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# Optimization, Kinetics Isotherm, and Reusability Studies of Methylene Blue Dye Adsorption using Acrylic Acid Grafted Rubber Hydrogel

(Pengoptimuman, Isoterma Kinetik dan Kajian Kebolehgunaan Semula Penjerapan Pewarna Biru Metilena menggunakan Hidrogel Getah Cantuman Asid Akrilik)

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ABSTRACT

Hydrogel based on liquid natural rubber (LNR) crosslinked with acrylic acid (AAc) was synthesised and applied for the adsorption of methylene blue (MB) in aqueous solutions. The LNR/AAc hydrogel was prepared by free-radical polymerisation using potassium persulfate (KPS) and N,N-methylenebisacrylamide (MBA) as the initiator and the crosslinking agent, respectively. The effect of three variables (i.e., AAc:LNR weight ratio, KPS concentration and MBA concentration) on the hydrogel preparation for MB removal was further investigated using response surface methodology (RSM). A quadratic polynomial model with the analysis of variance (ANOVA) results yielding $R^2$ value of 0.9833 was consequently obtained. The optimum conditions for the hydrogel preparation were identified as AAc:LNR weight ratio of 2.59 g/g, KPS concentration of 0.08 M and MBA concentrations of 0.08 M and resulting a high percentage of MB removal about 92.57% was obtained. Therefore, the kinetic and isotherm models of MB removal were represented by the pseudo-second order and Freundlich model, respectively, and reusability studies were also investigated resulting in the hydrogel can be used up to four cycles.

Keywords: Adsorption; dye removal; polymer gels; rubber; response surface methodology

ABSTRAK

Hidrogel berasaskan getah asli cecair (LNR) yang ditaut silang dengan asid akrilik (AAc) telah disintesis dan digunakan untuk penjerapan metilena biru (MB) dalam larutan akueus. Hidrogel LNR/AAc telah disediakan melalui pempolimeran radikal bebas menggunakan kalium persulfat (KPS) dan N,N-metilenabisakrilamida (MBA) sebagai pemula bersama agen taut silang. Kesan tiga pemboleh ubah iaitu (nisbah berat AAc:LNR, kepekatan KPS dan kepekatan MBA) ke atas penyediaan hidrogel untuk penyingkiran MB telah dikaji selanjutnya menggunakan kaedah rangsangan permukaan tindak balas (RSM). Model polinomial kuadratik dengan keputusan analisis varians (ANOVA) yang menghasilkan nilai pekali penentuan, $R^2$ sebanyak 0.9833 telah diperoleh. Keadaan optimum untuk penyediaan hidrogel dikenal pasti iaitu nisbah berat AAc:LNR 2.59 g/g, kepekatan KPS 0.08 M dan kepekatan MBA 0.08 M dengan peratusan penyingkiran MB yang tinggi sebanyak 92.57%. Oleh itu, model kinetik dan isoterma bagi penyingkiran MB diwakili oleh tertib pseudo kedua dan model Freundlich. Tambahan pula, kajian kebolehgunaan semula hidrogel turut dikaji dan didapati hidrogel boleh digunakan sehingga empat kitaran dalam penyingkiran MB.

Kata kunci: Getah; gel polimer; kaedah rangsangan permukaan tindak balas; penjerapan; penyingkiran pewarna

## Introduction

Dyes and heavy metals found in industrial wastewater can cause various environmental problems, such as water quality deterioration, aquatic habitat destruction, and pollution (Rajasulochana & Preethy 2016). Generally, dyes like methylene blue (MB) are widely used for colouring, coating paper, and dyeing purposes (Jeyagowri & Yamuna 2015). Their molecules are stable and non-degradable, thus causing them to exhibit properties like high toxicity and potentially carcinogenic, mutagenic, and allergenic to organisms (Pereira et al. 2021). Therefore, various techniques have been implemented to remove these dyes from aqueous solution, such as chemical precipitation, solvent extraction, ultrafiltration, ion exchange, and adsorption. Among these techniques, adsorption is the most practical technique as it is inexpensive and known for its high selectivity and efficiency. Recently, hydrogel adsorbents based on natural polymers are being preferred among others as they can be synthesised using renewable resources and green technology (Bao et al. 2019; Ozdes et al. 2014).

Hydrogels are defined as three-dimensional (3D) flexible polymeric networks that can hold a large amount of water or biological fluids in their swollen state (Ahmad et al. 2020). Hydrogels with hydrophilic polymer chains are effective adsorbents for dyes and heavy metals (Singh et al. 2021). However, their poor mechanical properties like being soft and brittle limit their use in certain applications. The product of hydrogel has weakness in terms of adsorption ability and mechanical strength (Aiza Jaafar et al. 2021). Natural rubber (NR) is therefore used as the based material in this research to overcome these weaknesses. This is because of the elevated mechanical characteristics of natural rubber specifically done by crosslinking of natural rubber with various monomer.

NR with a hydrophilic monomer can improves the hydrogel strength that will provides high mechanical strength and excellent elasticity, thus providing good water uptake and swelling properties to the hydrogels (Firdaus et al. 2019). These criteria are required to remove heavy metals and dyes from water, as well as for applications in the agricultural field (Sukumar & Nair 2014). Moreover, NR crosslinked with hydrophilic monomers having specific functional groups (e.g., –OH, $–NH_2$, $–SO_3H$, –COOH, $–CONH_2$) is extensively used for the adsorptive removal and recovery of aqueous pollutants, such as dyes and heavy metal ions (Singh et al. 2021). Different kinds of base materials were researched to improve hydrogel's effectiveness as an adsorbent. Each ingredient has its own benefits. Cellulose (Zainal et al. 2021), starch (Abdel-Halim & Al-deyab 2014), gelatine (Fosso-Kankeu et al. 2017) and synthetic polymers were among the based-materials studied.

