the plain rice husk hydrogel (Fig. 4a). This difference in surface morphology is likely due to the modification of the hydrogel with acrylic acid, which changed the surface properties of the material.

Additionally, the SEM images showed that the size and distribution of the MB particles adsorbed onto the surface of MRH hydrogel (Fig. 4d) were more uniform compared to the PRH hydrogel (Fig. 4b). This suggests that the acrylic acid modification improved the adsorption capacity and efficiency of the hydrogel.

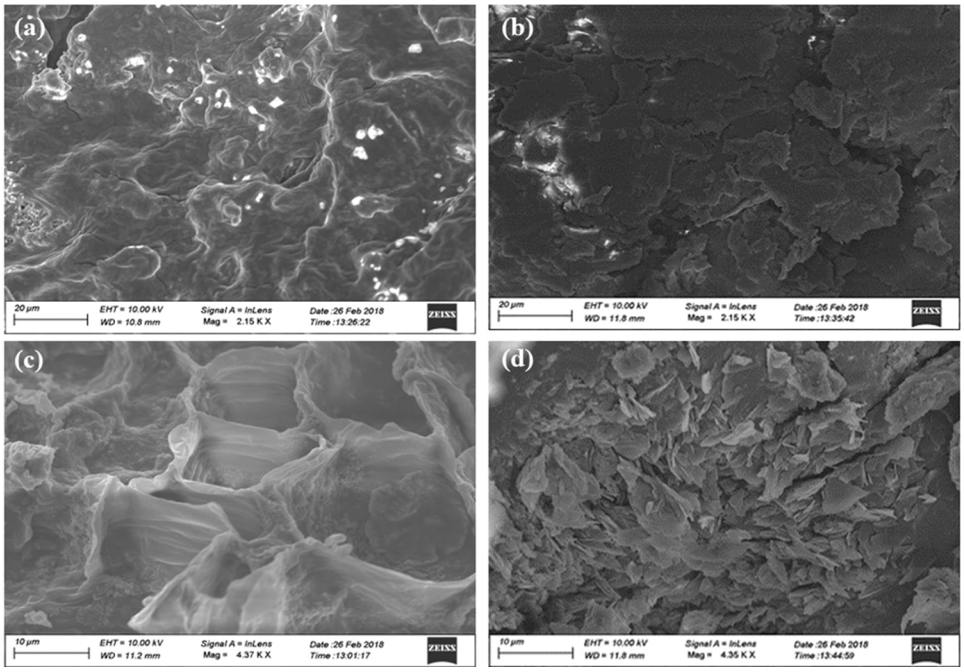

Fig. 4 — SEM images of (a and c) before dye adsorption and (b and d) after dye adsorption in PRH & MRH hydrogels, respectively

