Sains Malaysiana 53(5)(2024): 1149-1166
http://doi.org/10.17576/jsm-2024-5305-14

Optimizing Methylene Blue Dye Adsorption onto Liquid Natural Rubber-Based Hydrogel: Kinetics, Isotherms and Reusability

(Mengoptimumkan Penjerapan Pewarna Biru Metilena pada Hidrogel Berasaskan Getah Asli Cecair: Kinetik, Isoterma dan Kebolehgunaan Semula)

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Received: 21 January 2024/Accepted: 26 March 2024

ABSTRACT

In recent years, notable advancements have taken place in the textile industry, particularly with the widespread use of synthetic dyes such as methylene blue (MB). However, the environmental impact of these dyes has raised significant concerns. Their potential to influence both chemical and biochemical demand poses risks, leading to potential disruptions in aquatic plant photosynthesis. Additionally, concerns exist regarding the toxicity and potential carcinogenicity of these dyes to humans. This study achieved successful hydrogel synthesis through the efficient utilization of ultrasonic methods, combining liquid natural rubber (LNR), acrylic acid (AAc), and pectin (Pc) to adsorb MB from aqueous solutions. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were employed to analyze the structure. Utilizing Response Surface Methodology (RSM), the study investigated the effects of the AAc:LNR weight ratio and Pc weight on hydrogel preparation for MB removal. This led to the development of a quadratic polynomial model with an ANOVA-derived R^2 value of 0.9970. Optimal conditions for hydrogel production were identified as a 3.00 g/g AAc:LNR weight ratio and 0.0325g of Pc, resulting in an impressive 99.07% MB removal effectiveness. The limit of detection (LOD) for methylene blue adsorption was calculated at 0.64 ppm. The kinetics and isotherms of MB removal were described by the pseudo-second-order and Freundlich models, respectively. Furthermore, the investigation into hydrogel reusability demonstrated its capability for up to five utilization cycles. The LNR/AAc/Pc hydrogel exhibits promising potential as an effective, cost-efficient, and environmentally conscious adsorbent for MB removal. This makes it applicable to water treatment scenarios involving cationic dyes.

Keywords: Acrylic acid; adsorption; natural rubber; pectin; Response Surface Methodology

ABSTRAK

Beberapa tahun kebelakangan ini, terdapat kemajuan yang signifikan dalam industri tekstil, khususnya dengan penggunaan pewarna sintetik seperti metilina biru (MB). Walau bagaimanapun, kesan alam sekitar daripada pewarna ini telah menimbulkan kebimbangan yang ketara. Pewarna ini berpotensi untuk mempengaruhi permintaan kimia dan biokimia yang boleh menyebabkan gangguan dalam fotosintesis tumbuhan akuatik. Selain itu, terdapat risiko berkaitan dengan ketoksikan dan potensi karsinogen kepada manusia. Kajian ini telah berjaya mensintesis hidrogel melalui penggunaan kaedah ultrasonik yang cekap dengan menggabungkan getah asli cecair (LNR), asid akrilik (AAc) dan pektin (Pc) untuk menjerap MB daripada larutan akues. Spektroskopi Inframerah Transformasi *Fourier* (FTIR) dan Mikroskopi Elektron Imbasan (SEM) digunakan untuk menganalisis struktur hidrogel. Dengan menggunakan Kaedah Gerak Balas Permukaan (RSM), penyelidikan ini mengkaji kesan nisbah berat AAc:LNR dan berat Pc terhadap penghasilan hidrogel dalam penyingkiran MB. Ini menghasilkan model polinomial kuadratik dengan nilai R^2 yang

diperoleh daripada ANOVA sebanyak 0.9970. Keadaan optimum untuk penyingkiran hidrogel dikenal pasti sebagai nisbah berat AAc:LNR sebanyak 3.00 g/g dan 0.0325 g Pc yang menghasilkan keberkesanan penyingkiran MB sebanyak 99.07%. Had umum penemuan (LOD) bagi penjerapan biru metilina telah dihitung pada 0.64 ppm. Kinetik dan isoterma penyingkiran MB masing-masing dijelaskan oleh model pseudo-tertib kedua dan Freundlich. Selain itu, kajian mengenai kebolehgunaan semula hidrogel menunjukkan keupayaannya untuk sehingga lima kitaran kegunaan. Hidrogel LNR/AAc/Pc menunjukkan potensi yang baik sebagai penjerap yang berkesan, kos-cekap dan peka alam sekitar untuk penyingkiran MB. Ini menjadikannya sesuai untuk senario rawatan air yang melibatkan pewarna kation.

Kata kunci: Asid akrilik; getah asli; Kaedah Gerak Balas Permukaan; pektin; penjerapan

Introduction

Pollution is becoming a major issue, especially in developing nations, because it poses long-term dangers to both people and the environment. Essentially, untreated wastewater from domestic and industrial effluents is the leading cause of this issue. These effluents include dye ions in the wastewater and employ dyes as the primary ingredient (Yan et al. 2015). Nowadays, dyes are widely used in various industries, including cosmetics, clothing, printing, plastics, paper, leather, and food (Ma et al. 2017). However, these industries commonly discharge their dye-containing effluents into the environment without adequate water treatment. Even in minute concentrations, most dyes exhibit toxicity, carcinogenicity, and mutagenicity, thus posing substantial threats to human health (Mittal, Maity & Ray 2015). These wastes also harm aquatic life by lowering the quality of the water. Because dye-contaminated water restricts light penetration, most photosynthesizing organisms are also in danger. The cationic dye methylene blue (MB), also known as 3,7-bis (dimethyl amino)-phenothiazin-5-ium chloride, is thought to be more poisonous than those anionic dyes (Gomes et al. 2015) as it can quickly enter cells by interacting with the negatively charged surface of cell membranes. This is why effectively and promptly removing MB dye from industrial effluents has been a difficult area of research (Jiao et al. 2015). There are several methods available to remove these pigments from watery solutions, such as adsorption, ion exchange, solvent extraction, chemical precipitation, and ultrafiltration. Among these methods, adsorption is considered the most useful due to its affordability and reputation for being selective and effective.

Hydrogel adsorbents made from natural polymers are becoming more popular because they are manufactured with green technology and renewable resources (Abdel-Halim & Al-Deyab 2014; Bao et al. 2019). Hydrogels are three-dimensional networks of hydrophilic polymers, which can be natural or synthetic. By chemically or physically crosslinking these polymers the polymers undergo chemical or physical crosslinking to form flexible networks, allowing them to retain water or biological fluids when swelling (Ahmad, Mohamed & Yusoff 2020; Primo et al. 2016). These materials have garnered considerable interest as functional materials with biological, agricultural, and eco-friendly applications. They have demonstrated effectiveness as adsorbents for dyes and heavy metals (Singh et al. 2021; Wei et al. 2016; Xu et al. 2016). The poverty of their mechanical properties, which include brittleness and softness, limits their use in different fields. The hydrogel product has specific drawbacks when it comes to adsorption capacity and mechanical strength (Aiza Jaafar et al. 2021). Also, natural rubber (NR) is employed as the primary material to address these challenges, leveraging its superior mechanical properties achieved by crosslinking natural rubber with acrylic acid and pectin. Adding acrylic acid and pectin to natural rubber (NR) enhances the strength of the hydrogel, resulting in improved mechanical properties such as strength and elasticity. This modification also improves the hydrogel's water uptake and swelling properties (Firdaus et al. 2019). These standards play a vital role in removing heavy metals and dyes from water and their utilization in agricultural practices (Vudjung & Saengsuwan 2018). In treating water, scientists often mix hydrophilic monomers with unique functional groups such as -OH, -NH2, -SO_3H, -COOH, and -$CONH_2$ with cross-linked NR. The crosslinked polymer has promising capabilities for the adsorption and retrieval of waterborne contaminants, including dyes and heavy metal ions (Polgar et al. 2016). Researchers extensively investigated different base

materials such as cassava starch (Junlapong et al. 2020), chitosan (Yang et al. 2021), cellulose (Mohd et al. 2021), and synthetic polymers to enhance the effectiveness of hydrogels as adsorbents, with each ingredient offering distinctive advantages.