For the past years, modification on rubber-based hydrogel has been studied thoroughly. The hydrophilic polymer, acrylic acid is crosslinked in order to improve the adsorption flux and hydrogel selectivity because this hydrophilic polymer has a functional group that can react specifically with water molecules (Amnuaypanich & Kongchana 2009; Singh et al. 2021). As an example, previous research has synthesised rubber based hydrogel grafted maleic anhydride (MaH) by using benzoyl peroxide (BPO) as radical initiator (Mohd Noor & Yusoff 2020). This grafting of MaH to introduce functional group with higher polarity inside the LNR chain (Nakason et al. 2004; Pongsathit & Pattamaprom 2018). It is proven that the grafting will give effect towards the ability of hydrogel to adsorb dyes as the result for these studies shows that the maximum adsorption of malachite green dye was 94.13%.

In this study, free-radical polymerisation between liquid natural rubber (LNR) and acrylic acid (AAc) using potassium persulfate (KPS) as the initiator and N,N-methylenebisacrylamide (MBA) as the crosslinking agent was performed. MBA was chosen as crosslinker due to its basic characteristic that would provide additional stability towards the hydrogel structure (Mathew et al. 2020). Crosslinking of acrylic acid into LNR chain will increase the interaction with water molecules due to functional group of the hydrophilic polymer (Krishnamoorthy et al. 2021). The optimisation of preparation condition of hydrogel were performed by varying three parameters: AAc:LNR weight ratio, KPS concentration and MBA concentration for removal of MB dye. The kinetic and isotherm models were calculated to determine the adsorption mechanism system. The adsorption-desorption process was carried out to determine the cycle of reusability.

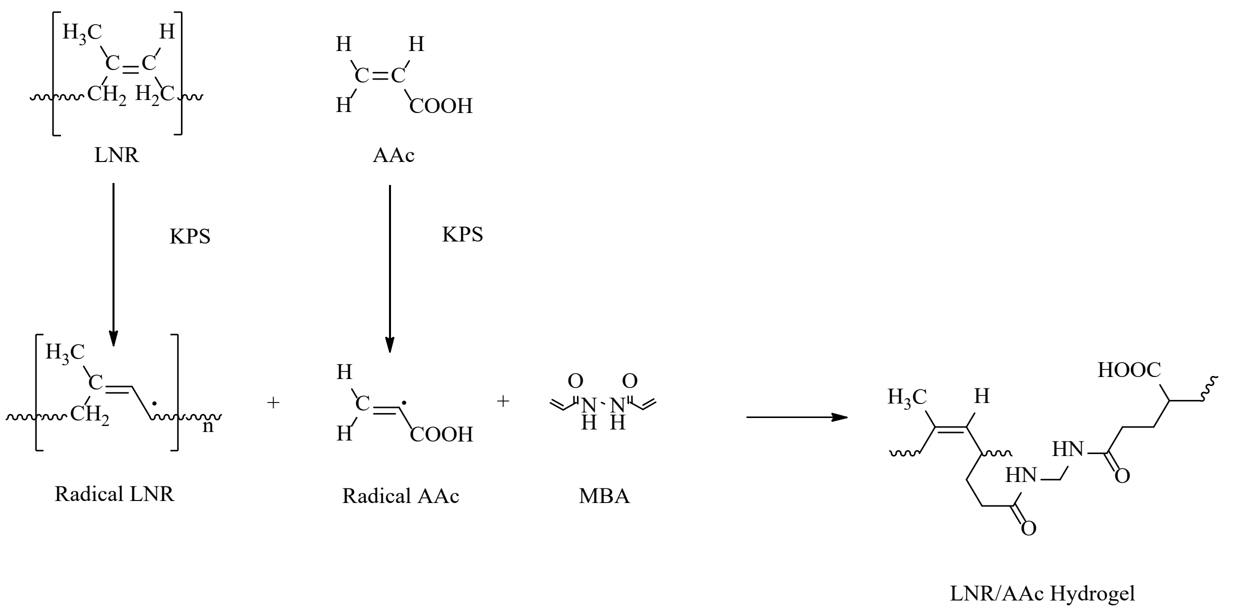
## Materials and Methods

### materials

NR was supplied by the Rubber Research Institute of Malaysia (RRIM), whereby the LNR was prepared using the method reported by Jamaluddin et al. (2016). At first, NR was soaked in toluene until it was completely swollen. A few amounts of methanol, rose Bengal, and methylene blue was added into the swollen NR. This mixture then was stirred for about 10 days using mechanical stirrer under visible light and room temperature. Meanwhile, AAc, KPS and MBA were supplied by Sigma Aldrich (USA). Sodium dodecyl sulfate (SDS) from Systerm (Malaysia) was used as the surfactant, while MB for the adsorption study was also purchased from Sigma Aldrich (USA).

### PREPARATION OF LNR/AAc HYDROGEL

LNR/AAc hydrogel was synthesised by adding distilled water and 1% SDS into a flask containing LNR. Then, diluted KPS was added into the solution, following which the mixture was stirred at 70 °C for 30 min. At the same time, KPS solution was added into AAc and stirred at room temperature for 30 min. Next, both mixtures were combined and MBA solution was added dropwise. The mixture was then continuously stirred at 70 °C until a solid hydrogel was formed. The formed hydrogel was dried in oven at 60 °C until a constant mass was achieved.