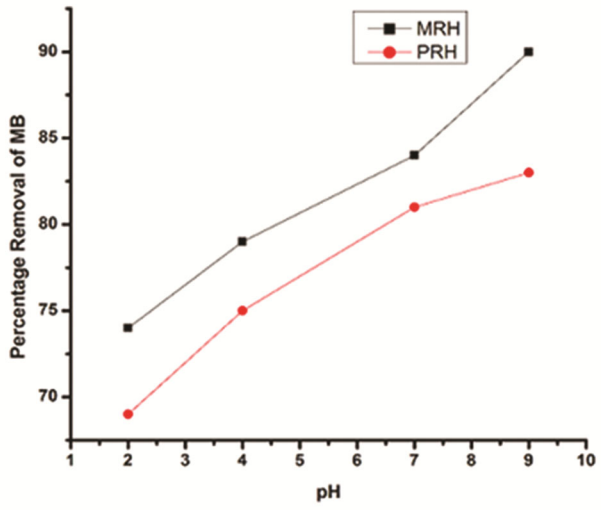

Fig. 5 — Effect of pH on PRH and MRH hydrogel for MB adsorption process

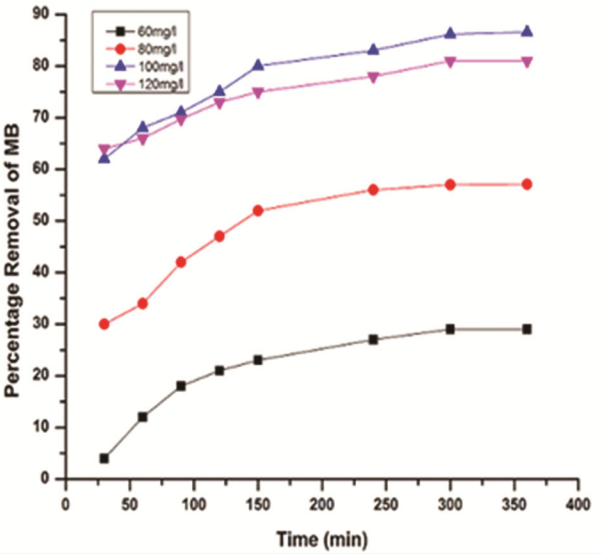

Fig. 6 — Effect of concentration on MRH hydrogel for MB dye adsorption process

Effect of pH on MB adsorption

The pH of dye solution plays an important role in the adsorption of dye as it influences charge density on the surface of the adsorbent. At pH 2 with 0.37g of adsorbent dose, 68% of MB is removed by PRH and 73% by MRH. When the pH of the dye solution is increased from 2 to 9, the adsorption of MB is found to increase to 90% by MRH from 85% by PRH. Therefore, maximum MB removal was observed at pH 9. The basic cationic dye when dissolved in water releases positively charged ions in the solution. Thus, in an acidic medium or at lower pH, the adsorbent surface having a positive charge opposes the

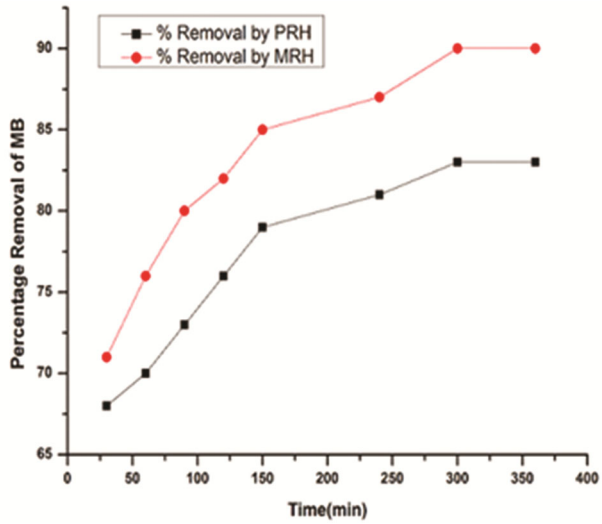

Fig. 7 — Effect of contact time on Methylene blue dye removal using PRH and MRH

adsorption of the adsorbate which is cationic in nature (Fig. 5). The adsorbent surface becomes negatively charged, at the higher pH of the dye solution, resulting in enhanced adsorption of MB. This is because of the significant increase in electrostatic interaction between the positively charged dye and the negatively charged adsorbent surface[19,20].

Effect of MB concentration on MRH Hydrogel

The effect of dye concentration on the adsorption of MB onto the surface of MRH hydrogel (0.5 g/L) was done at pH 9 and varying concentrations of MB from 60-120 mg/L at different time intervals was studied and the results are shown in Fig. 6. Equilibrium adsorption capacity increased with an increase in MB concentration because the driving force for mass transfer also increases with the increased dye concentration. The observations from the graph indicate that the maximum removal of MB was observed at 100 mg/L until 300 min; at pH 9 and an adsorbent dose of 0.5 g/L.

Effect of contact time on MRH hydrogel for adsorption process

85-90% of MB removal takes place by using MRH with an adsorbent dose of 0.37 g and a state of equilibrium is attained after 300 min. This transition in the rate of removal of dye can be explained by the fact that in the beginning, the sites of the adsorbent are free for dye adsorption and the gradient of solute concentration is also high to facilitate the process of adsorption. However, the rate of adsorption tends to decline as the number of vacant sites on the surface of the adsorbent decreases (Fig. 7). Due to the formation

Table 1 — Comparison of MB adsorption capacities on different adsorbents

S. No.	Adsorbent	Initial MB conc. (mg/L)	MB adsorption capacity (mg/g)	Ref.
1	sodium alginite/cellolose	100	328.36	22
2	Carboxymethylcellulose/Poly acrylic acid/ Graphene oxide	100	138.4	17
3	Pineapple peel carboxymethyl cellulose/acrylic acid/Acrylamide/graphene oxide	200	133.32	23
4	Cellulose/activated carbon	100	103.66	24
5	SAP-AC	50	213.2	25
6	PRH	0.37	315	Current study
7	MRH	0.37	333	Current study