Over the past few years, there have been numerous studies investigating changes to rubber-based hydrogels. One method involves crosslinking acrylic acid, which is a hydrophilic polymer. To improve the hydrogel's ability to absorb and select substances, this hydrophilic polymer includes specific functional groups that can interact with water molecules (Amnuaypanich & Kongchana 2009; Cui et al. 2020). The grafting of maleic anhydride (MaH) into the LNR chain introduces a highly polar functional group (Nakason, Kaesaman & Supasanthitikul 2004; Pongsathit & Pattamaprom 2018). The grafting process significantly enhances the hydrogel's dye adsorption capacity. The studies have demonstrated maximum adsorption of 94.13% for malachite green dye. Pectin is a naturally occurring anionic heteropolysaccharide with a high concentration of COO-. It is made up of (1-4) -D-galacturonic acid (GaIA) and can be found abundantly in plant bio-waste, like citrus rind. Extracting pectin from such sources is a simple process. Because of its unique characteristics, such as affordability, easy availability, non-toxicity, and biodegradability, pectin has gained considerable attention in various fields, including food, wastewater treatment for pollutant removal, and pharmaceutical applications (Nesic, Velickovic & Antonovic 2014; Thakur et al. 2019). The novelty of this study lies in the production and synthesis of an innovative negatively-charged adsorbent, achieved through the combination of natural polymers such as pectin and liquid natural rubber, along with a synthetic monomer, acrylic acid. In this study, we employed the ultra-sonication method to conduct free-radical polymerization between liquid natural rubber (LNR), acrylic acid (AAc), and pectin (Pc), with potassium persulfate (KPS) serving as the initiator and N, N-methylene bisacrylamide (MBA) as the crosslinking agent. MBA was selected as the cross-linker due to its ability to leverage the bifunctional crosslinking properties, thereby enhancing the stability of the hydrogel structure (Mathew, Sasidharan & Rakesh 2020). It facilitates the initiation of copolymerization between natural polymers and monomers, namely LNR, acrylic acid (AAc), and pectin (Pc), forming a robust hydrogel network the hydrogel's preparation conditions were optimized by changing two parameters: the AAc:LNR weight ratio and the pectin weight. This was done to enhance its performance and remove MB dye. The system's adsorption mechanism was determined using kinetic and isotherm models. Furthermore, an adsorption-desorption procedure has been conducted to evaluate the hydrogel's reusability.

EXPERIMENTAL DETAILS

REAGENTS AND SOLUTIONS

The peels of bitter oranges (*Citrus aurantium*) were obtained from a fruit plantation in Baqubah, Diyala, Iraq. Natural Rubber (NR) was provided by the Rubber Research Institute of Malaysia (RRIM). Therefore, we used the method described in the study by Jamaluddin et al. (2016) to prepare the LNR. Sigma Aldrich supplied acrylic acid (AAc), potassium persulfate (KPS), ethanol, and MBA. SDS, which is a detergent, was sourced from Systerm in Malaysia. For the adsorption study, MB was obtained from Sigma Aldrich.

PECTIN EXTRACTION

First, 20 g of bitter orange peels were added to standard borosilicate glass vials. The peels were then dried using a Mono Wave 450 microwave reactor, with the process's adjustment to utilize microwave power levels of 450 W for 170 s (Kratchanova, Pavlova & Panchev 2004). Once dry, 5 g of the sample was obtained by adding 250 mL of water. Citric acid was used to lower the pH of the distilled water to 2, resulting in acidified distilled water at a concentration of 0.5 M. The mixture was heated to a temperature between 80 °C and 82 °C and stirred constantly for 30 min during extraction. After heating, the mixture was filtered through a cloth. The obtained filtrate was then combined with an equal volume of 96% ethanol and left to stand for an hour, leading to solidification. The coagulated pectin underwent filtration and three rounds of washing: first with 70% acidic ethanol (0.5% acidity), then with 70% ethanol to achieve a neutral pH, and finally with 96% ethanol. Subsequently, the pectin was dried in a laboratory dryer at 60 °C. The analysis of pectin extraction from bitter orange peels involved Fourier Transform Infrared (FTIR) spectroscopy.

PREPARATION OF LNR/AAc/Pc HYDROGELS

By employing the method described in Jamaluddin et al. (2016) study, the LNR was prepared. LNR,

distilled water, 1% SDS, and a specified quantity of KPS were combined in a beaker. The mixture underwent ultrasonication at 70 °C for 30 min. The AAc and Pc solutions were concurrently mixed with KPS and then sonicated for 30 min. The procedure was repeated with the dropwise addition of MBA until a firm gel formed. Afterwards, the produced hydrogel was dried at 60 °C until it attained a consistent mass. The analysis of rubber hydrogel involved the utilization of two techniques: Fourier Transform Infrared (FTIR) and Scanning Electron microscopy X-ray (SEM).

METHYLENE BLUE DYE ADSORPTION

The hydrogel sample (0.10 g) was placed in 20 mL of 5 ppm MB at room temperature until it reached a balance. The concentration of MB was measured using UV-Vis spectrophotometer before and after the hydrogel was added and removed from the solution. The absorbance of the MB dye was measured at 664 nm. Equation (1), with C_i as the initial concentration and C_e as the final concentration (mg/L) of MB, was used to calculate the percentage of MB dye removal.

$$\text{Percentage removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

OPTIMIZING THE PARAMETERS OF THE ADSORPTION OF MB DYE

RSM is an optimization tool that combines several statistical and mathematical techniques. This tool's base is the empirical model-experiment data fit, which relies on the experimental design's relationship to the experimental data. Additionally, in this study, we used a central composite rotatable design (CCRD) with two factors and five levels. RSM was applied to analyze the data. The AAc/LNR weight ratio varied from 1.00 to 3.00 g, while the weight of pectin was adjusted between 0.0375 and 0.0625 g during the optimization process using RSM (Table 1). The response variable evaluated in this study was the percentage of MB removal (%). The mass of the MBA, the mass of the initiator, and the temperature were kept constant throughout the experimental process. ANOVA with an F-test was carried out to ascertain the association between the factors and the response. Subsequently, the model's significance was verified with F-values with a significance level of $p \leq 0.05$, which showed how well the model fit.

STUDIES ON ISOTHERMAL EQUILIBRIUM

Hydrogels (0.1 g) have been placed into 20 mL methylene blue (MB) solutions, with starting concentrations ranging from 1 to 10 mg L^{-1}, to obtain adsorption isotherms at equilibrium. A temperature of 25 °C, a reaction duration of 24 h, and a pH of 6.55 were all consistent. The adsorbent's absorption capacity was calculated using Equation (1). After filtering the samples, the residual MB concentration was measured. The Langmuir and Freundlich isotherm models were employed to fit the equilibrium data, allowing for the calculation of the relevant parameters.