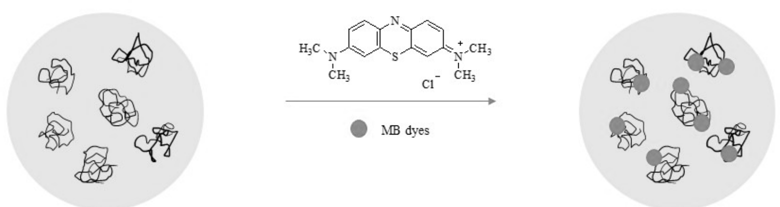



SCHEME 1. Reaction scheme of LNR/AAc hydrogel (Firdaus et al. 2019)

### METHYLENE BLUE DYE REMOVAL

The hydrogel sample (0.10 g) was immersed in 20 mL of 5 ppm MB in room temperature until equilibrium was reached. The hydrogel was then removed from the solution. Following this, the concentration of MB before and after the addition of the hydrogel was determined using UV-Vis spectrophotometry. The absorbance of the MB dyes was observed at 664 nm. The percentage of removal for the MB dye was subsequently calculated using the equation (1) shown below, where $C_i$ and $C_f$ are the initial and final concentrations (mg/L) of MB, respectively.

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




SCHEME 2. Interaction mechanism between MB dyes and LNR/AAc hydrogel

### CENTRAL COMPOSITE ROTATABLE DESIGN (CCRD)

CCRD is an efficient optimisation method for the prediction of linear and quadratic interactions between factors that will influence the consequent response. It also ensures less experimental runs compared to other optimisation methods, such as full factorial design (FFD) and Bohn-Behnken Design. In this research, the parameter and its range were set based on the preliminary test. Therefore, preparation variables chosen consisted of the weight ratio of AAc/LNR (1.00-3.00 g/g), concentration of KPS (0.05-0.20 M), and concentration of MBA (0.05-0.20 M), whereas the evaluated response was MB removal percentage (%). Using the Design Expert Software, a three-factor-five-level CCRD comprised of 20 experimental runs was applied for the optimisation of the preparation conditions of the hydrogel (Table 1). The model was then subjected to a statistical analysis, which was performed by an ANOVA analysis with F-test to obtain the correlation between the variables and response. Following this, the significance of the model was confirmed by the F-values with $p \leq 0.05$, which showed the goodness of fit for the model. Additionally, the quality of the suggested polynomial was also confirmed according to the $R^2$ values, adjusted $R^2$ and predicted $R^2$ values, lack-of-fit, and adequate precision of the model.

TABLE 1. Experimental variables and their coded levels for CCRD

| Variables | Coded variables level | | | | |
|---|---|---|---|---|---|
| | -2 | -1 | 0 | 1 | 2 |
| Weight ratio of AAc/LNR (g/g) | 1.00 | 1.41 | 2.00 | 2.59 | 3.0 |
| KPS concentration (M) | 0.05 | 0.08 | 0.13 | 0.17 | 0.20 |
| MBA concentration (M) | 0.05 | 0.08 | 0.13 | 0.17 | 0.20 |

### KINETIC STUDIES

Kinetic studies were performed by using 0.1 g of optimum hydrogel obtained and immersed in 5 ppm of MB dyes. pH of distilled water (6.55) and room temperature (25 °C) were fixed. This study relies on adsorption time, where the sample will be checked at the appropriate interval time until the adsorption in equilibrium state. The hydrogels were then filtered, whereby the final concentration of MB was determined, and the experimental data was fitted to pseudo-first order and pseudo-second order models accordingly. The pseudo-first order obtained through Equation (2) founded by Lagergren (1898). Whereas, Equation (3) introduced the pseudo-second order (Ho & McKay 1999).

$$\textit{Pseudo-first order: } \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (2)$$

$$\textit{Pseudo-second order: } \frac{t}{q_t} = \frac{1}{(k_2 q_e{}^2)} + \frac{1}{q_e}(t) \quad (3)$$

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

### ISOTHERMAL EQUILIBRIUM STUDIES

The isotherm equilibrium study for MB adsorption was determined by the immersed 0.1 g of hydrogel with 50 mL of MB solutions in different initial concentrations of MB (1-10 mgL$^{-1}$). Each sample was filtered, and residual MB concentration was then determined. Finally, the equilibrium data was fitted to Langmuir and Freundlich isotherm model and its parameters were subsequently calculated. The Langmuir model is represented by Equation (4) proposed by Clarke and Langmuir (1916) while the Freundlich model is represented by Equation (5) based on (Langmuir 1917).

$$\textit{Model Langmuir: } \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (4)$$

$$\textit{Model Freundlich: } \ln Q_e = \ln K_f + \frac{1}{n}(\ln C_e) \quad (5)$$

where $C_e$ is equilibrium concentration MB (mgL$^{-1}$); $Q_e$ is equilibrium adsorption capacity (mg/g); $Q_m$ and $K_f$ is expectation adsorption capacity (mg/g). In addition, the intensity of the adsorption can be calculated by value of $n$ in Freundlich model based on the intercept and gradient of the plot.

### REUSABILITY STUDIES

The reusability studies of LNR/AAc hydrogel was carried out by using methanol as desorbing agent (Lazim et al. 2019) and follow the method reported by Allouss et al. (2019). At first, 0.6 g of the hydrogel was immersed in 5 ppm of MB dye for about 50 mL for 120 min. After 120 min of adsorption process, the hydrogel was separated from the dye solution and immediately soaked into methanol for about 60 min. After soaking, the hydrogel was dried using silica gel approximately for 1 day. Then the dried hydrogel was used back for another adsorption-desorption process. Percentage of dye removal was recorded for each cycle of the adsorption-desorption process.