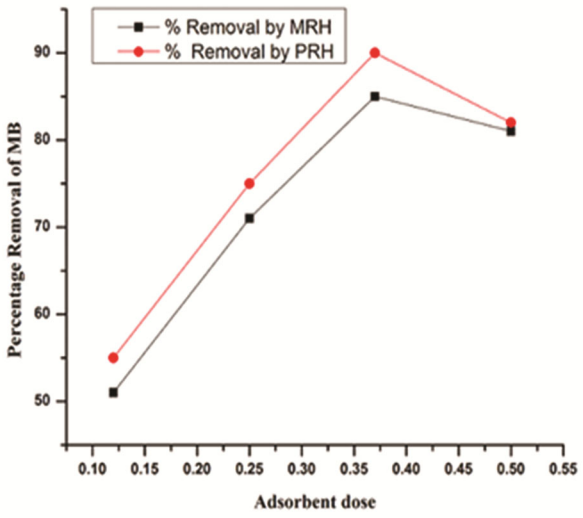

Fig. 8 — Effect of adsorbent dosage (PRH and MRH Hydrogel) for MB adsorption process

of a layer of MB on the surface of the adsorbent, the rate of adsorption tends to decrease. Lack of active site available on the surface of the adsorbent no further uptake of MB becomes possible after 300 min and hence equilibrium is attained.

Effect of adsorbent dose on MB adsorption

To investigate the effect of adsorbent dosage on MB removal, varying doses of MRH hydrogel were taken from 0.12 to 0.5 g in 100 ppm of MB solution at pH 9. At 0.12 g of adsorbent dose maximum adsorption of 55% was obtained by MRH and 43% by PRH till 300 min. It is clearly shown through the obtained graph that the MB removal tends to increase with an increase in the adsorbent dose from 0.12 to 0.5 g. This is due to the presence of more binding sites on the surface of the adsorbent as well as greater surface availability. However, no significant increase in removal efficiency was observed beyond 0.37 g of adsorbent dose (Fig. 8). At 100 ppm concentration of MB solution, when 0.37g of adsorbent was used, the maximum adsorption observed was 85% by PRH and 90% by MRH till 300 min. Thereafter no further adsorption was observed. This can be due to the agglomeration of adsorbent particles on the surface as there is no increase in the effective surface area of a hydrogel. Therefore, 0.37 g of hydrogel is considered the optimal dose for dye removal thereafter the adsorption tends to decrease and becomes constant.

Comparison with other adsorbents

Table 1 compares the MB adsorption capacity between the current study and earlier studies that have been published in the literature. It is evident that at various initial MB concentrations, the MB adsorption capabilities observed in the current study were significantly higher. Furthermore, the adsorption of MB reached maximum values of 90% (333 mg/g) for MRH and 85% (315 mg/g) for PRH.

Kinetic Study

The linear version of Lagergren's pseudo-first-order[26] (Eq. 3) was applied to study the kinetics of MB adsorption:

$$lnC_e = lnC_o - K_1 t \quad \ldots(3)$$

C_o and C_e are the initial and final concentrations of dye solution at time t. K_1 (min^{-1}) is the rate constant of the adsorption process for pseudo-first-order. K_1 can be determined from Fig. 9a which indicate the linear plots between ln(C_e) *vs.* t.

It is noticeable from the low correlation coefficients (R_2) that the process did not follow Lagergren's first-order model. In order to model the data, a pseudo-second-order kinetic equation (Eq. 4) was used[27].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} - \frac{t}{q_e} \quad \ldots(4)$$

The rate constant for pseudo-second-order kinetic models at 27°C is given in Eq. (4) as K_2 (g/mg/min). The intercept and slope of the plot of $1/C_e$ *vs.* t, as depicted in Fig. 9b, can be used to determine K_2 and C_o. The pseudo-second-order correlation coefficient