Equation (2) is the Langmuir model, which was initially provided by Clarke and Langmuir 1916 . It is based on the Freundlich model and can be represented by Equation (3), as shown by Langmuir (Langmuir 1917).

$$Model\ Langmuir: \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \qquad (2)$$

$$Model\ Freundlich: lnQ_e = \ln k_f + \frac{1}{n}(lnC_e) \qquad (3)$$

C_e represents the equilibrium concentration of MB (mg/L); Qe denotes the equilibrium adsorption capacity (mg/g); Q_m and K_f represent the expected adsorption capacity (mg/g). Additionally, the intercept and gradient of the curve can be used in conjunction with the value of n in the Freundlich model to calculate the intensity of adsorption.

TABLE 1. Lists of the experimental variables for the central Composite Rotatable Design (CCRD) and their corresponding levels

Variables/factors	Coded level				
	-2	-1	0	+1	+2
Weight ratio of AAc: LNR, A (g/g)	0.58	1.00	2.00	3.00	3.41
Weight of Pc, B (g)	0.0323	0.0375	0.050	0.0625	0.0677

KINETIC STUDIES

In this study, the kinetics were investigated by adding 0.1 g of hydrogels to a 20 mL solution with a pH of 6.55 and room temperature, containing 5 mg L^{-1} of MB. The focus of this work is to measure duration of dye adsorption. The sample will be monitored at regular intervals until the adsorption reaches equilibrium. Subsequently, the hydrogels were filtered to ascertain the final concentration of MB. This research employed two commonly employed models to analyze the kinetics of MB adsorption on hydrogels, one of which was the pseudo-first-order model derived from Lagergren's Equation (4) (Lagergren 1898). Pseudo-second-order Equation 5 (Ho & McKay 1999).

$$\text{Pseudo} - \text{first order: } \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}\text{t} \quad (4)$$

$$\text{pseudo} - \text{second order: } \frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e}(t) \quad (5)$$

where q_t is the adsorption capacity by time (mg/g); q_e is the adsorption capacity at equilibrium (mg/g); k_1 and k_2 are the rate constants of kinetic in order (min^{-1}); and t is the time of adsorption (min).

REUSABILITY STUDY OF HYDROGEL

When evaluating the performance of the adsorbent in a specific application, reusability is an important factor to consider (Peng et al. 2018). The study includes reusability experiments on LNR/AAc/Pc hydrogel using methanol as the desorbing agent. These experiments follow the method described by Allouss et al. (2019) and Lazim et al. (2019). Initially, 0.4 g of the hydrogel was added into 50 mL of 5 ppm MB dye. After 120 min of adsorption, the hydrogel was removed from the dye solution and soaked in methanol for 60 min. Following the soaking process, the hydrogel was dried using silica gel approximately for one day. The dried hydrogel was subsequently utilized once again for the adsorption-desorption cycles, with each cycle's percentage of dye removal was recorded.

RESULTS AND DISCUSSION

STRUCTURAL ANALYSIS OF EXTRACTED PECTIN

Figure 1 illustrates the FTIR spectrum of a pectin sample extracted using citric acid as the combined solvent. The FTIR signal of pectin falls within the range of 3000 to 3700 cm-1 due to the presence of OH functional groups in

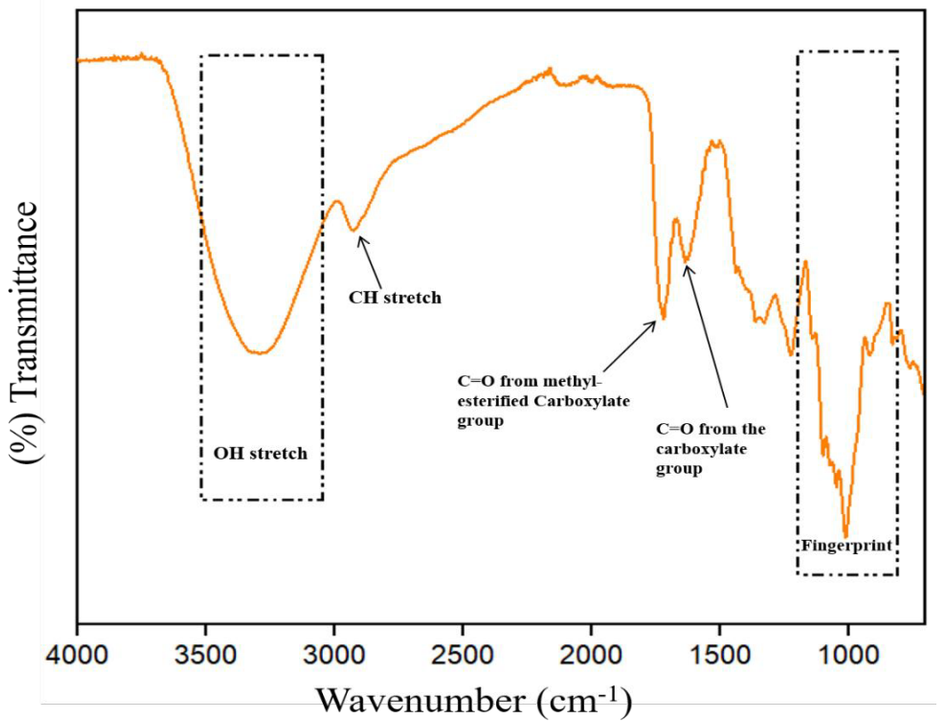


FIGURE 1. FTIR spectrum of pectin recovered from bitter orange peel using citric acid

its molecular structure. This area showed hydrogen bonds within and between molecules in the pectin molecule's galacturonic acid structure (Hamidon, Abang Zaidel & Mohd Jusoh 2020; Santos et al. 2013). An additional peak in the 2800-3000 cm-1 range demonstrated the existence of the CH group. The stretching vibration of carbonyl functional groups (C=O) within the methyl-esterified carboxylic groups produces an absorption peak falling in the range of 1680 to 1810 cm-1, as documented in references Nouri and Mokhtarian (2020) and Gnanasambandam and Proctor (2000). A peak in the wavenumber between 1490 and 1700 cm-1 provided further evidence of the stretching vibration of the C=O group inside the carboxylate functional groups (COO-) in the pectin structure.

The absorption spectrum, spanning from 800 to 1200 cm^{-1} showed the peculiar properties of the pectin molecule (Tongkham et al. 2017), which was the fingerprint zone, was challenging to comprehend due to the functional groups (Oliveira et al. 2016). The pectin fingerprint zone, which falls between 950 and 1200 cm^{-1}, exhibits a complex absorption pattern commonly utilized for chemical identification. This zone shows the potential to detect the vibration of the pyranose cycle (Lee & Choo 2020).