## RESULTS AND DISCUSSION

### SYNTHESIS OF LNR/AAC HYDROGEL

In general, hydrogel can be easily produced through solution polymerization (homogeneous) which all of the constituents are soluble in the medium, including the monomer (or polymer), initiator, and crosslinking agent (Du et al. 2020). The LNR/AAc hydrogel was synthesised from LNR and AAc using KPS as the initiator and MBA as the crosslink agent. The active site of crosslinking was generated by the decomposition of persulfate, which produced sulphate radical. The sulphate radical then abstracted hydrogen and initiated the polymerisation process before started to grow. Upon the addition of MBA into the reaction, both of the growing polymer chains crosslinked to each other and produced a hydrogel network (Ashri et al. 2018). The crosslinker content can influence the water absorption capacity of the hydrogel (Zhang et al. 2019). This method and characterization for LNR/AAc hydrogels following the same research reported earlier by our group (Firdaus et al. 2019). Figure 1 shows the SEM images for the LNR/AAc hydrogel that has been synthesised. It can be observed that 0.01 M MBA in LNR/AAc display a porous of hydrogel as compared to 0.06 M and 0.10 M of MBA, respectively, which have an undulant and coarse surface. When the content of crosslinker is high, voids in the network structure of the polymer would shrink due to the effects of the graft copolymerization reaction thus changes surface of the hydrogel (Zhang et al. 2019).

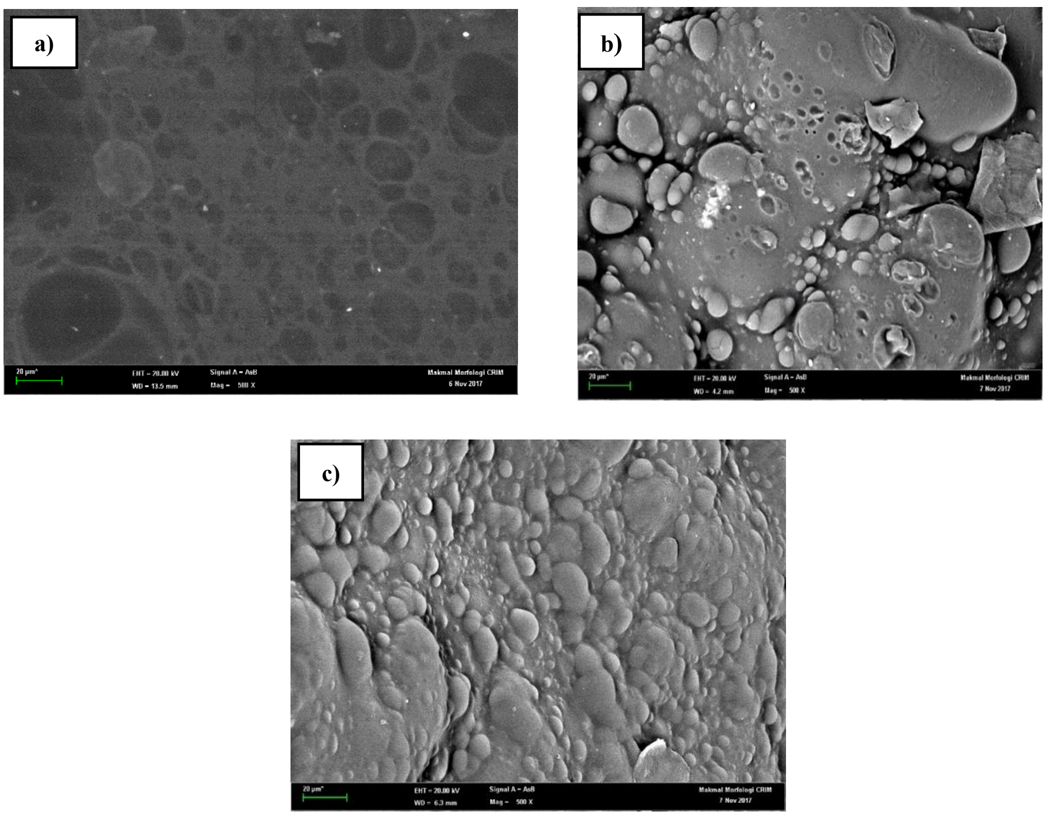



FIGURE 1. SEM images for surface of LNR/AAc hydrogel at concentration of MBA a) 0.01 M b) 0.06 M and c) 0.10 M at magnification of 500x

### OPTIMISATION USING RSM APPROACH

The evaluated response for the 20 experimental runs carried out is presented in Table 2, which consist of 8 factorial points, 8 axial points, and 6 centre points. The results were then used to determine the polynomial equation.

TABLE 2. CCRD table for preparation of LNR/AAc hydrogel parameters

| Run | Weight ratio of AAc/ LNR (g/g) | KPS concentration (M) | MBA concentration (M) | Removal percentage (%) | |
|---|---|---|---|---|---|
| | | | | Actual | Predicted |
| 1 | 1.41 | 0.08 | 0.08 | 85.91 | 86.57 |
| 2 | 2.59 | 0.08 | 0.08 | 93.69 | 93.04 |
| 3 | 1.41 | 0.17 | 0.08 | 85.02 | 85.70 |
| 4 | 2.59 | 0.17 | 0.08 | 85.69 | 86.22 |
| 5 | 1.41 | 0.08 | 0.17 | 83.69 | 83.15 |
| 6 | 2.59 | 0.08 | 0.17 | 95.47 | 94.79 |
| 7 | 1.41 | 0.17 | 0.17 | 77.91 | 78.56 |
| 8 | 2.59 | 0.17 | 0.17 | 84.91 | 84.25 |
| 9 | 1.00 | 0.13 | 0.13 | 82.36 | 81.50 |
| 10 | 3.00 | 0.13 | 0.13 | 90.87 | 91.73 |
| 11 | 2.00 | 0.05 | 0.13 | 98.13 | 98.85 |
| 12 | 2.00 | 0.20 | 0.13 | 89.96 | 89.25 |
| 13 | 2.00 | 0.13 | 0.05 | 81.24 | 80.51 |
| 14 | 2.00 | 0.13 | 0.20 | 75.25 | 75.98 |
| 15 | 2.00 | 0.13 | 0.13 | 83.02 | 82.48 |
| 16 | 2.00 | 0.13 | 0.13 | 83.24 | 82.48 |
| 17 | 2.00 | 0.13 | 0.13 | 83.36 | 82.48 |
| 18 | 2.00 | 0.13 | 0.13 | 82.24 | 82.48 |
| 19 | 2.00 | 0.13 | 0.13 | 81.80 | 82.48 |
| 20 | 2.00 | 0.13 | 0.13 | 81.24 | 82.48 |