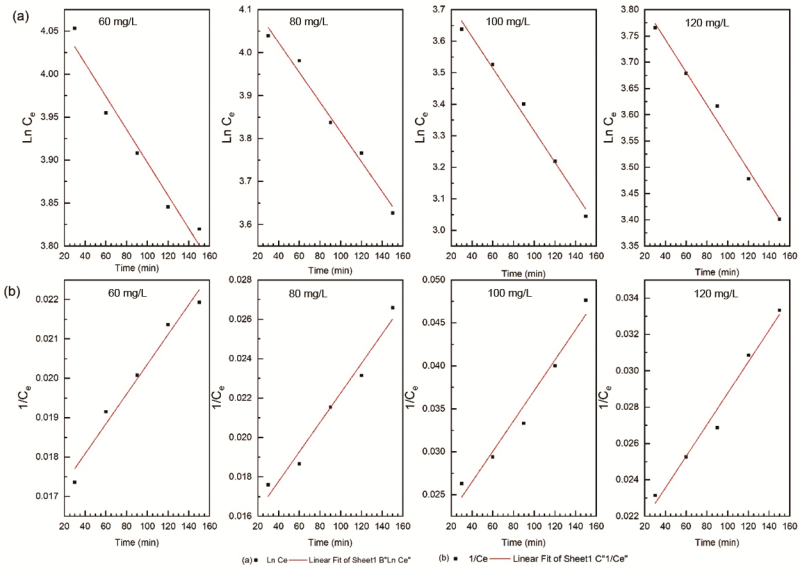

Fig. 9 — (a) Lagergren's pseudo-first and (b) pseudo-second-order, linear plots for the adsorption of dyes onto MRH at different concentrations of dye solution (60, 80, 100, 120 mg/L)

Table 2 — Regression Coefficient for the pseudo-first and second-order models for different concentrations

Dye conc. (mg/L)	Regression Coefficient (R_2)	
	First Order	Second Order
60	0.808	0.98
80	0.866	0.956
100	0.942	0.994
120	0.954	0.998

values for MB at various concentrations were 0.98, 0.956, 0.994, and 0.998, indicating that the kinetic adsorption model, as presented in Table 2, fit the data well.

The experimental data in Fig. 10 were used to further recalculate and confirm the suitability of pseudo-second-order and first order to characterize the adsorption kinetic data.

Isotherm Study

Langmuir and Freundlich Isotherm established the experimental data for dye uptake as well as the homogeneity and heterogeneity by adsorbent. The Langmuir model is based on the production of adsorbate molecules on the homogenous surface of the adsorbent. The linear form of the Langmuir model can be represented as shown in Eq. 5:

$$\frac{1}{q_e} = \frac{1}{K_l q_{max} C_e} + \frac{1}{q_{max}} \quad \ldots(5)$$

where, C_e is the maximum amount of dye that can be adsorbent by MRH (in mg/g), q_{max} is the maximum amount of dye that can be adsorbent by MRH (in mg/g), K_L is the Langmuir isotherm constant related to the binding energy between the adsorbate (MB) and adsorbent (MRH), and q_e is the retention capacity of the dye at equilibrium time[26,27]. When C_e/q_e was plotted against C_e, as illustrated in Fig. 11a, a straight line was produced. Using the slope and intercepts, the q_{max} and K_L were determined and given in Table 3.

The linear form of the Freundlich model can be presented as in Eq. 6.

$$lnC_e = lnK_f + \frac{1}{n} lnC_e \quad \ldots(6)$$

where n represents the Freundlich exponent, C_e the adsorbate concentrations, q_e the amount of MB in equilibrium, and K_F the capacity-designating Freundlich constant. K_F and n were found using the plot of lnq_e vs. lnC_e in Fig. 11b. It is common practice to assess the suitability of the adsorption process using the n value. 1/n <1 represents a typical process, but 1/n > 1 indicates a cooperative process. The value of 1/n was 2.632 as MB was adhering to the MRH.

A conclusion can be drawn that the Freundlich adsorption model offered the best fit with experimental data by comparing the values of R_2 from Table 3. From the Freundlich adsorption isotherm, theoretical maximum levels of dye were estimated, and they were quite close to the experimentally measured values (Fig. 11c). Although the Freundlich adsorption isotherm predicts monolayer adsorption, the maximum coverage is unconstrained. It explains both the surface's heterogeneity and the exponential distribution of the active sites' energy.