SYNTHESIS OF LNR/AAc/Pc HYDROGEL

Ultrasound method was used to create hydrogels by combining natural rubber with LNR, AAc, and Pc through a process called free radical copolymerization

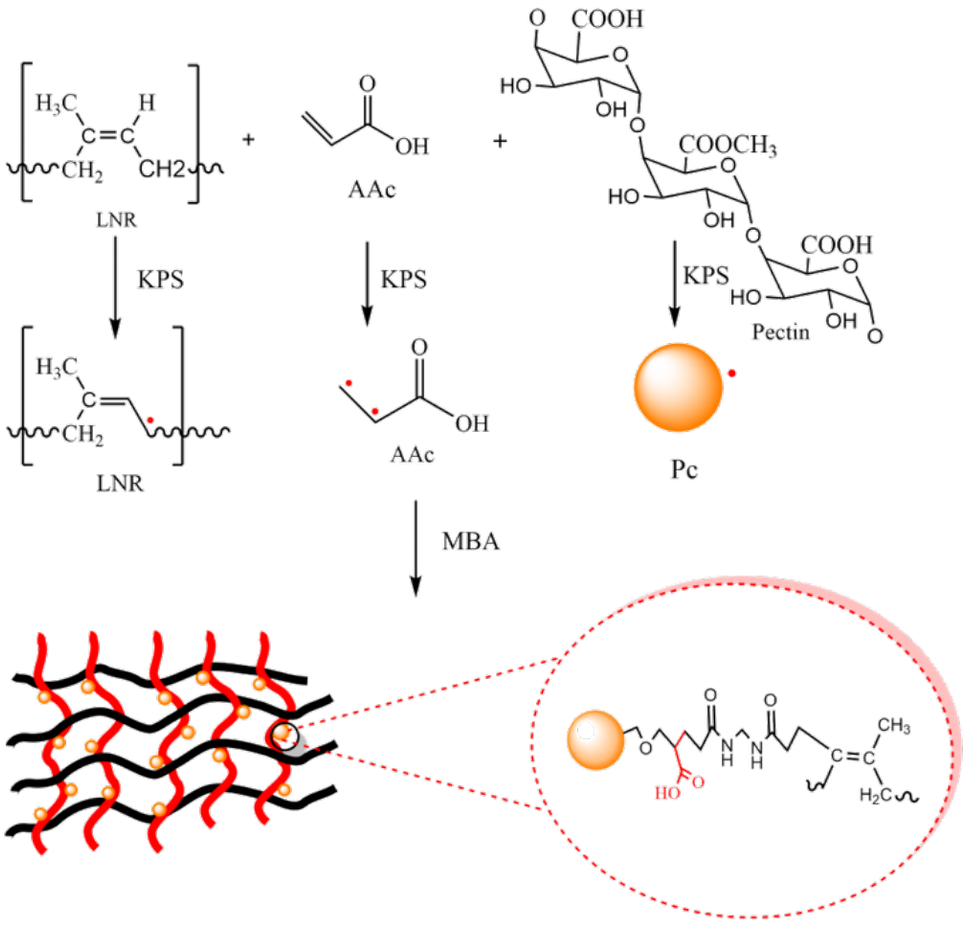


FIGURE 2. Reaction scheme of LNR/AAc/Pc hydrogel

as shown in Figure 2. KPS was used as the initiator, while MBA played the role of crosslinking agent. During the initiation step, KPS vigorously triggered polymerization by decomposing persulfate, which generated initial free radicals upon heating to 70 °C. These radicals abstracted hydrogen from the LNR chain, AAc, and the hydroxyl groups of pectin (Mohd Noor & Yusoff 2020). Free radicals actively interact with the pectin chain, abstracting hydrogen and creating pectin free radicals (Pandey et al. 2021). Moreover, molecule AAc is pivotal as a cross-linker between LNR and pectin, producing the final hydrogel product (Scheme 1). Finally, MBA was employed to crosslink the polymer chains, forming the ultimate hydrogel product.

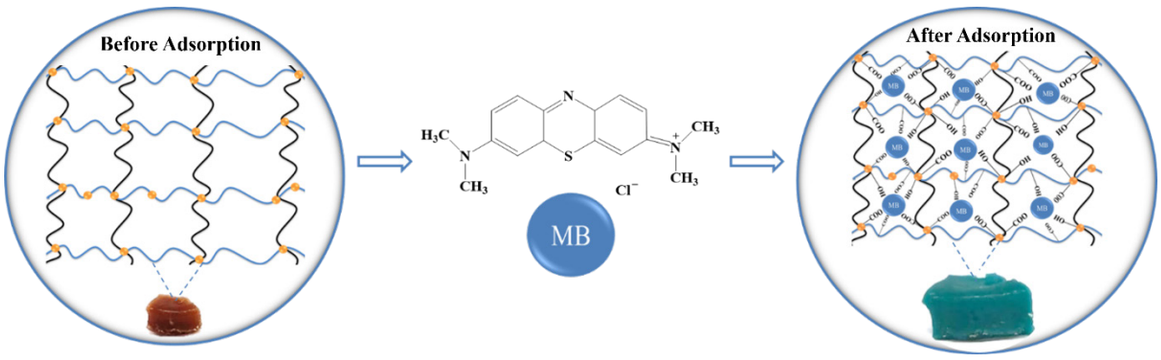
STRUCTURAL ANALYSIS OF LNR/AAc/Pc HYDROGEL

Figure 3 depicts the FTIR spectra of LNR, AAc, Pc, and LNR/AAc/Pc hydrogel. The FTIR spectra of unaltered LNR display bands at 3050-2850 cm^{-1} and 1664 cm^{-1} correspond to sp^3 CH and C=C stretching, respectively. The AAc spectrum shows a wide-ranging band spanning from 3300 to 2730 cm^{-1}, signifying the presence of the -OH group. A distinct peak becomes evident at 1700 cm^{-1}, corresponding to the -OH group, and a significant height at 1700 cm^{-1}. Within the AAc structure, there are bands at 1408 cm^{-1} for the C-OH in-plane deformation and bands at 1180 cm^{-1} for the CO stretching (Taheri et al. 2016). Within the hydrogel's FTIR spectrum, the -OH and -C=O groups are correlated with peaks at 3600 and 1650 cm^{-1}, while A peak at 1150 cm^{-1} is caused by the -CO stretching of the carboxylic acid group. Pectin's molecular structure contains OH functional groups, as seen by the broad peak in the Pc spectrum that ranges from 3000 to 3700 cm^{-1}. This segment of the galacturonic acid structure in pectin exhibited intramolecular and intermolecular hydrogen bonding (Hamidon, Abang Zaidel & Mohd Jusoh 2020; Santos et al. 2013). Another discernible peak, ranging from 2800 to 3000 cm^{-1}, confirmed the presence of the CH group. Within the pectin structure, the stretching vibration associated with the carboxylate functional group (COO-) of the C=O group was detected within 1490 to 1700 cm^{-1} range (Oliveira et al. 2016). The 3000 to 2850 cm^{-1} signal indicated the stretching of C-H bonds in the polymer chains in a sp^3 configuration. The presence of peaks between 3000 and 3700 cm^{-1} implied the elongation of the polymer chain, while the mountain within the 3000 to 2850 cm^{-1} range confirmed the presence of sp^3 C-H bonds. This outcome signifies the successful grafting of AAc and Pc onto the LNR.

OPTIMIZING HYDROGEL PERFORMANCE IN MB DYE REMOVAL

Table 2 shows the assessed response for the 13 experimental runs. The two independent factors were the mass ratio of LNR:AAc (g/g) and Pc (g); these two independent variables had a significant impact. The experiment included 13 data points, with four factorial points, four axial points, and five center points. They afterwards utilized these results to establish the polynomial Equation. Equation (6) shows the quadratic model regarding the coded factors based on the trial runs. A and B are the corresponding AAc:LNR weight ratio and pectin weight.

$$\text{Removal MBA (\%)} = + 97.37 + 2.06\,A - 0.824\,B - 4.632\,AB - 2.23975 - 3.282\,B^2A^2 \quad (6)$$



SCHEME 1. The mechanism in which MB dyes and LNR/AAc/Pc hydrogel interact

The equation's positive and negative signs represented the elements' complementary and antagonistic impacts. Factor A in the Equation, representing the LNR/AAc weight ratio, shows a synergistic impact. Increasing the LNR/AAc weight ratio can enhance adsorption efficiency. The convenience of crosslinking with hydrophilic polymers in LNR arises from polar or charged functional groups in hydrophilic monomers, allowing them to react in water readily (Wongthep et al. 2013).