Based on the experimental runs conducted, the quadratic model that is generated in terms of the coded variables is shown in Equation (6).

MB removal percentage (%) =

$$+82.48 + 23.04A - 2.85B - 1.35C - 1.49\,AB + 1.29\,AC - 0.93\,BC + 1.46\,A^2 + 4.09\,B^2 - 1.50\,C^2 \quad (6)$$

where A, B, and C represent the weight ratio of AAc:LNR, KPS concentration, and MBA concentration, respectively. The positive signs in the equation indicated synergetic effects of the factors, while the negative signs indicated the antagonistic effects. Based on the equation, factor A which is LNR/AAc weight ratio give synergetic effect. It shows that the higher LNR/AAc weight ratio may increase the adsorption capability. This is because, performing the crosslinked with hydrophilic polymers in LNR is convenient because hydrophilic monomers contain polar or charged functional groups that rendering them to react in water (Wongthep et al. 2012). While, factor B and C which are KPS concentration and MBA concentration, respectively, give the antagonistic effects. This statement being supported by the morphological analysis that has been conducted before using similar hydrogel, it proves that over concentration of MBA and KPS lead to the formation of denser polymer networks in the hydrogel and smaller pore size was observed leading to higher adsorption capacity. Then, ANOVA analysis was conducted as the removal percentage of MB was used to validate the importance and adequacy of the model. The results are presented in Table 3, which depicts the F-values and Prob>F values for the model at 65.49 and <0.0001, respectively. Therefore, this research was successfully justified the significance of the quadratic model. All model terms were significant to the response as each of the Prob>F values was less than 0.05. Regardless, the lack of fit value indicated that the systematic variation was unaccounted in the hypothesised model, thereby necessitating the insignificance of lack of fit value. In this study, the Prob>F value for the lack of fit was 0.2612, which exceeded the suggested value of 0.05.

TABLE 3. ANOVA results for preparation conditions of LNR/AAc hydrogel for MB removal

| Source | Sum of squares | Degree of freedom | Mean square | F-value | Prob> F |
|---|---|---|---|---|---|
| Model | 616.00 | 9 | 68.44 | 65.49 | < 0.0001 |
| A | 126.36 | 1 | 126.36 | 120.91 | < 0.0001 |
| B | 111.20 | 1 | 111.20 | 106.40 | < 0.0001 |
| C | 24.80 | 1 | 24.80 | 23.73 | 0.0007 |
| AB | 17.67 | 1 | 17.67 | 16.91 | 0.0021 |
| AC | 13.34 | 1 | 13.34 | 12.76 | 0.0051 |
| BC | 6.94 | 1 | 6.94 | 6.64 | 0.0276 |
| $A^2$ | 30.75 | 1 | 30.75 | 29.43 | 0.0003 |
| $B^2$ | 240.81 | 1 | 240.81 | 230.41 | < 0.0001 |
| $C^2$ | 32.36 | 1 | 32.36 | 30.96 | 0.0002 |
| Residual | 10.45 | 10 | 1.05 | | |
| Lack of fit | 6.76 | 5 | 1.35 | 1.83 | 0.2612 |
| Pure error | 3.69 | 5 | 0.74 | | |
| Cor total | 626.45 | 19 | | | |

Coefficient variation (CV) indicates the ratio of the standard error to the mean value of the observed response and reproducibility of the model. Therefore, CV values less than 15% are generally considered as reasonable. Besides, the difference between the predicted $R^2$ (Pred-$R^2$) and the adjusted $R^2$ (Adj-$R^2$) must be less than 0.2 for it to be considered as a reasonable agreement. In this study, the value of CV was 1.20%, whereas the Adj-$R^2$ and Pred-$R^2$ value difference was less than 0.2. Therefore, the $R^2$ value that was close to unity showed that the model had a good agreement between the actual and predicted values of the response, with the $R^2$ value of 0.9833 for the quadratic model. This indicated that the quadratic model provided 98.33% of accuracy for the output prediction.

The plots of the predicted values against the actual values for removal percentage of MB are presented accordingly in Figure 2. The good agreement between both values consequently confirmed the validity of the model.