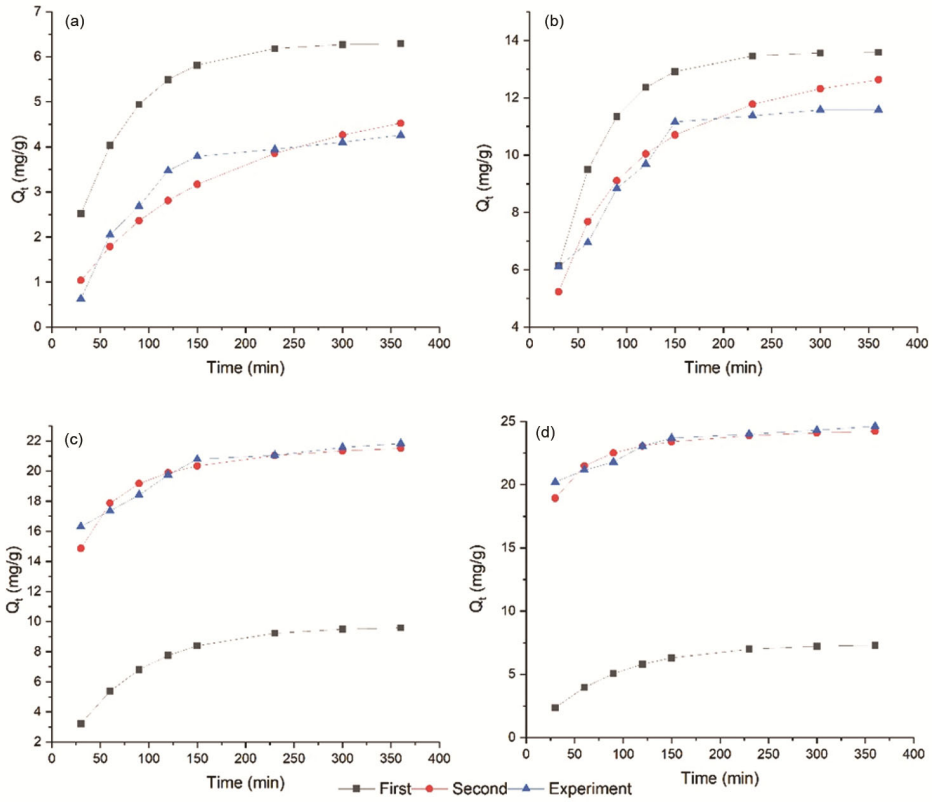

Fig. 10 — Comparison of kinetic Lagergren's pseudo-first, pseudo-second-order, and experimental data plot at different dye concentrations (a) 60, (b) 80, (c) 100, and (d) 120 mg/L for the adsorption of dyes onto MRH

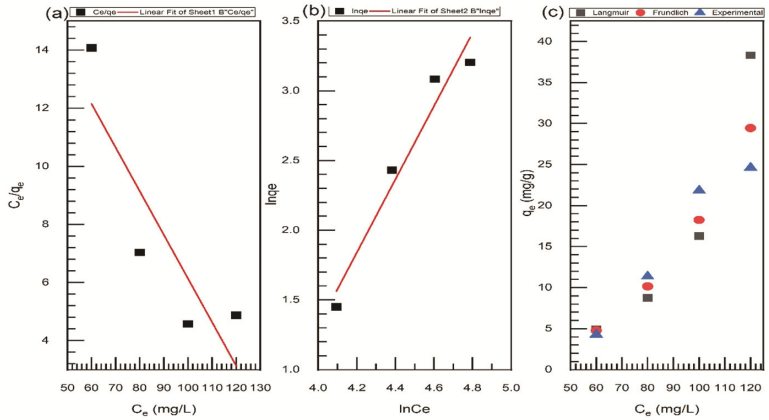

Fig. 11 — (a) Langmuir, (b) Freundlich Isotherm, linear plots and (c) experimental data fitted with all adsorption isotherms for MB adsorption onto MRH

Table 3 — Isotherm parameters in the adsorption process

Isotherm Model	Parameters	Values
Langmuir	Q_e	38.336
	K_L	0.0071
	R_2	0.769
Freundlich	Q_e	29.46
	K_f	0.000102
	n	0.38
	R_2	0.954

Conclusion

Overall, the results of this study suggest that the PRH and MRH have great potential as low-cost and effective materials for the selective remediation of methylene blue from water. The hydrogel demonstrated high removal efficiency, with maximum removal efficiency of PRH and MRH for methylene blue was found to be 85% (315 mg/g) & 90%

(333 mg/g) at 0.37 g of adsorbent dose, 300 min of contact time and pH 9. The study also showed that the removal efficiency increased with increasing the amount of hydrogel used. SEM images revealed the porous nature of the PRH and MRH adsorbent before MB adsorption. The hydrogel may be employed successfully for several adsorption and desorption cycles. This research may contribute to the development of sustainable and cost-effective solutions for the remediation of dye from wastewater.

Acknowledgments

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