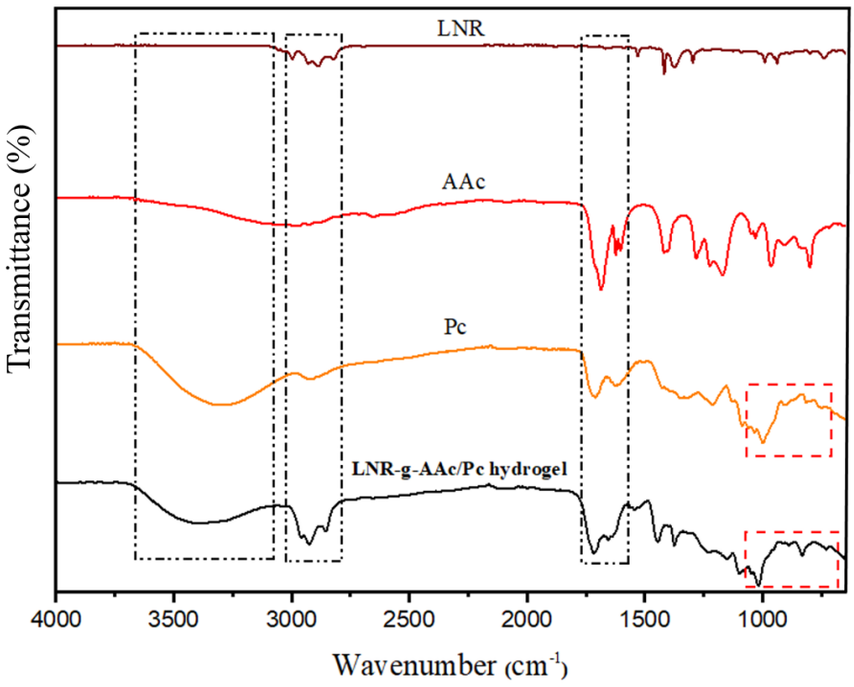


FIGURE 3. FTIR spectrum of LNR/AAc/Pc and a rubber-based hydrogel

TABLE 2. Central composite rotatable design (CCRD) for the LNR/AAc/Pc hydrogel

No	Weight ratio of LNR: AAc, A (g/g)	Weight of Pc B (g)	Removal Percentage (%)	
			Actual	Predicted
1	2	0.05	97.53	97.37
2	3.41	0.05	96.07	95.81
3	2	0.067	89.68	89.64
4	3	0.0375	99.07	99.37
5	3	0.0625	88.31	88.46
6	2	0.0323	92.23	91.97
7	0.58	0.05	90.01	89.97
8	2	0.05	96.84	97.37
9	1	0.0625	93.6	93.59
10	2	0.05	97.61	97.37
11	2	0.05	97.31	97.37
12	2	0.05	97.57	97.37
13	1	0.0375	85.83	85.98

Factor A in the Equation, representing the LNR/AAc weight ratio, shows a synergistic impact. Increasing the LNR/AAc weight ratio can enhance adsorption efficiency. The convenience of crosslinking with hydrophilic polymers in LNR arises from polar or charged functional groups in hydrophilic monomers, allowing them to readily react in water (Wongthep et al. 2013). The evidence for this statement is reinforced by conducting a morphological analysis before utilizing the hydrogel. The study shows that denser polymer networks form within the hydrogel by adjusting the weight ratio (LNR:AAc) and decreasing the amount of pectin. As a result, this modification significantly improves the absorption capacity of the hydrogel. After that, an ANOVA test was done to ensure the model was significant and good enough, employing the removal percentage of MB as the metric. The results are shown in Table 3, which shows that the F-values are 462.13 and the Prob>F values are <0.0001. In the end, this study proved that the quadratic model was significant. All model terms had Prob>F values below 0.05, which showed that they were significant and affected the response. On the other hand, the lack of fit value meant that the hypothesized model did not account for all regular changes. This meant that the lack of fit value was not significant. The Prob>F number for the lack of fit in this study was 0.5221, which is higher than the suggested level of 0.05.

The coefficient of variation (CV), which measures the model's repeatability, is the standard error ratio to the observed response's mean value. Additionally, the low values of C.V (0.331 for MBA removal percentage) showed the experimental data's higher dependability. For an agreement to be considered acceptable, the predicted R-squared (Pred-R^2) and the adjusted R-squared (Adj-R^2) should exhibit a difference of less than 0.2. The difference between the Adj-R^2 and Pred-R^2 values was less than 0.2, resulting in a CV value of 0.33%. Consequently, the R^2 value of 0.9970 for the quadratic model indicates high agreement between the actual and expected response values. The perfect agreement between these values confirms the model's validity. For the removal percentage of MB, Figure 4 shows the plots of projected values vs actual values. The perfect agreement between these values confirms the model's validity.

The plot of the three-dimensional reaction surface illustrates how the factors interact to identify the optimal levels for achieving the maximum removal of MB dyes. Based on Figure 4, 99.07% of MB dyes are removed when the AAc/LNR weight ratio by weight increases and the weight of pectin decreases. A greater concentration of carboxylic functional groups inside the polymer hydrogel network is shown by the rise in the weight ratio of AAc to LNR. The ability of these carboxylic groups of function to connect with MB dye molecules is essential. The more functional groups there are, the more MB dye molecules can be absorbed into a hydrogel network (Bhattacharyya & Ray 2015). The graph shows that the weight ratio AAc/LNR has an enormous effect on removing MB dyes than the weight of pectin.

TABLE 3. Results of the ANOVA for the LNR/AAc/Pc hydrogel preparation variables for the removal of MB

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	p-value
Model	223.56	5	44.71	462.13	< 0.0001
A-LNR:AAC	34.11	1	34.11	352.59	< 0.0001
B-PC	5.44	1	5.44	56.21	0.0001
AB	85.84	1	85.84	887.21	< 0.0001
A^2	34.90	1	34.90	360.68	< 0.0001
B^2	74.94	1	74.94	774.59	< 0.0001
Residual	0.6773	7	0.0968		
Lack of Fit	0.2696	3	0.0899	0.8817	0.5221
Pure Error	0.4077	4	0.1019	-	-
Corrected Total	224.24	12	-	-	-

The hydrogel preparation was optimized for maximum MB removal by increasing the AAc:LNR weight ratio and decreasing the pectin weight ratio. The experimental conditions yielding the highest desirability were selected and validated using the optimization feature of Design Expert software. the predicted (99.07) and actual (99.37) MB removal values under optimal conditions, showing a strong match with a minimal error of only 0.30%. The study notably achieved optimal removal of MB, surpassing the findings of previous research documented in the literature (Mohafezatkar Gohari et al. 2022; Sharma et al. 2019; Yusoff et al. 2022). Additionally, Table 4 established the detection limit (LOD) for methylene blue dye at 0.64 ppm using UV-visible spectrophotometry and a standard calibration curve, as demonstrated in Figure 5 through Equation (7). The figure illustrates the minimal concentration required for confident detection of methylene blue, underscoring the method's high sensitivity and confirming its suitability for detecting trace amounts of the dye across various samples.

$$\mathrm{LoD} = \frac{3.3 * \infty}{\mathrm{S}} \tag{7}$$

where ∞ standard deviation and S slope calibration curve.