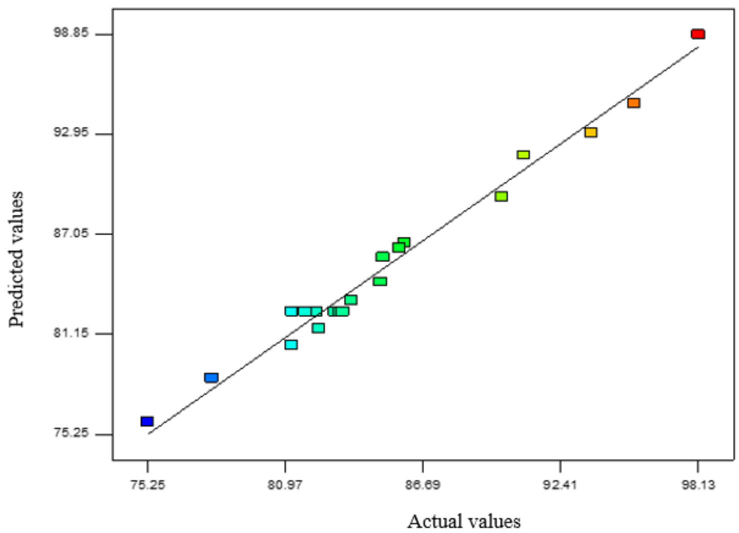



FIGURE 2. Plots of predicted values against actual values for preparation condition of LNR/AAc hydrogel for MB removal

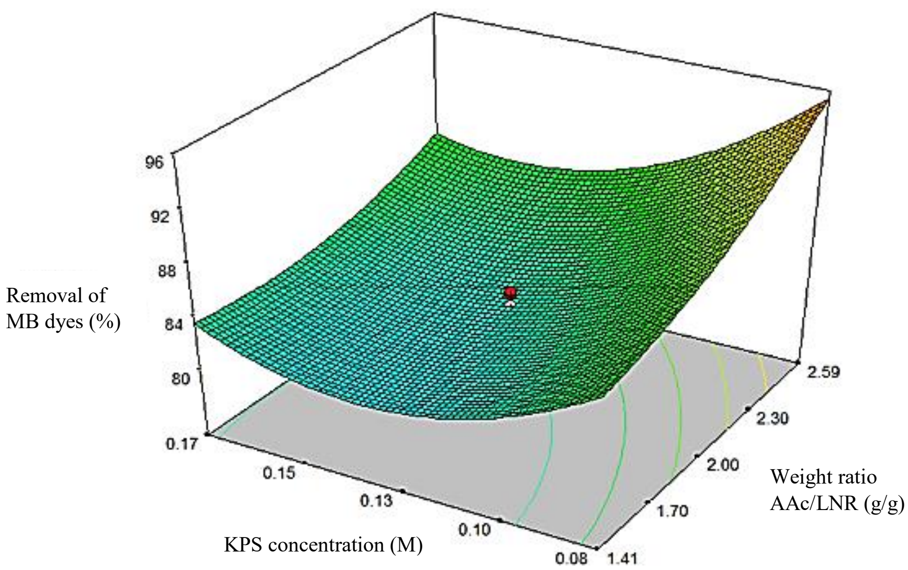



FIGURE 3. Response surface interaction between parameters weight ratio AAc/LNR and KPS concentration

Three dimensional response surface plot shows the interaction between factors to determine optimum level for each factors to achieve maximum removal of MB dyes. Figure 3 shows the interaction between parameters weight ratio of AAc/LNR and KPS concentration. Based on Figure 3, removal percentage of MB dyes at lower concentration of KPS and lower weight ratio of AAc/LNR is at lower percentage and increasing with the increase of weight ratio of AAc/LNR. The increase in weight ratio AAc/LNR means more carboxylic functional group inside the polymer hidrogel network. This carboxylic functional group takes an important roles in adsorption of MB dyes. The higher the functional group the more MB dyes molecules can be adsorbed into hydrogel network (Bhattacharyya & Ray 2015). Through this plot, it shows that weight ratio AAc/LNR give significant effect towards the removal of MB dyes compare to KPS concentration.

Next, interaction between parameters of weight ratio AAc/LNR and MBA concentration with constant KPS concentration shown in Figure 4. Based on the plot, highest percentage removal of MB can be achieved at higher weight ratio AAc/LNR and lower MBA concentration. This is due to at more concentration of MBA, the degree of crosslinking of the hydrogel increase, hence making the structure of the hydrogel become less elastic and expansion of space inside the hydrogel linkage (He et al. 2016; Wang et al. 2011). Based on this plot, weight ratio of AAc/LNR give significant effect towards the percentage removal of MB compare to MBA concentration.

Figure 5 shows plot of interaction between parameters of KPS concentration and MBA concentration with constant weight ratio AAc/LNR. Based on the plot, the removal percentage of MB decreased at higher concentration of KPS and MBA. The removal

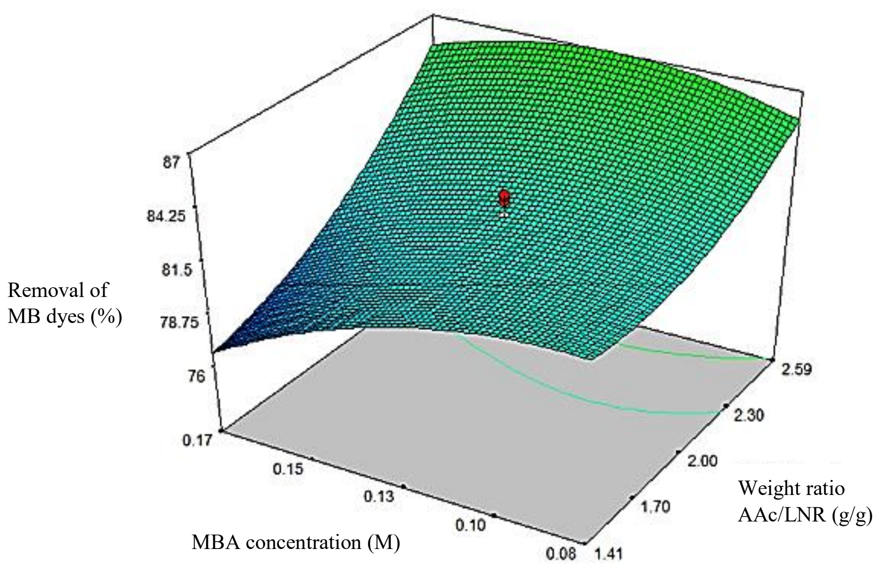



FIGURE 4. Response surface interaction between parameters weight ratio AAc/LNR and MBA concentration

percentage increase at concentration of MBA between 0.08 M – 0.13 M. This shows that MBA can form optimum crosslinking for the formation of hydrogel (Mandal & Ray 2014). Unfortunately, when the concentration exceeding 0.13 M, hydrogel become more dense and less elastic resulting in blockage the adsorption of MB molecules inside the hydrogel (Yang et al. 2010). Next, percentage removal of MB dyes decrease with the increasing of KPS concentration. This situation already explained based on Figure 3.

Optimization of the hydrogel preparation was conducted to achieve maximum MB removal under suitable conditions, namely higher AAc:LNR weight ratio, and lower KPS and MBA concentration. Therefore,

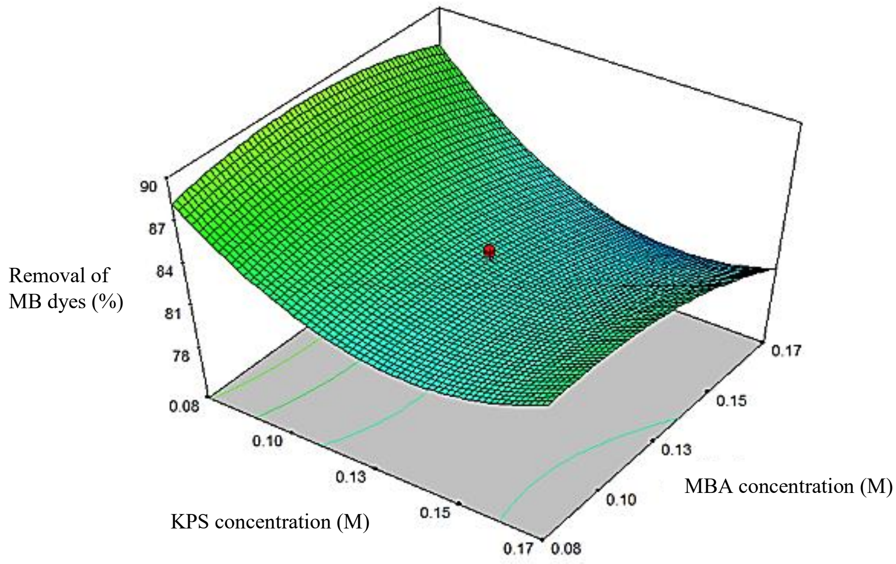



FIGURE 5. Response surface interaction between parameters KPS concentration and MBA concentration

the experimental conditions with higher desirability were selected and verified using the optimisation function in the Design Expert software. Table 4 shows the predicted and experimental values of MB removal obtained at the optimum condition, showing a good agreement with an error of 0.47%. Result shows the amount of KPS and MBA used is 1:1 ratio indicating that the initiator produce the concentration of free radicals in the solution thus increasing the crosslinking site and density of hydrogel. However, too many free radicals and crosslinkers will cause a chain termination reaction, shortening the graft chain of polymer and making the spatial network structure difficult to form, causing the hydrogel to shrink and decreasing the adsorption performance towards MB (Zhang et al. 2019).

TABLE 4. The optimum condition of preparation condition of LNR/AAc hydrogel for MB removal

| AAc:LNR weight ratio (g/g) | KPS concentration (M) | MBA concentration (M) | MB removal (%) | | |
|---|---|---|---|---|---|
| | | | Predicted | Actual | Error |
| 2.59 | 0.08 | 0.08 | 93.04 | 92.57 | 0.47 |

## KINETIC STUDY OF MB ADSORPTION ONTO LNR/AAc HYDROGEL

Two common adsorption kinetic models were used in this study, specifically the pseudo-first order and pseudo-second order models (Jamnongkan et al. 2014). They were usually utilised to investigate the mechanism of adsorption processes. The value of $k_1$, the rate constant for pseudo-first order was obtained by plotting log $(q_e - q_t)$ versus t. Meanwhile, the rate constant of pseudo-second order equation was represented by $k_2$ ($gmg^{-1}min^{-1}$). The $k_2$ value was obtained from the intercept of the plot graph for $t/q_t$ versus t. From the pseudo-second order equation, it was assumed that the adsorption capacity of an adsorbent was directly proportional to the number of its active sites (Sharifpour et al. 2018).

The kinetic constants and correlation coefficients ($R^2$) of both kinetic models are presented accordingly in Table 5. A high $R^2$ value that was close to unity showed a good agreement of experimental and calculated adsorption capacity. Based on the data, the $R^2$ value of the pseudo-second order was higher than that of the pseudo-first order kinetic model. Moreover, the calculated adsorption capacity at the equilibrium state was lower (0.2160 mg/g) than the experimental value of 0.5911 mg/g, whereas the $q_{e\ (calculated)}$ for the pseudo-second order kinetic model was the closest, at 0.6211 mg/g. Therefore, the pseudo-second kinetic model was more suited for describing the adsorption kinetic of MB adsorption onto LNR/AAc hydrogel. Adsorption kinetics following the pseudo-second order were assumed to be chemisorption, which involved the sharing of electrons or an exchange between the adsorbent and adsorbate (Gürses et al. 2006). Adsorption capacity is the rate of amount of adsorbate adsorbed into adsorbent depending on several other factors such as concentration, pH and temperature of solution (Tran et al. 2017). To achieve a good adsorption capacity, all these factors need to be controlled carefully the entire time until equilibrium reached. For this study, the maximum adsorption capacity is relatively low as compared to the other research work due to the saturation of adsorbate-adsorbent system. The lower concentration of solute, no adjustment of pH and temperature of reaction also affected towards adsorbent where the value of adsorption capacity remains unchanged. Besides, the adsorption of MB by LNR/AAc hydrogel was heterogeneous, involving reverse adsorption and no single layer formation.