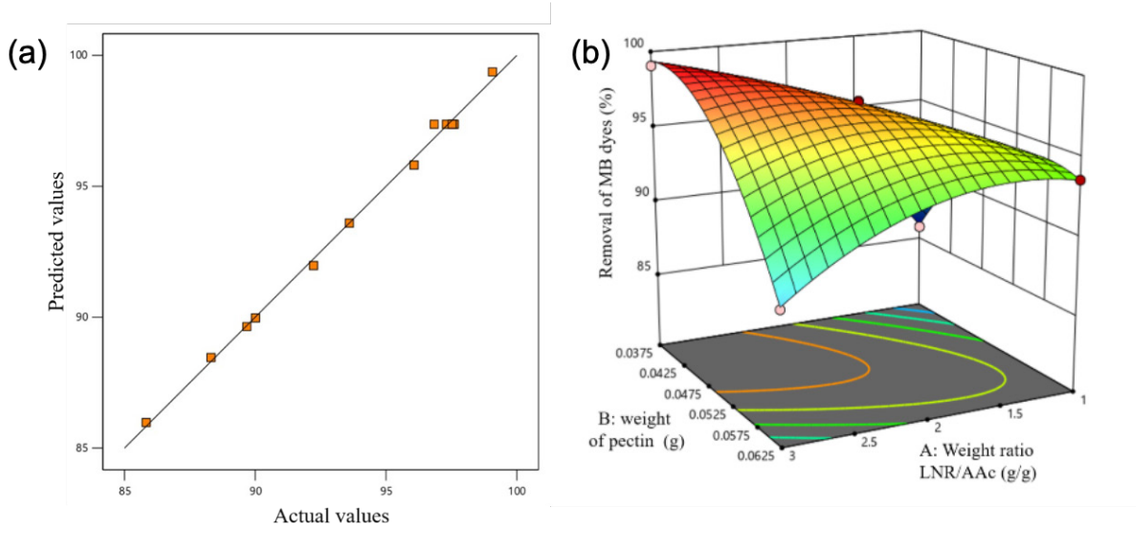


FIGURE 4. (a) Predicted and actual values, representing the LNR/AAc/Pc hydrogel preparation conditions for Methylene Blue (MB) removal, (b) interaction of response surface parameters weight ratio LNR/AAc/Pc and weight of pectin

TABLE 4. The calibration curve data and calculated limit of detection (LOD) for the methylene blue using the proposed method

Standard Error	Intercept	Standard deviation (SD)	Slope of calibration curve (S)	Limit of Detection (LoD) ppm	R^2
0.01	0.0562	0.022	0.1159	0.64	0.9993

MORPHOLOGY ANALYSIS

Figure 6 presents the micrograph of the hydrogel, showing discernible surface pores within the polymer that are unevenly distributed. These pores serve a crucial function by facilitating both the movement and retention of water molecules within the hydrogel networks (Hakam et al. 2015). An augmented presence of pores indicates a larger surface area, consequently enhancing the adsorption capacity for heavy metals and cationic dyes (Mohd Noor & Yusoff 2020).

KINETIC STUDY THE PROCESS OF MB ADSORPTION ONTO LNR/AAc/Pc HYDROGEL

Studying adsorption kinetics is essential in order to assess the rate of adsorption and the time required for the hydrogel to reach equilibrium after dye absorption (Mohd Noor & Yusoff 2020). Two different kinetic models were used to fit the experimental data and look into the rate of MB adsorption. The experiment was repeated at intervals of 60 min, and the adsorption percentage increased in tandem with the increase in contact duration. Equilibrium was attained in the MB dye adsorption process in around 17 h. As a result, 17 h of interaction duration was chosen for further experimental research. To investigate the adsorption kinetics of the composite, we utilized pseudo-first-order and pseudo-second-order kinetic models in this study. Figure 7(a) and 7(b) shows the graphs for the pseudo-first order and pseudo-second-order kinetic parameters. The results from the experiment fit the pseudo-second-order kinetic model better than

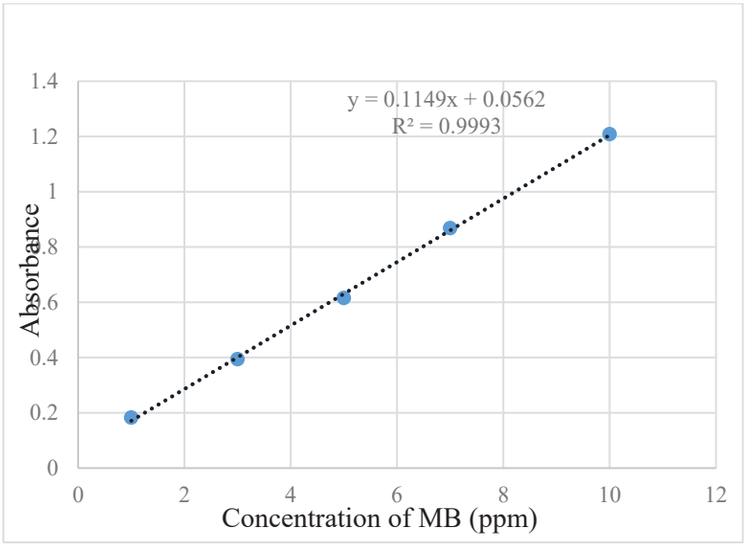


FIGURE 5. Limit of detection (LOD) for adsorption of methylene blue by UV-visible for standard calibration curve at different concentrations

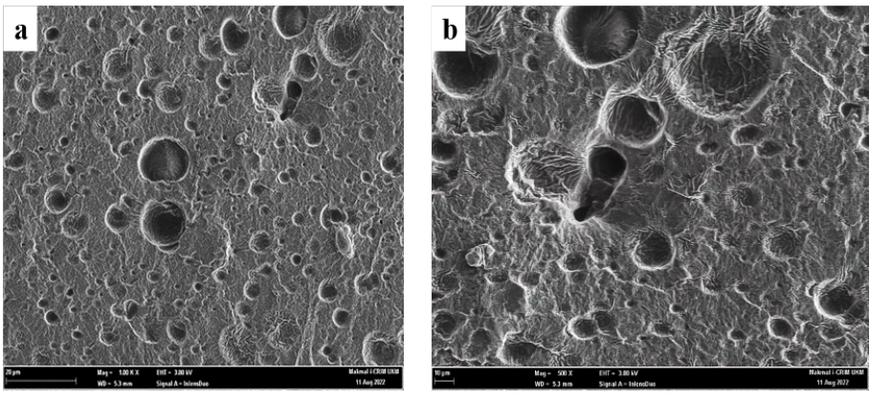


FIGURE 6. SEM image for a surface of a) LNR/AAc/Pc hydrogel b) a magnification (a) of 10 µm at (500x)

the pseudo-first-order kinetic model, as shown by the graph and the amount of association (R^2). The pseudo-second-order model has an R^2 value of 0.9828, higher than the pseudo-first-order model's R^2 value of 0.9396. Furthermore, the computed $q_{e,\ calc}$ obtained from the pseudo-second-order model, as determined by Equation (5), exhibited a closer agreement with the experimental $qe,_{exp}$ compared to the $qe,_{cal}$ obtained from the pseudo-first-order model, as presented in Table 5. Therefore, the experimental results strongly support the suitability of the pseudo-second-order kinetic model in representing the adsorption data. This result implies that chemisorption is essential and probably controls adsorption (Foo & Hameed 2010).