TABLE 5. Constant parameters and correlation coefficients of the kinetic models

| Model | | Pseudo-first order | | | Pseudo-second order | | |
|---|---|---|---|---|---|---|---|
| Parameters | $q_{e\ (exp)}$ | $k_1$ | $q_{e\ (calc)}$ | $R^2$ | $k_2$ | $q_{e\ (calc)}$ | $R^2$ |
| Units | mg/g | $min^{-1}$ | mg/g | - | $min^{-1}$ | mg/g | - |
| | 0.5911 | 0.0115 | 0.2160 | 0.7983 | 0.104 | 0.6211 | 0.9915 |

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

The isotherm models were used to explain the equilibrium characteristics of adsorption, specifically between the mass of dye adsorbed per unit mass of sorbent and the dye concentration. In this study, the two isotherm models of Langmuir and Freundlich were utilised to analyse the data. The Langmuir isotherm model was used to elucidate monolayer sorption of surface containing a finite number of identical active sites (Jeyagowri & Yamuna 2015). In contrast, the Freundlich isotherm model was implemented to assume heterogeneous adsorption, where stronger binding sites would be occupied first before decreasing exponentially upon the completion of the adsorption process. Values of 1/n below 0 showed adsorption by chemisorption, whereas values above 1 indicated cooperative adsorption.

Based on Table 6, Freundlich isotherm model is shown to have a better fit compared to the Langmuir isotherm model, which is justified by its higher $R^2$ value (0.9971). Therefore, this data supported the heterogeneous adsorption of MB onto the LNR/AAc hydrogel. Moreover, its heterogeneity factor of below 0 also explained the adsorption mechanism of MB onto hydrogel via chemisorption, which was explained by the pseudo-second kinetic model. Based on the research findings, we proposed that the mechanism for MB adsorption onto LNR/AAc hydrogel is due to the active site of the hydrogel that can bind the MB via electrostatic attraction, where the large number of anionic carboxylate groups that contribute to the adsorbent's negative charge can provide many adsorption sites for the MB molecules (Maijan et al. 2021; Yan et al. 2015).

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

| Dye | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $K_L$ (L/mg) | $Q_m$ (mg/g) | $R^2$ | $K_F$ | n | $R^2$ |
| Methylene blue | 0.8143 | 181.818 | 0.0011 | 0.8143 | 0.9953 | 0.9971 |

## REUSABILITY STUDIES

A good adsorbent should have the ability to adsorb at high capacity and also to regenerate its adsorption sites for recycling use which is energy saving. In this research, the reusability of LNR/AAc was inspected by performing several cycles of adsorption-desorption where methanol was used as a desorbing medium. Based on Figure 6, we found the LNR/AAc hydrogels can be recycle for up to four consecutive cycles where dye removal percentage decreasing with the increasing of recycle times. The results indicate that the MB removal percentage was relatively high in the first cycle and decreased significantly as more desorption cycles were performed. This suggested that the adsorbents' physical properties deteriorated, reducing the number of reusable cycles. In spite of slight decline, the mechanical strength of hydrogel was maintained showing durability for repeated use. The synthesized hydrogels based on natural rubber showed good water retention, mechanical properties, and thermal stability as stated by Maijan et al. (2021). The ability of material withstands the stress of physical forces makes hydrogel rigid and firm.

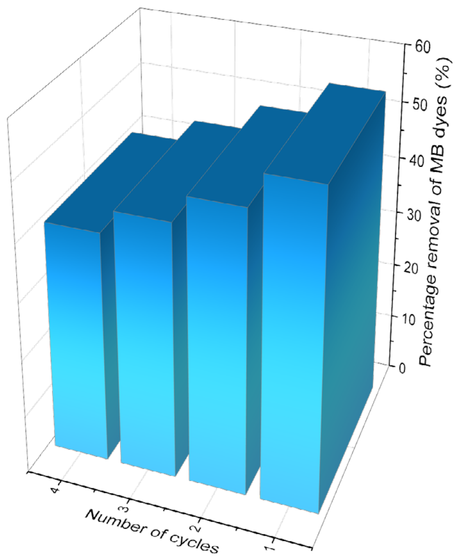



FIGURE 6. The reusability of LNR/AAc hydrogel for MB adsorption

## CONCLUSION

LNR/AAc hydrogel was successfully synthesised using KPS as the initiator and MBA as the crosslinking agent. The optimisation of this hydrogel was done using response surface methodology and the optimum condition is at weight ratio AAc/LNR (2.59 g/g), concentration KPS (0.08 M) and concentration MBA (0.08 M). This hydrogel subsequently achieved the maximum MB dye removal percentage of 94.53% with the maximum adsorption capacity (0.59 mg/g) was best described by the pseudo-second order and Freundlich isotherm model. The addition of MBA and AA as crosslinkers would provide additional stability towards the hydrogel structure and increase the interaction with water molecules due to functional group of the hydrophilic polymer. These results consequently confirmed its ability as an application for dye removal but at lower adsorption capacity due to other factors that not being considered during adsorption such as concentration, pH and temperature of solution. The reusability studies for the LNR/AAc were done and result shows that the hydrogel can be recycle for several times thus showing good mechanical strength. Hence, the hydrogel has shown a vast potential to act as an effective adsorbent by considering the factors involving in adsorption such as concentration, pH and temperature of solution. This also may be an instrumental in widening the opportunities for rubber-based hydrogel research in the future.

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