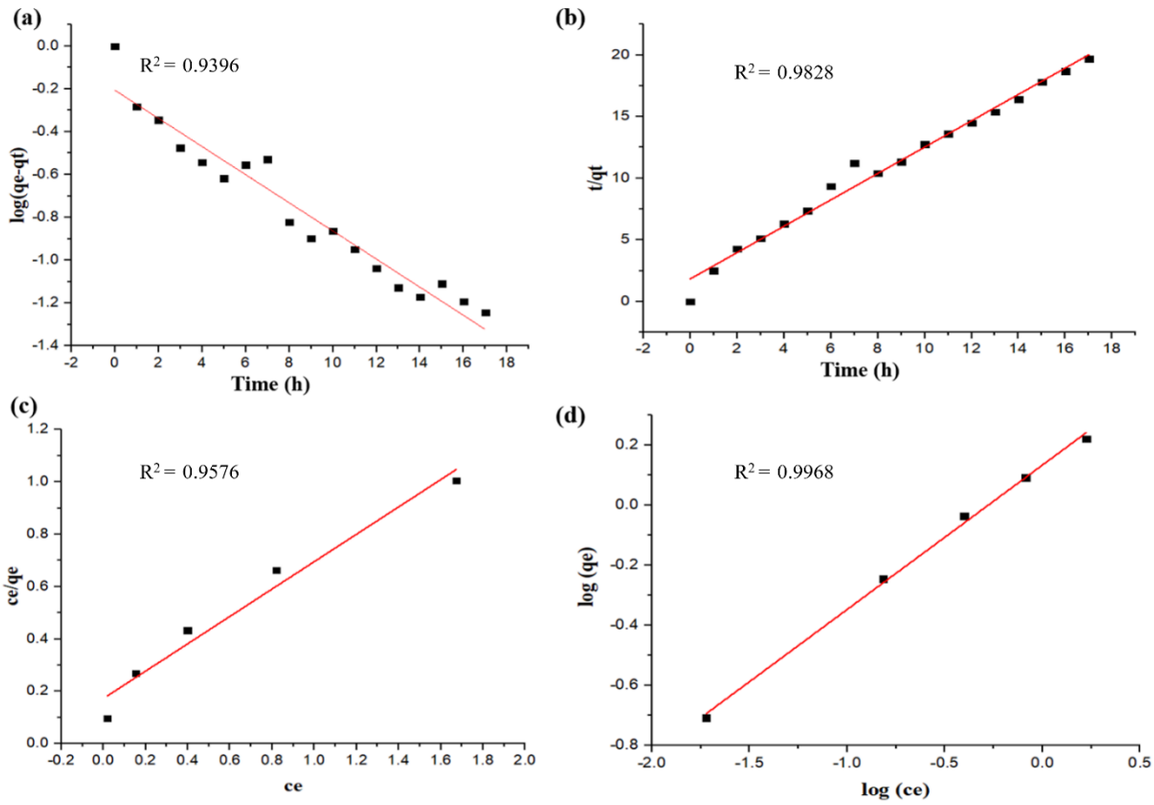


FIGURE 7. (a) Pseudo-first-order (b) pseudo-second-order kinetic model (c) Langmuir (d) Freundlich isotherm model for MB dye adsorption on the LNR/AAc/Pc

TABLE 5. The kinetic models' constant values and association coefficients

	Pseudo-first order				Pseudo-second order		
Parameters	$q_{e(exp)}$	K_1	$q_{e\ (calc)}$	$^R2$	K_2	$q_{e(calc)}$	R^2
Units	mg/g	min^{-1}	mg/g	-	min^{-1}	mg/g	-
	0.9204	0.00387	0.8136	0.9396	0.6204	0.9356	0.9828

STUDY OF ISOTHERM MB ADSORPTION ONTO LNR/AAc/Pc HYDROGEL

To specify the effectiveness of the adsorption process for methylene blue dye, adsorption isotherm models describe the interaction between the adsorbent and the solution. The hydrogel composite's effectiveness was studied by analyzing isotherm data to determine its maximum adsorption capacity (Asgari, Roshani & Ghanizadeh 2012). Additionally, the study of this isotherm can provide additional insights into the properties of hydrogel adsorption. The determined adsorption parameters demonstrate the effectiveness of the system's adsorption capabilities (Ahmad, Mohamed & Yusoff 2020). The Langmuir and Freundlich isotherm models, which are commonly used, were employed to analyze and explain the adsorption isotherm in this study (Yusoff et al. 2022). The adsorbent's formation of an adsorbate monolayer on the exterior surface of the adsorbent is explained by the Langmuir adsorption isotherm model. This isotherm model focuses exclusively on monolayer adsorption on surfaces (Dada et al. 2012), specifically on surfaces with comparable energy and adsorption sites. The Langmuir constants Q_m and KL represent the adsorption capacity and energy of the monolayer, respectively. In contrast, for heterogeneous surfaces, the Freundlich isotherm model is used to describe non-ideal adsorption. This phenomenon is brought on by interactions between adsorbent and adsorbate and different functional groups on the surface (Krishnamoorthy et al. 2021). The Freundlich constants, k_f, and n, represent the adsorption capacity and intensity, respectively (Senthil Kumar 2014). Figure 7(c) and 7(d) shows plot graphs for the Freundlich and Langmuir isotherm models. According to the findings, the Freundlich isotherm model best fits this study by looking at the correlation values (R^2) and the constants found in the plots. Table 6 illustrates that the Freundlich model's R^2 value (0.9968) was more significant than the Langmuir model's (0.9576). Hence, the Freundlich isotherm model is the most suitable for describing this study's MB dye adsorption process within the LNR/AAc/Pc composite. A heterogeneous distribution of active sites on the hydrogel surface indicates a heterogeneous adsorption process.

Furthermore, the value of n in the Freundlich isotherm model equation plays a crucial role in identifying the process of MB's adsorption onto the hydrogel surface. As per Ahmad, Mohamed and Yusoff (2020) and Krishnamoorthy et al. (2021), value less than 0 indicates that MB is adsorbed onto the hydrogel surface by a chemical process.

HYDROGEL COMPOSITE REUSABILITY

It is important for an adsorbent to have a high capacity for adsorption and the ability to regenerate its adsorption sites for recycling purposes, which can lead to energy-saving advantages. This study aimed to assess the reusability of LNR/AAc/Pc by conducting multiple cycles of adsorption and desorption using methanol as the desorbing medium. The results indicated that LNR/AAc/Pc hydrogels could be used again for up to five cycles. However, there was a gradual decrease in dye removal with each cycle, as depicted in Figure 8(a). This suggests that the physical properties of the adsorbents deteriorated over time, limiting their reusability. As a result, the dye removal percentage was 94.64% during the first cycle and gradually decreased to 29.34% in the fifth cycle. The colour intensity of the MB dye for the five successive cycles is shown in Figure 8(b). The adsorption efficiency markedly decreased in the fifth cycle, dropping from 52.21% in the fourth cycle to 29.34% in the fifth cycle. The results of our study indicate that the hydrogel reached its highest level of adsorption capacity in the fifth cycle of absorption.

TABLE 6. Parameters for the Freundlich and Langmuir isotherm models of the adsorption of MB on LNR/AAc/Pc hydrogel

Langmuir			Freundlich		
K_L(L/mg)	Q_m (mg/g)	R^2	K_F	n	R^2
0.330	5.783	0.9576	1.3629	0.480	0.9968

It is important to note that significant changes were observed on the surface of the hydrogel, which differed from the SEM micrograph of LNR/AAc/Pc and resulted in the porosity being indiscernible, as shown in Figure 8(c). Based on this study, it is evident that the resulting hydrogel composite demonstrated reasonable reusability for five cycles of adsorption. Despite the slight decline, the hydrogel's mechanical strength remained intact, demonstrating its durability for repeated use. According to Yusoff et al. (2022), the hydrogels synthesized from natural rubber exhibited favourable characteristics, including good water retention, mechanical properties, and thermal stability. The material's capacity to endure physical forces allows the hydrogel to maintain a rigid and firm structure.

COMPARISON WITH OTHER ADSORBENTS

The literature shows that researchers have explored various adsorbents for removing methylene blue (MB) from water. Our study scrutinized the effectiveness of our adsorbent in comparison with previously reported ones. The data in Table 7 indicate that our adsorbent competes well in adsorption capacity and affinity for MB relative to other adsorbents. Furthermore, the developed adsorbent stands out as novel, competitive, effective, practical, and cost-efficient. Therefore, we highly recommend the prepared LNR/AAc/Pc hydrogel as an efficient adsorbent because of its straightforward preparation and reusability, making it ideal for treating containing dyes effluent.

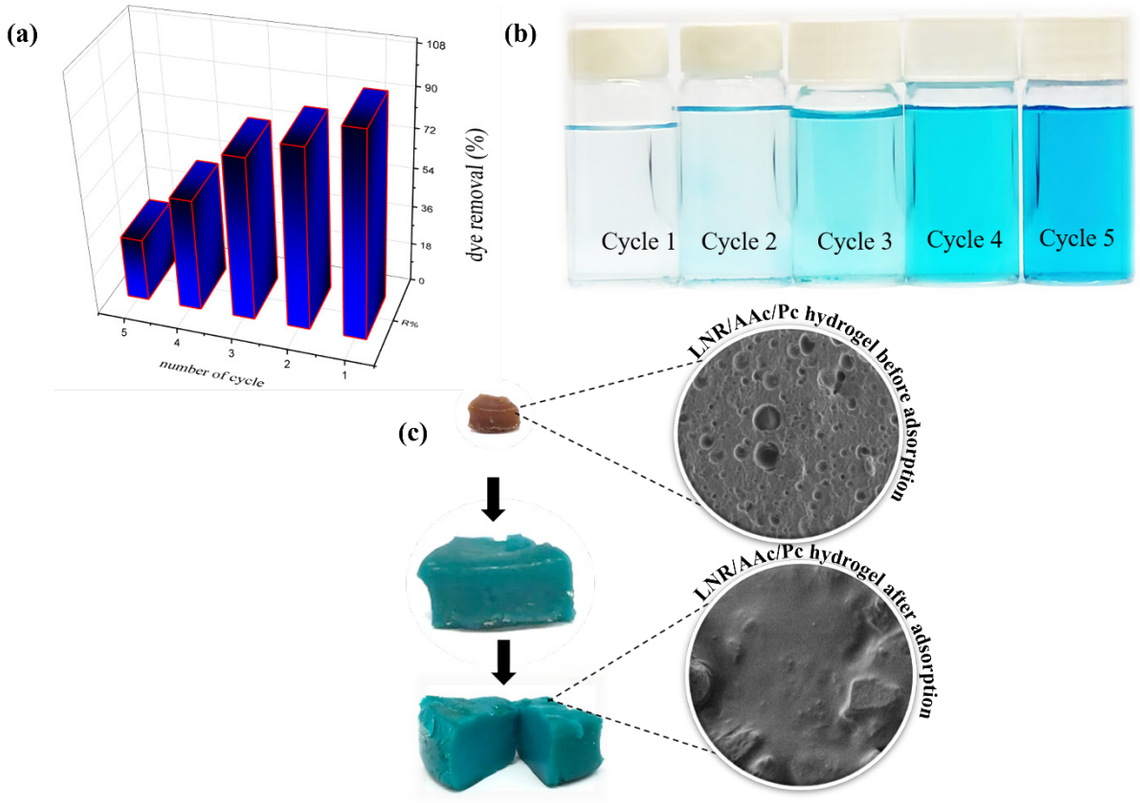


FIGURE 8. (a) The reusability of LNR/AAc/Pc hydrogel for MB adsorption (b) LNR/AAc/Pc hydrogel at first cycle and fifth cycle of MB adsorption (c) Photograph: LNR/AAc/Pc hydrogel after the first and fifth cycles, along with SEM after the fifth cycle of reusability

TABLE 7. The percentage adsorption capacity of MB utilizing LNR/AAc/Pc hydrogel and various adsorbents

Adsorbents	Removal (%)	References
Alginate/almond peanut bio-composite	90	(Erfani & Javanbakht 2018)
CMC-Alg/GO hydrogel beads	96.2	(Allouss et al. 2019)alginate (Alg
APTES/lignocellulose hydrogel	98	(Zhang et al. 2019)
CMC/kC/MMT composite	92	(Liu, Omer & Ouyang 2018)
polyacrylamide/cellulose hydrogel	90	(Zhou et al. 2014)
Tannin-immobilized cellulose hydrogel	91	(Pei et al. 2017)
Carboxymethyl cellulose-graft-poly(acrylic acid-co-itaconic acid)/ carbon black nanocomposite hydrogel	98.76	(Mohammadzadeh Pakdel et al. 2022)
LNR/AAc hydrogel	94.53	(Yusoff et al. 2022)
LNR/AAc/Pc hydrogel	99.07	Current study

CONCLUSION

The LNR/AAc/Pc hydrogel was successfully synthesized with KPS as the starting material and MBA as the crosslinking agent. The best conditions for this hydrogel were found using response surface methodology. The weight ratio of AAc/LNR is 3.00 g/g, and the weight of the pectin is 0.0375 g. The structural stability and water affinity of hydrogels are improved when pectin, a hydrophilic polymer, is included due to the presence of functional groups inherent in this type of polymer. With a maximum adsorption capacity of 0.92 mg/g and a maximum MB dye removal percentage of 99.07%, this hydrogel was best represented by the pseudo-second-order and Freundlich isotherm model. The findings from the experiments on the reusability of the LNR/AAc/Pc hydrogel indicate that it maintains its strong mechanical properties even after multiple recycling cycles. This implies that the LNR/AAc/Pc hydrogel has promising applications as an affordable, efficient, and environmentally friendly adsorbent for purifying water contaminated with cationic substances such as dyes or heavy metal ions.

ACKNOWLEDGMENTS

Universiti Kebangsaan Malaysia (UKM) supported this study through a research grant (ST-2022-022). At the same time, the facilities offered by the Centre of Research and Instrumentation (CRIM) and the Department of Chemical Sciences, Faculty of Science and Technology, UKM significantly contributed to the research. Additionally, we would like to thank Diyala University Iraq, College of Sciences, Department of Chemistry.

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